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A NEW POLYENE SYNTHESIS

A dissertation submitted to the faculty of the
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by

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CONTENTS

Introduction

Transportation difficulties and blockade brought about by the war have caused a serious shortage of drying oils. Tung oil had been imported from China, oiticia from Brazil, perilla from Japan, and linseed mainly from Argentina. As a consequence, considerable effort has been directed towards the synthesis of drying oils from non-drying types, such as castor oil, through dehydration, or from semi-drying fish oils through saponification, distillation, and separation of the fatty acids into the drying and non-drying components, susequently reesterifying the drying acids with glycerol or pentaerythitol.

Because the excellent drying properties of tung oil are attributed to the conjugated triene structure of eleostearic acid, which constitutes 80 percent of its fatty acids, it has been thought advisable to study the drying properties of trienes and their polymers in general.

Historical Background

The synthesis of poly unsaturated compounds was given added impetus with Karrer's elucidation of the structure of Vitamin A in 1931[1]. Before this vitamin or its predecessor, carotene, or pro-vitamin A, could be synthesized, it was necessary that methods be developed for the synthesis of

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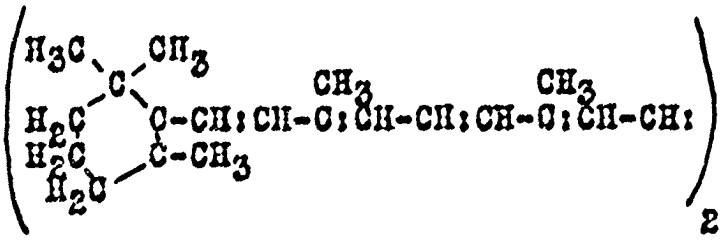
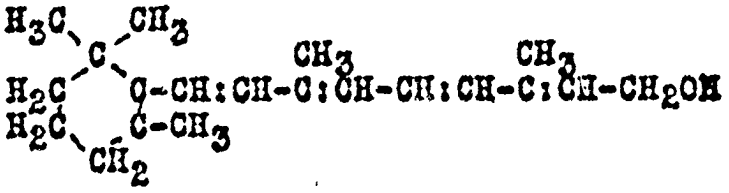
1. Karrer, Morf, and Schopp, Helv. chim. acta. 14,1431 (1931); 16, 557, 625(1933)

polyenes with conjugated unsaturation.



beta-Carotene



Vitamin A

A large body of literature pertaining to the chemistry of polyenes has been built up in recent years. Most of this has had as its ultimate goal the total synthesis of carotene, or compounds of a similar nature. The reviews of Kuhn[2] and Sobotka and Bloch[3] are the best entries to this literature.

Compounds very similar to carotene have been synthesized by Kuhn and Wallenfels[4]. In their method, which is the best available for high molecular weight compounds, polyene seleno or thio aldehydes were prepared through reaction of the corresponding polyene aldehydes with hydrogen selenide or hydrogen sulphide. When the sulphur or selenium was removed through the action of metals such as copper, two of the parent nuclei dimerized, and a diphenyl polyene with an odd number

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2. Kuhn, J. Chem. Soc., 1938, 605
3. Sobotka and Bloch, Chem. Rev., 34, 435 (1944)
4. Kuhn and Wallenfels, Angew. Chem., 50, 703 (1937)

of double bonds resulted. The similarity between compounds of this type and carotene is obvious, but the difference represents a very difficult synthesis.

$$R\text{-}CH{:}CH\text{-}CHO + H_2S \longrightarrow R\text{-}CH{:}CH\text{-}CHS + H_2O$$

$$R\text{-}CH{:}CH\text{-}CHS + SHC\text{-}CH{:}CH\text{-}R \xrightarrow{Cu} R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}R$$

Three other syntheses for symmetrical diphenyl polyenes can be found in the literature. Kuhn[2] has described the reduction of diphenyl polyene glycols, such as dihydrocinnamoin, to the corresponding diphenyl polyenes, in this instance diphenyl hexatriene. P_2I_4 in ethyl ether was used as the reducing agent, and theoretical yields were obtained.

$$Ph\text{-}CH{:}CH\text{-}\overset{OH}{\underset{}{CH}}\text{-}\overset{OH}{\underset{}{CH}}\text{-}CH{:}CH\text{-}Ph \xrightarrow{P_2I_4} Ph\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}Ph$$

There is no reference to this reaction in the purely aliphatic series.

Diphenyl polyenes with either an even or odd number of double bonds have been synthesized through the Perkin reaction. In this manner two mols of phenyl polyene aldehyde have been condensed with succinic acid in the presence of lead oxide, acetic acid, and acetic anhydride[5,6]. In every instance a diphenyl polyene with an even number of double bonds was

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5. Kuhn and Winterstein, Helv. Chim. Acta., 11, 87, 116, 144 (1928)
6. Bernhauer, Woldan, Neubauer, Irrgang, Drobnick, and Skudrzyk, J. Pract. Chem., 155, 310 (1940); Biochem. Zeit. 249, 199; 251, 173; 254, 434 (1932); 266, 197 (1933); 525, 45 (1936)

isolated. Using essentially the same reaction, Kuhn and Grundmann[7] have prepared a series of diphenyl polyenes with an odd number of double bonds by substituting dihydromuconic acid for succinic.

$$2\ R\text{-}CH{:}CH\text{-}CHO + HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH \longrightarrow R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}R + 2H_2O + 2CO_2$$

$$2\ R\text{-}CH{:}CH\text{-}CHO + HOOC\text{-}CH_2\text{-}CH{:}CH\text{-}CH_2\text{-}COOH \longrightarrow R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}R + 2H_2O + 2CO_2$$

A great number of mono and diphenyl polyenes are available through the Grignard synthesis. Kuhn and coworkers[4,8] have shown that the normal reaction takes place between unsaturated aldehydes and benzyl Grignard reagent. The carbinols resulting from these reactions are readily dehydrated to polyenes with a 2 percent solution of p-toluene sulfonic acid in ether[9]. It is obvious that these reactions can lead to many symmetrical or unsymmetrical polyenes in either the aromatic or aliphatic series.

$$R\text{-}CH{:}CH\text{-}CHO + Ph\text{-}CH_2MgBr \longrightarrow R\text{-}CH{:}CH\text{-}\underset{H}{\overset{CH_2\text{-}Ph}{C}}\text{-}OMgBr \xrightarrow{H_2O} R\text{-}CH{:}CH\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}Ph$$

$$R\text{-}CH{:}CH\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}Ph \xrightarrow{-H_2O} R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}Ph$$

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7. Kuhn and Grundmann, Ber., 69, 1757 (1936)
8. Kuhn and Wallenfels, Ber., 70, 1331 (1937); 71, 1889 (1938)
9. Kuhn and Grundmann, Ber., 71, 442, (1938)

The Knoevenagle condensation is perhaps the most useful reaction which has been developed in the polyene series. This reaction furnishes the polyene aldehydes, basic materials for most of the other syntheses described. Kuhn and Grundmann[10] have obtained a series of vinylene homologs of crotonaldehyde with up to 8 conjugated double bonds through successive condensations of acetaldehyde in the presence of acid amine salts as catalysts. It is of interest to note that in this work Kuhn and Grundmann discovered that the essential catalyst for the Knoevenagle reaction was an acid amine salt, and not the free amine as had been previously supposed.

$$R\text{-}CH{:}CH\text{-}CHO + H_3C\text{-}CHO \xrightarrow[\text{salts}]{\text{amine}} R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CHO + H_2O$$

With the polyene aldehydes as starting material, it is possible to obtain monocarboxylic acids in any of three ways, the most direct being oxidation of the aldehyde with silver oxide[6,11]. If these same aldehydes are condensed with malonic acid in pyridine, the polyene monocarboxylic acids with one more double bond and two more carbon atoms are obtained.

$$R\text{-}CH{:}CH\text{-}CHO + H_2C(COOH)_2 \xrightarrow{\text{pyridine}} R\text{-}CH{:}CH\text{-}CH{:}C(COOH)_2 \xrightarrow{-CO_2} R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}COOH$$

In this manner Kuhn and Grundmann[12] have prepared compounds of the type $CH_3(CH{:}CH)_nCOOH$ with n as large as 8. The decarboxylatio

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10. Kuhn and Grundmann, Ber., 70, 1318, (1937)
11. Reichstein, Ammann and Trivelli, Helv. Chim. Acta., 15, 261, 1074 (1932)
12. Kuhn and Grundmann, Ber., 70, 1318 (1937)

occurs spontaneously in the course of reaction when the lower members of the series are being prepared. It is necessary in the case of the higher members, however, to decarboxylate the dicarboxy acid by refluxing in acetic acid and acetic anhydride.

The third synthesis for polyene monocarboxylic acids involves the Reformatsky reaction with polyene aldehydes and ethylbromacetate. In this manner, the cis-trans pairs of 3-methyloctatrienic acid and 3,7-dimethyloctatrienic acid were prepared after dehydration of the carbinols obtained from crotonylidene acetone and 6-methyl-3,5-heptadiene, respectively[13,14].

$$R\text{-}CH{:}CH\text{-}CHO + CH_2BrCOOEt \xrightarrow{Zn} \xrightarrow{H_2O} R\text{-}CH{:}CH\text{-}\underset{H}{\overset{OH}{C}}\text{-}CH_2COOEt \xrightarrow{-H_2O}$$

$$R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}COOEt$$

In some instances, the dehydration of the intermediate hydroxy acid is attended with decarboxylation and the product isolated is a polyene hydrocarbon[13].

Kuhn and Grundmann have prepared a series of dicarboxylic acids using a fairly complicated synthesis which they generalized[7,11,15]. They utilized as starting materials the polyene monocarboxylic esters of one less double bond than was to be present in the final molecule. These were condensed with oxalic ester in the presence of potassium ethoxide or pyridine, yielding an oxalo-polyene ester.

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13. Fischer and Lowenberg, Ann., 494, 263 (1932)
14. Kuhn and Hoffer, Ber., 65, 651 (1932)
15. Kuhn and Grundmann, Ber., 69, 1979 (1936)

$$EtOOC\text{-}(CH{:}CH)_n\text{-}CH_3 + EtOOC\text{-}COOEt \xrightarrow{\text{pyridine}} EtOOC\text{-}(CH{:}CH)_nCH_2C(=O)\text{-}COOEt$$

The enol form of this compound was acetylated with acetic anhydride and reduced with aluminum amalgam.

$$EtOOC\text{-}(CH{:}CH)_n\text{-}C(H){:}C(OH)\text{-}COOEt + CH_3CO\text{-}O\text{-}OC\text{-}CH_3 \longrightarrow$$

$$EtOOC\text{-}(CH{:}CH)_n\text{-}C(H){:}C(OAc)\text{-}COOEt \xrightarrow[H_2]{Al\text{-}Hg} EtOOC\text{-}CH_2\text{-}(CH{:}CH)_n\text{-}CH(OAc)\text{-}COOEt$$

When the product of these reactions was treated with aqueous or alcoholic alkali, the free dicarboxylic polyene, or its diester, was obtained through removal of the elements of acetic acid and ester interchange with the solvent.

$$EtOOC\text{-}CH_2\text{-}(CH{:}CH)_n\text{-}CH(OAc)\text{-}COOEt \xrightarrow[H_2O]{KOH} HOOC\text{-}(CH{:}CH)_n\text{-}CH{:}CH\text{-}COOH$$

Of more interest to the present investigation than the preceding material, which was directed towards the synthesis of carotene, is the synthesis of purely aliphatic polyenes with special reference to the aliphatic trienes. To correlate the syntheses in the aliphatic series, it might be well to reference again to their synthesis from polyene carbinols[9,13] and their appearance as by-products in the synthesis of monocarboxylic polyenes through the Reformatsky synthesis[13].

Thermal dehydration and dehydrogenation of 1,2 glycols yields, along with a complex mixture of other materials, a certain amount of polyene. Thus Urion[16] first prepared

16. Urion, Ann. chim., (11), 1, 5 (1934)

1,6 dimethyl-hexatriene-1,3,5 through thermal decomposition of dipropylene glycol over copper.

$$CH_3\text{-}CH{:}CH\text{-}\underset{OH}{CH}\text{-}\underset{OH}{CH}\text{-}CH{:}CH\text{-}CH_3 \xrightarrow[Cu]{-H_2,-H_2O} CH_3CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH_3$$

Quite similar in nature to this synthesis is one referred to by Kharasch, Nudenberg, and Sternfeld[17]. They cite the reduction of unsaturated carbonyl compounds to the pinacols, replacement of the hydroxyls with halogen, and removal of the halogen with zinc as a general scheme which, however, does not furnish satisfactory yields. In the same work these authors report a triene synthesis which seems quite general whenever the reactants are available. After a study of many possible dehydrohalogenating agents, they determined that sodamide in liquid ammonia caused the condensation of allyl halides and substituted allyl halides in such a manner that two mols of hydrogenhalide split out, and a conjugated triene was produced.

$$R\text{-}CH{:}CH\text{-}CH_2Br \quad + \quad Br_2HC\text{-}CH{:}CH\text{-}R \xrightarrow[NH_3]{NaNH_2} R\text{-}CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CH\text{-}R$$

Yields are good, and this is undoubtedly the best synthesis whenever the proper allyl halide is available.

Several attempts have been made to dehydrate the olefin-1,4-glycols produced from acetylene dimagnesiumbromide and

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17. Kharasch, Nudenberg, and Sternfeld, J.Am.Chem.Soc., 61, 2318 (1939); 62, 2034 (1940)

aliphatic carbonyl compounds. In every instance save one the result has been a substituted dihydrofuran[18]. The successful synthesis of 2,5-dimethylhexatriene by Kharash et al[17] through the sodamide condensation has cast considerable doubt upon the synthesis of the same compound through dehydration of 2,5-dimethyl-2,5-dihydroxy-3-hexene with aqueous hydrochloric acid at 95° for eight days[19]. Thus the bulk of evidence seems to indicate that dehydration of aliphatic olefin-1,4-glycols is not feasable as a triene synthesis. Kuhn and Wallenfels, however, have reported one such dehydration in the aromatic series[8]. It is possible that steric considerations prevent the formation of phenyl substituted dihydrofurans, making the triene synthesis possible.

Semi-hydrogenation of substituted acetylenes

When substituted or di-substituted acetylenes are hydrogenated in the presence of platinum black, there seems to be no evidence of a stepwise reaction. Instead the reaction proceeds directly to the saturated compound, and, if it is interrupted after the addition of one equivalent of hydrogen, a mixture of acetylene, olefin and saturated hydrocarbon is obtained[20,21]. If colloidal palladium is used, it becomes possible to obtain good yields of the olefins by halting the

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18. Blomquist and Marvel, J. Am. Chem. Soc., 55, 1658 (1933)
19. Bourguel and Rambaud, Bull. Soc. Chim., (4), 47, 173(1930)
20. Bourguel, Bull, Soc. Chim., (4), 41, 1443, 1475 (1927)
21. Dupont, Compt. Rend., 156, 1623 (1913)

reaction after one mole of hydrogen has been absorbed[20 to 28,inc].

This selectivity is not due to a more rapid reduction of the acetylene compound than that of the corresponding olefin, for, in some cases, (monosubstituted acetylenes[23], arryl acetylenes[24,29], acetylenic alcohols and some unsymmetrical acetylenic glycols[29]) the olefins reduce as rapidly or even more rapidly than the acetylenes.

The selective properties associated with colloidal palladium are also exhibited by Raney nickel and a similar catalyst prepared from an iron aluminum alloy[30,31,32,33].

Farkas[34] considers that the selective action is connected with preferential adsorption of the acetylene upon the surface of the catalyst. Because no olefin may be adsorbed while there is any acetylene present to cover the catalyst surface, the reaction must proceed in steps.

In contrast to earlier literature, Bourguel and his students[22,23,25] have shown that the product of semi-hydrogenation of a disubstituted olefin with colloidal palladium on starch is almost always the cis form. As a consequence, Bourguel[22] has suggested that the primary product

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22. Bourguel, Bull.Soc.Chim., (4), 45, 1067 (1929)
23. Ibid. 51, 253 (1932)
24. Bourguel and Gredy, Compt. Rend., 189, 757 (1929)
25. Gredy, Bull.Soc.Chim., (5), 2, 1029 (1935)
26. Khrash, Walling, and Mayo, J.Am.Chem.Soc., 47, 1147 (1925)
27. Paal, Ber., 42, 3930 (1909)
28. Sherrill and Matlack, J.Am.Chem.Soc., 59, 2134 (1937)
29. Zalkind, Vishnyakov, and Morev, J.Gen.Chem.(USSR), 3, 91, (1933)
30. Dupont, Bull.Soc.Chim., (5), 3, 1030 (1936)
31. Campbell and O'Connor, J.Am.Chem.Soc., 61, 2897 (1939)
32. Paul and Hilly, Compt. Rend., 206, 608 (1938)
33. Thompson and Wyatt, J.Am.Chem.Soc., 62, 2655 (1940)
34. Farkas, Trans. Faraday Soc., 35, 906 (1935)

of such a semi-hydrogenation is the cis isomer, and that prolonged contact of this with the catalyst results in isomerization to the trans form. The work of Campbell and Eby and Dupont [30,35] indicates that the same considerations hold when Raney nickel is used as the catalyst.

There does not seem to have been a systematic study of the effect of the various factors, such as concentration of catalyst or acetylene derivative, upon the rate of hydrogenation. Ott and Schroeter[36] have investigated the effect of poisoned catalysts upon the steriochemical course of the reaction and have concluded that the more active catalysts produce more of the cis isomers, but this is probably explained by the concept advanced by Bourgel above.

Present Investigation

Results and Discussion

A new synthesis of potential generality has been developed for symmetrically substituted trienes. This is expected to be of special value in the production of high molecular weight symmetrical trienes, such as 3,5,7,- decatriene, which has been synthesized. The synthesis involves the preparation of acetylene-dimagnesiumbromide through interaction of acetylene and two mols of ethyl-magnesiumbromide. This, in turn, is reacted

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35. Campbell and Eby, J.Am.Chem.Soc., 63, 216,2683 (1941)
36. Ott and Schroeter, Ber., 60, 624 (1927)

with two mols of aldehyde or symmetrical ketone[37,38] and the product, an acetylene-1,4-glycol, semi-hydrogenated to the corresponding olefin glycol[39,40]. Because these olefin glycols in general do not dehydrate to trienes, but rather to dihydrofurans[18], the 1,4-dihaloolefins were prepared by reacting the glycols with anhydrous hydrogenchloride, and subsequently dehydrohalogenating by refluxing in pyridine to yield the substituted trienes.

In the course of the above work, an investigation of the effects of certain variables on the rate of semi-hydrogenation of 4,7-dihydroxy decene-5 was made.

Acetylene dimagnesiumbromide

This compound was first prepared by Jositsch[37] by passing acetylene through an etherial solution of ethyl magnesiumbromide at room temperature until the lower of the two layers which were formed no longer increased in volume. The product of this reaction is exclusively the dimagnesiumbromide, according to the equation below, although it is possible to prepare the mono magnesiumbromide by varying the conditions.

$$2\ C_2H_5MgBr + HC{:}CH \longrightarrow \underset{I}{BrMgC{:}CMgBr} + 2\ C_2H_6$$

It was first noted by Jositsch, and confirmed by others, that if acetylene was passed through the ethyl Grignard for too

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37. Jositsch, Bull.Soc.Chim., (3), 32, 552
38. Dupont, Ann.Chim.Phys., (8), 30, 485 (1913)
39. Salkind and Bessonowa, J.Phys.Chem. (USSR), 53, 284
40. Bourguel, Compt.Rend., 180, 1754 (1925)

long a period of time, the lower layer became pasty and difficult to handle.

In the present investigation it was found that the best yields of the acetylene di-Grignard reagent were obtained when a 50 percent excess of acetylene was passed into the solution of ethyl Grignard and the resulting mixture allowed to stand overnight. It was also noted that the addition of chlorbenzene to a reaction mixture of two layers caused the formation of a homogeneous solution. This led to an investigation of the effect of chlorbenzene upon the reaction. It was found to be an effective solvent for an acetylene di-Grignard that had been jelled through excess use of acetylene, but otherwise did not affect the reaction.

Acetylene glycol

After the proper amount of acetylene had been passed through the ether solution of ethyl Grignard, it was allowed to stand overnight before addition of the carbonyl component. In the preparation of 4,7-dihydroxy decyne-5 it was found that the best yields were obtained when freshly distilled butyraldehyde was added very slowly, without dilution, to a large batch (1.5 moles or more) of acetylene di-Grignard and the complex allowed to stand at least 24 hours. When tetramethyl butynediol (from I and acetone) was

prepared, yields were best from small batches, with hydrolysis necessary before the complex was 12 hours old. Variation of the method of hydrolysis had little effect upon the yield of 4,7-dihydroxy decyne-5, but in the case of tetramethyl butynediol[38] good yields could only be obtained if ammonium chloride were used to decompose the complex. This is undoubtedly because of the greater instability of a tertiary alcohol in the presence of acid. In either case the mixture was kept cold during hydrolysis by means of cracked ice. After the butyraldehyde complex had been stirred well for half an hour in dilute sulphuric acid, the organic layer was separated, washed, and carefully neutralized before removing the excess ether and distilling under vacuum.

$$CH_3CH_2CH_2CHO + BrMgC{\equiv}CMgBr + OHCCH_2CH_2CH_3 \longrightarrow$$

$$CH_3CH_2CH_2\underset{OMgBr}{CH}-C{\equiv}C-\underset{OMgBr}{CH}CH_2CH_2CH_3$$

$$CH_3CH_2CH_2\underset{OMgBr}{CH}-C{\equiv}C-\underset{OMgBr}{CH}CH_2CH_2CH_3 + H_2O \longrightarrow$$

$$CH_3CH_2CH_2\underset{OH}{CH}-C{\equiv}C-\underset{OH}{CH}CH_2CH_2CH_3 + 2\ MgBrOH$$

II

In this manner, overall yields of 70 percent of the acetylene glycols are not unusual when working with carbonyl compounds of seven carbon atoms[18].

Olefin Glycol

The semi-hydrogenation of the acetylene glycols has

previously been studied with respect to the steric-chemical aspects of the reaction. In many cases either the cis or trans isomer of these compounds may be isolated in the pure state by suitable choice of the method of hydrogenation. Thus, rapid catalytic hydrogenation in the presence of Raney nickel yields, in general, practically pure cis isomer. Since the aliphatic cis compounds are in many instances quite resistant to isomerization, it is possible that this configuration might be retained under the mild conditions of the remainder of the process.

There does not seem to be any data on the effect of the many variables upon the rate of reduction of the acetylene glycols. Therefore an investigation of this type was desirable in view of the higher purity of cis isomer obtained upon rapid reduction, and the possibility that some additional light might be shed on the mechanism of the reaction.

Effect of catalyst amount on semi-hydrogenation rate of 4,7- dihydroxy decyne-5, II

The data were obtained in the usual manner by following the pressure change occurring during the course of hydrogenation. The hydrogenator used was similar to that described in Organic Synthesis[41], and was calibrated with maleic acid and platinum black catalyst.

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41. Gilman and Blatt, Org.Syn., Vol. I, p. 61 (Wiley & Sons) Second Ed.

Raney nickel was the catalyst used in the reduction of 4,7-dihydroxy decyne-5 to the corresponding olefin, according to the equation below.

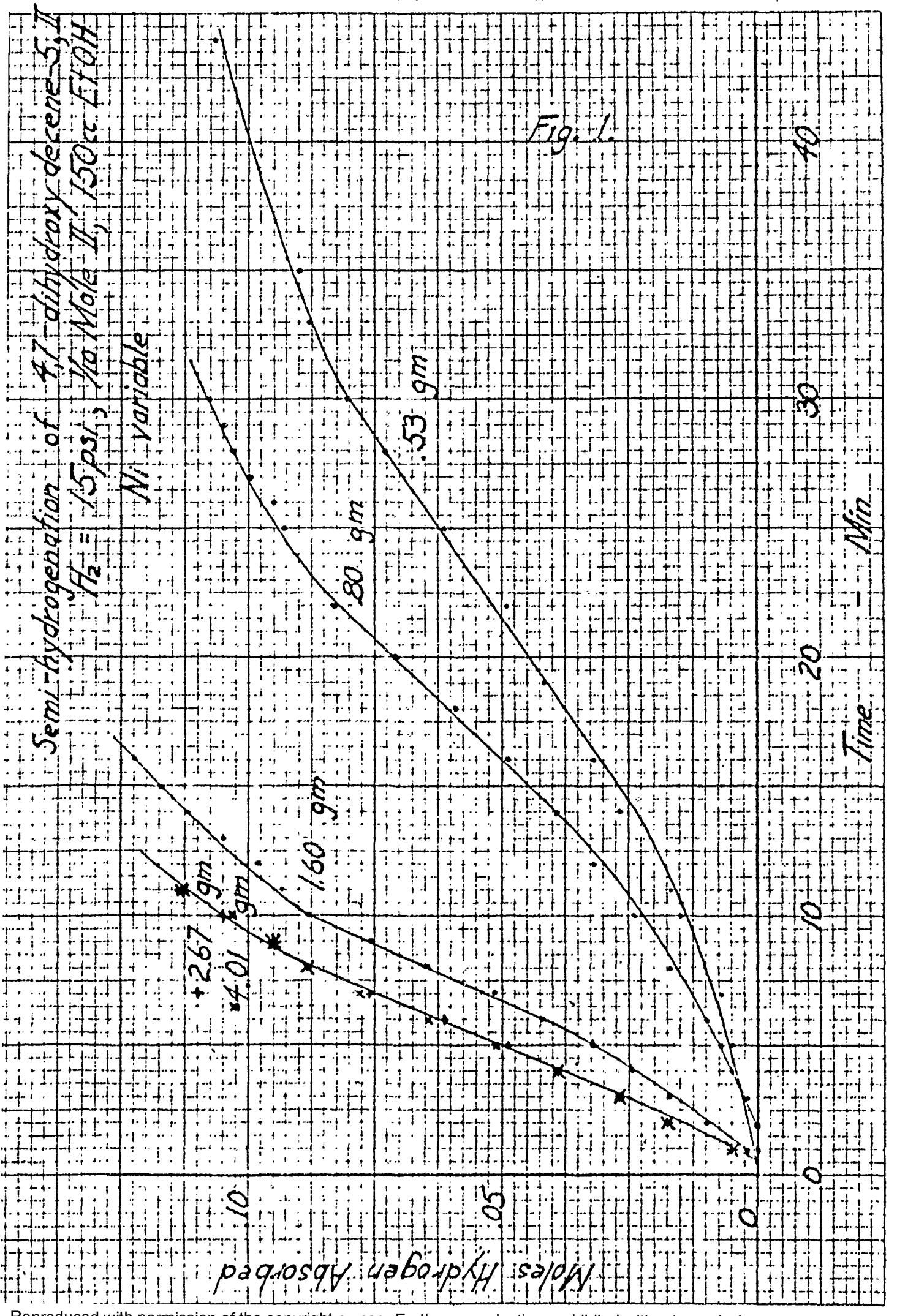
$$CH_3CH_2CH_2\underset{OH}{C}HC{\equiv}C\underset{OH}{C}HCH_2CH_2CH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2\underset{OH}{C}HCH{=}CH\underset{OH}{C}HCH_2CH_2CH_3$$

III

As a matter of convenience, the catalyst was utilized as a suspension in 95 percent ethyl alcohol. To make a run, it was then only necessary to measure a volume of suspension, after vigorously shaking the stock bottle, and add it to a solution of 0.1 moles of 4,7-dihydroxy decyne-5 in 95 percent alcohol. The volume of alcohol was then adjusted so that the total alcohol added was 150cc. Each run was made under an initial pressure of 15 psi of electrolytic Hydrogen.

The data are presented in the form of Figures 1 and 2 which show the moles of Hydrogen absorbed versus the time of reaction. Each curve in these figures represents a variation in the amount of catalyst present, with all other factors constant. The break in the curves at the semi-hydrogenation point is evident, although the reactions were not carried to the completely saturated decane-4,7-diol.

Each curve is linear over the middle portion of the reaction, and this section is taken as representing the inherent rate of reaction. The slope of each curve was determined by the graphical method which was thought to be accurate enought to represent the data. These slopes, or rates, are presented in Table 1.



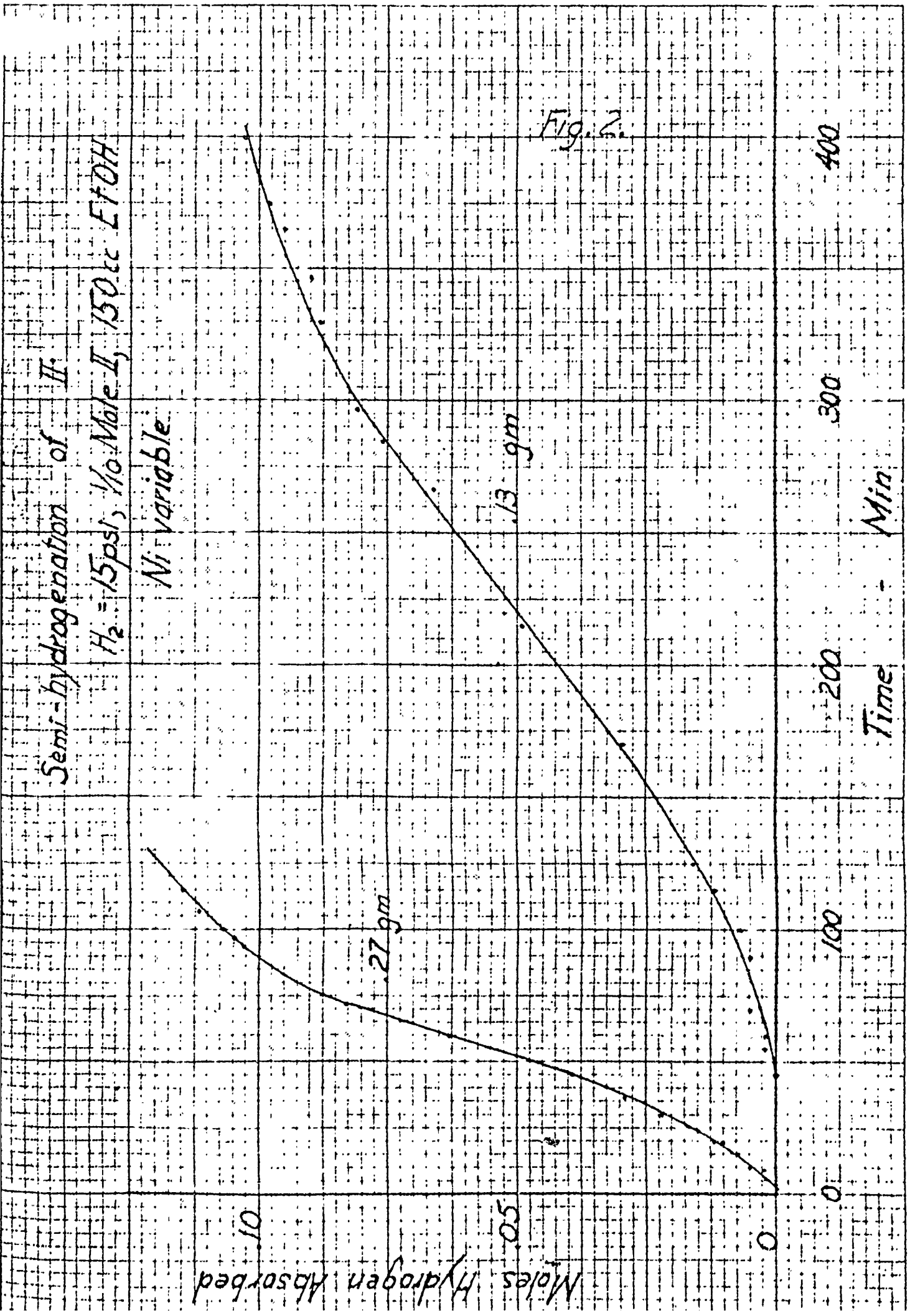


Table 1.

Amount of Catalyst (as grams of dry Ni)	Hydrogenation Rate (moles per min.)
0.13	0.00039
0.27	0.00167
0.53	0.00352
0.80	0.00522
1.60	0.0114
2.67	0.0123
4.01	0.0123

If the rates of Table 1 are plotted against the amount of catalyst which each represents, an interesting curve, Figure 3, is obtained. It is evident from Figure 3 that there is a point beyond which addition of more catalyst does not increase the rate of reaction, whereas below this point the rate is very nearly linear with increasing amount of catalyst.

A logical explanation of this phenomenon might be that as long as hydrogen is capable of dissolving in the liquid phase at a rate in excess of that at which it is used in the hydrogenation, the nickel surface available is the controlling factor in the hydrogenation rate. If, however, nickel is added in such an amount that hydrogenation becomes very rapid, then the rate at which hydrogen dissolves in the liquid phase becomes the slow step which controls the reaction rate. Since this would be determined by the hydrogen

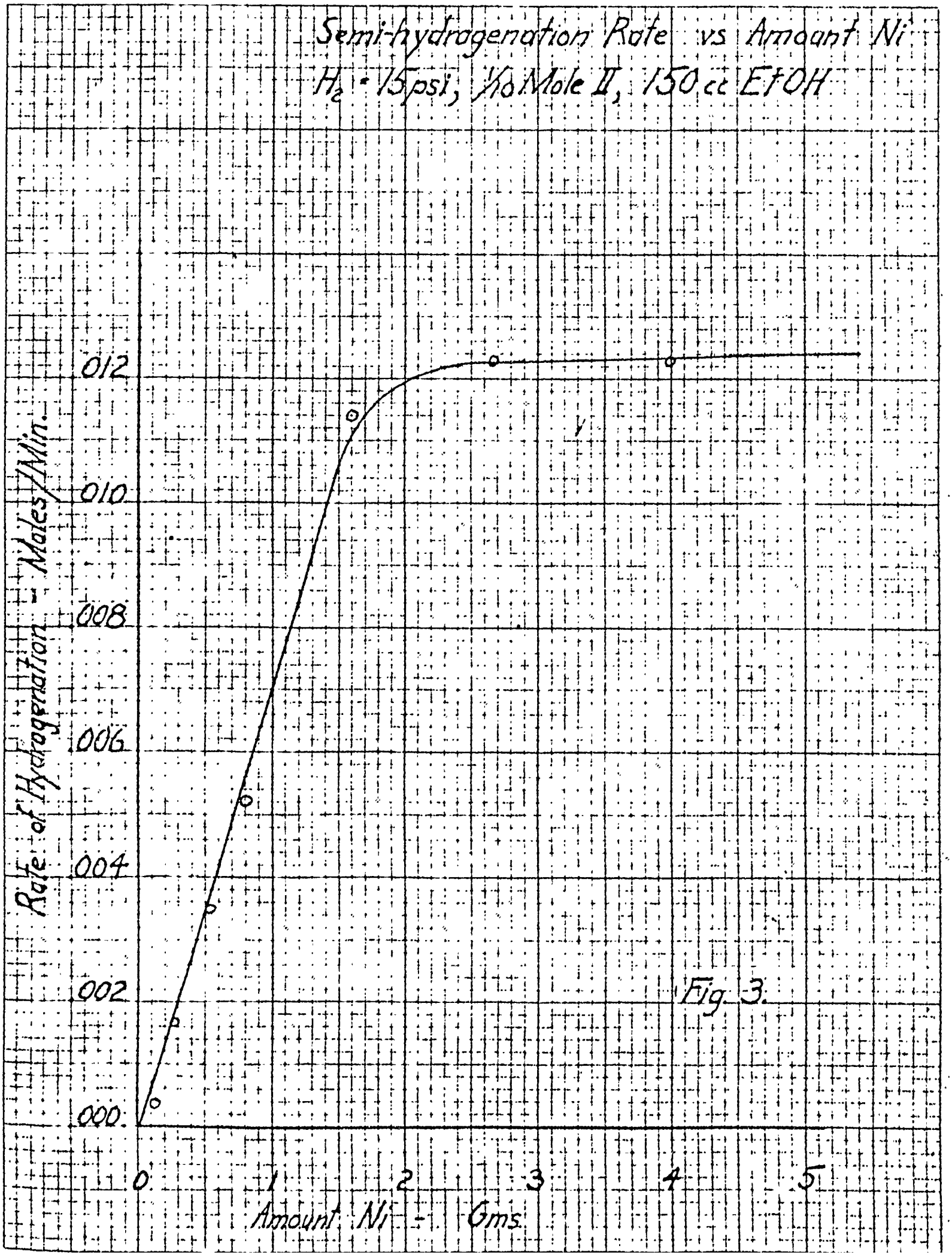


Fig. 3.

pressure, which is maintained equivalent for all experiments, the flat portion of the curve would be expected.

Effect of dilution on semi-hydrogenation rate of 4,7-dihydroxy decyne-5

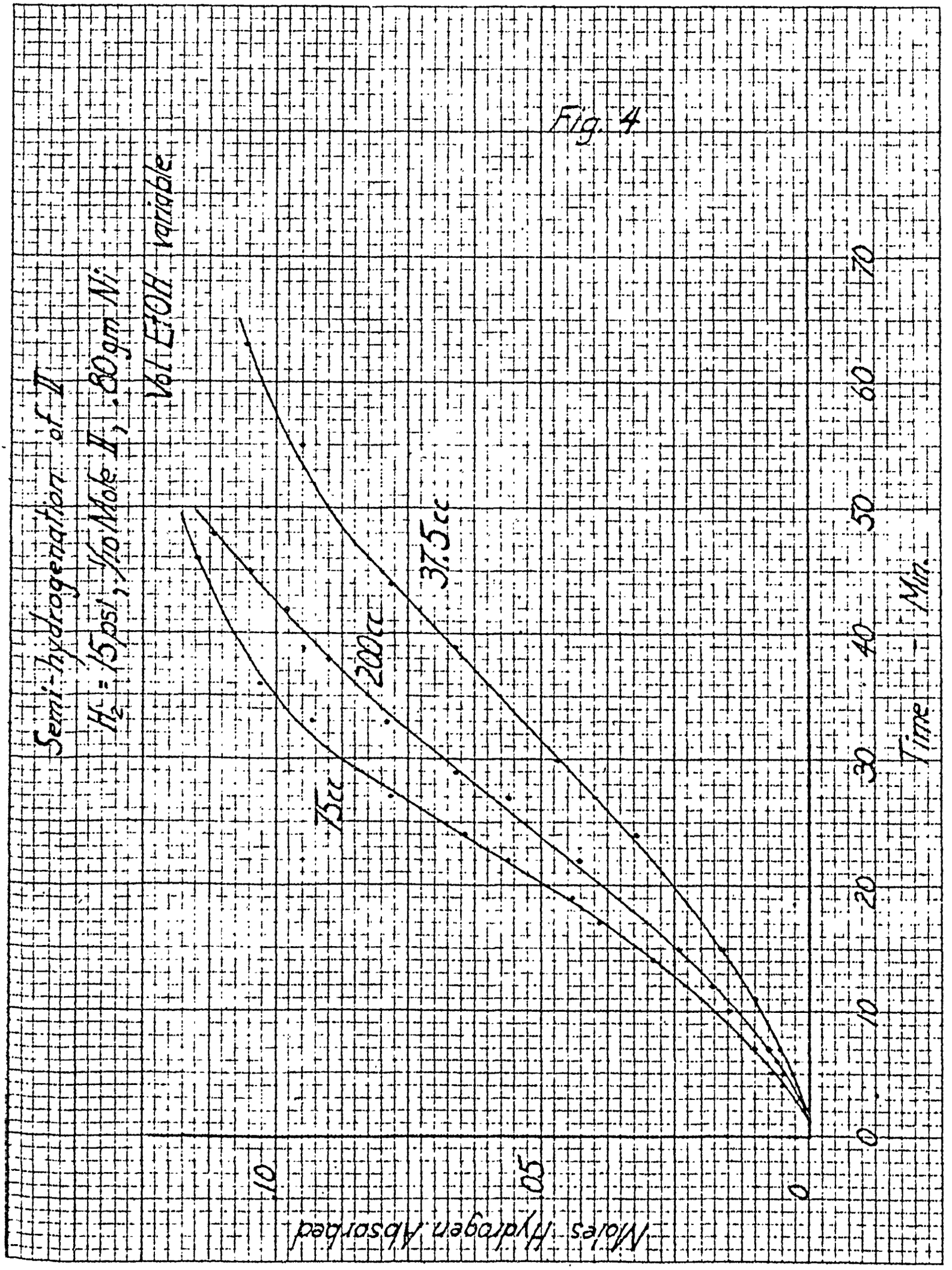
These data were collected in the manner described above and are presented in Figures 4 and 5. The essential feature of this set of data, in contrast to that which will follow, is that the ratio of catalyst to acetylene-diol is maintained constant while the concentration of acetylene-diol is varied.

The rates were once more determined as the slopes of the straight line portions of the curves obtained by the hydrogenation of 0.1 and 0.2 mole portions of 4,7-dihydroxy decyne-5 with 0.80 grams of nickel in various amounts of 95 percent ethyl alcohol. These results are presented in Tables 2 and 3.

Table 2.

0.10 mole II

Cc of Alcohol	Reaction Rate (moles/min.)
37.5	0.00224
75.	0.00387
150.	0.00522
200.	0.00302



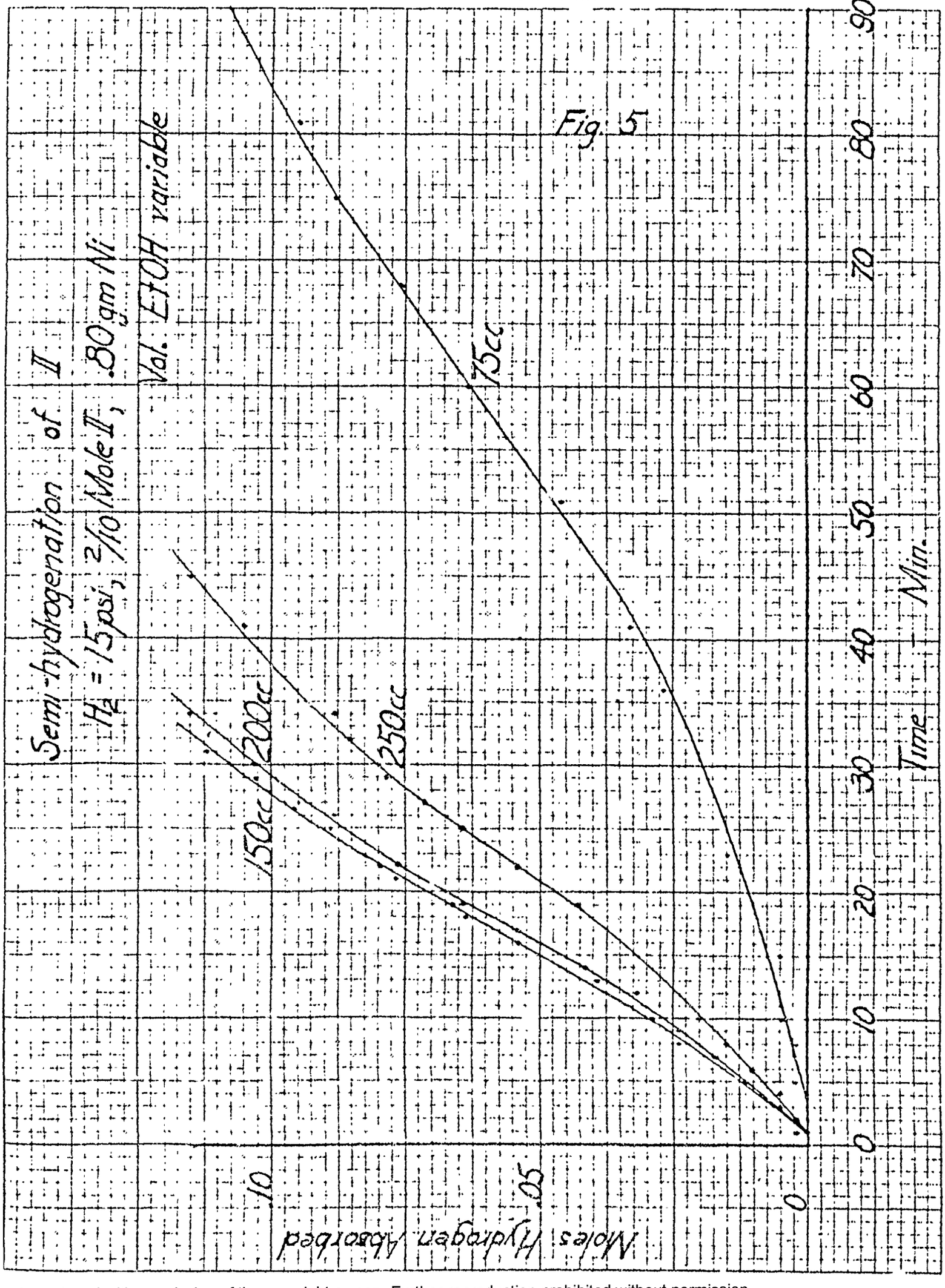


Table 3.

0.20 mole II

Cc of Alcohol	Reaction Rate
75	0.00168
150	0.00435
200	0.00438
250	0.00353

If the data of Tables 2 and 3 are plotted, Figure 6, two more curves of considerable interest result. A maximum is present in each, that for the 0.2 mole being run considerably below that for the 0.1 mole. Each curve might be explained separately by the following reasoning, but it is more difficult to correlate the two.

The activity, or solution pressure, of the dissolved 4,7-dihydroxy decyne-5 varies continuously from higher to lower values as the amount of alcohol in which it is dissolved is increased. Correspondingly, there is a variation in the amount of this compound adsorbed on the surface of the nickel catalyst. The activity of hydrogen is maintained constant throughout, however, through fixation of its pressure at 15 psi. Since it would be expected that the activity ratio of hydrogen to 4,7-dihydroxy decyne-5 would determine the relative amounts of the two compounds adsorbed on the surface of the catalyst, it would also be expected that a maximum would occur in the reaction rate at some dilution where the activity of the acetylene diol is such that an optimum

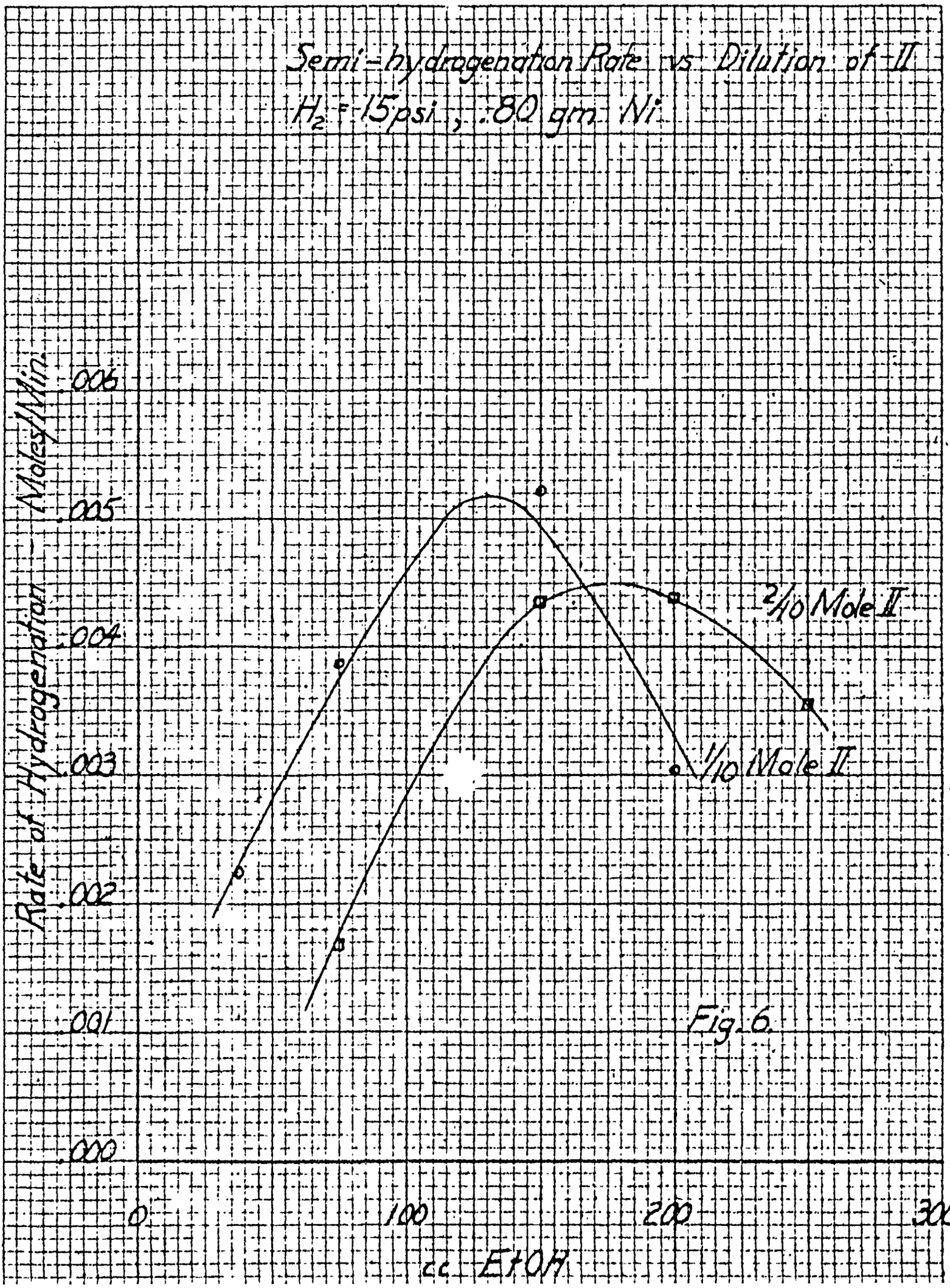


Fig. 6.

balance of such factors as adsorption and adsorption rate in respect to similar factors for the hydrogen is obtained.

If dilution of acetylene glycol were the only factor involved, it would be expected that the rate found for 0.1 mole at a dilution of 100cc would be duplicated for the 0.2 mole run at 200cc. While it is evident that the maximum of the 0.2 mole curve has been shifted in the proper direction, it has not moved far enough nor is it high enough to satisfy this concept.

Effect of concentration of 4,7-dihydroxy decyne-5 on its semi-hydrogenation rate.

The experimental data are presented in Figure 7 and the computed rates given in Table 4. The data represent determinations in which the amount of catalyst and volume of alcohol were maintained constant, while the amount of acetylene compound was varied. Here there is no question of variation of catalyst concentration, so that an explanation of the curve plotted from the data of Table 4 need not consider such a possibility.

Table 4.

Moles of II	Hydrogenation Rate (moles per min.)
0.05	0.00385
0.10	0.00522
0.20	0.00435
0.30	0.00337
0.50	0.00180

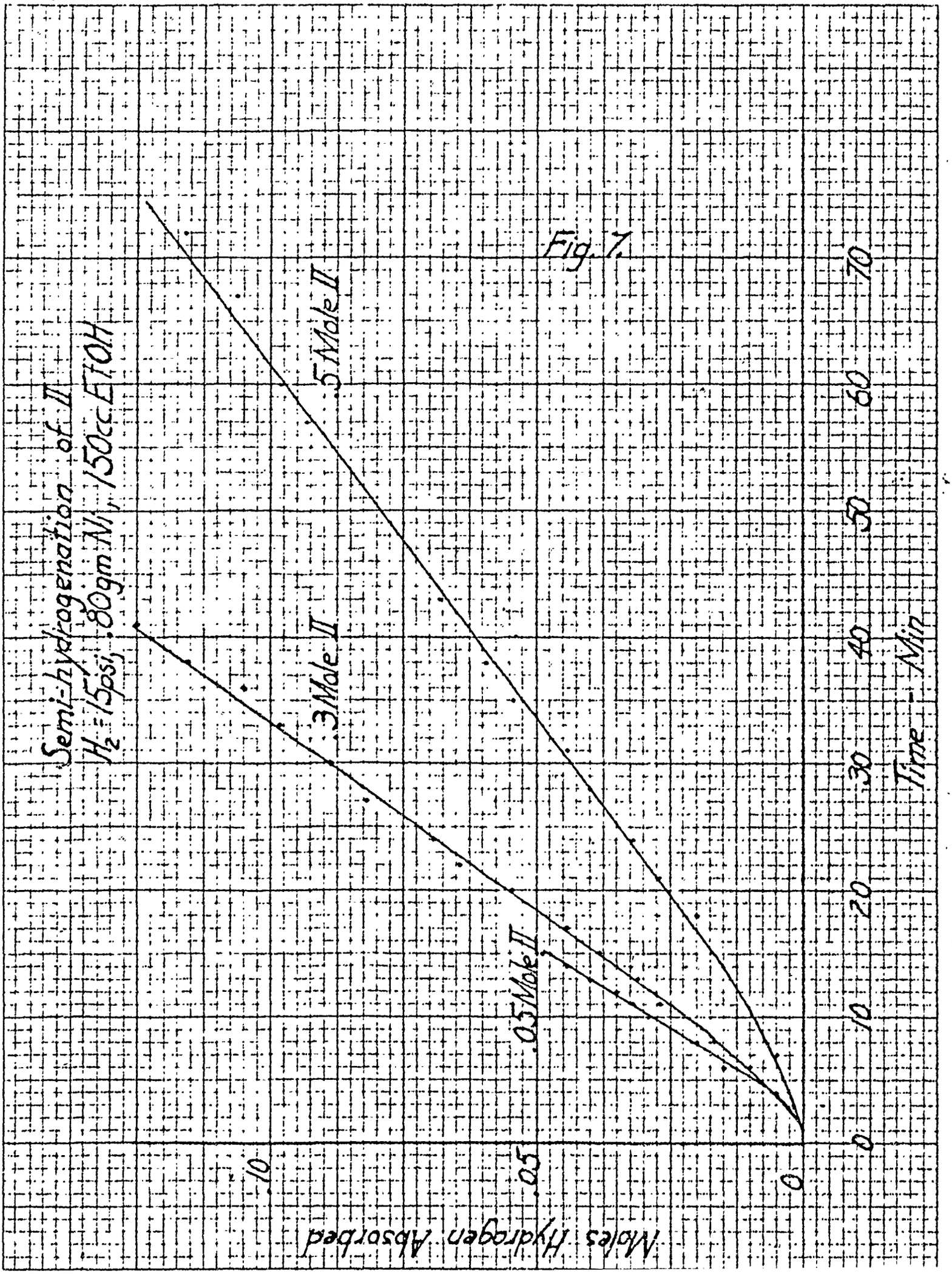


Fig. 7.

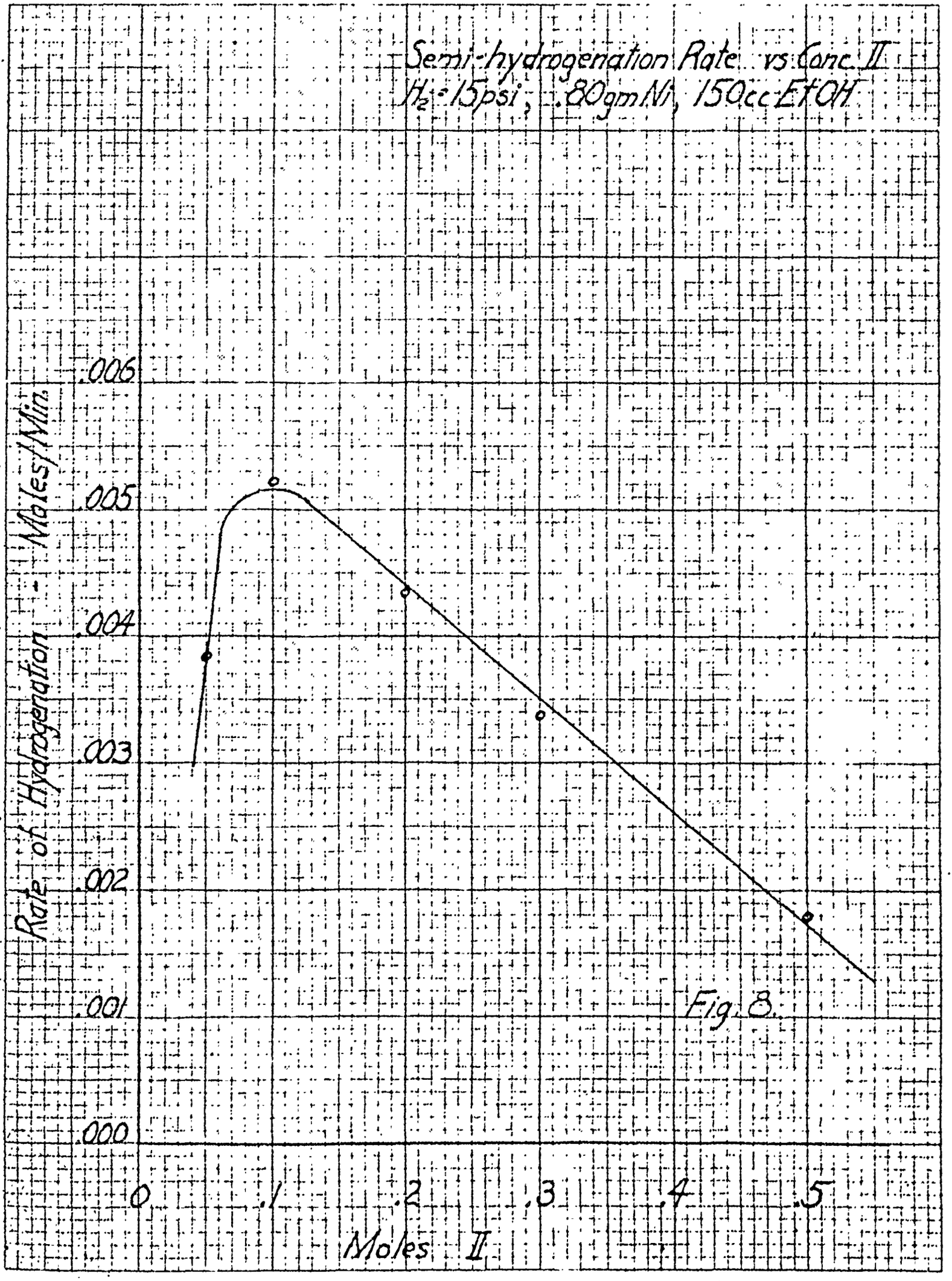


Fig. 8

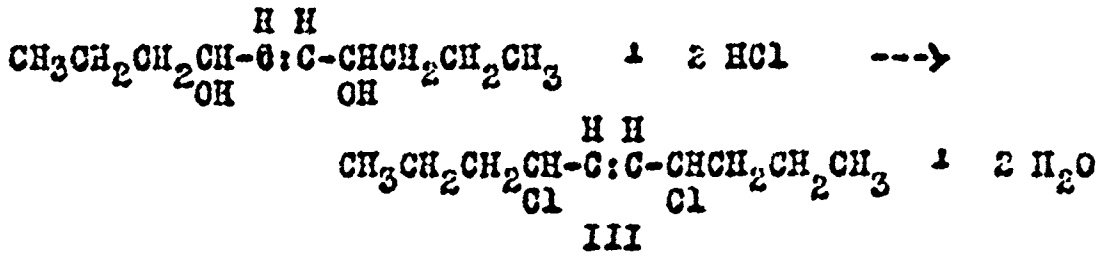
Thus, a possible explanation of the maximum appearing in Figure 6 would be essentially that proposed in the first part of the proceeding section. That is, increasing the amount of acetylene in solution causes an increase in its activity with an attendant change in the ratio of this activity to that of hydrogen, which is fixed by the total hydrogen pressure. Since the ratio of acetylene to hydrogen adsorbed on the surface of the catalyst would be expected to be a function of this activity ratio, there should be a certain acetylene concentration at which optimum adsorption takes place on the catalyst surface. At this concentration a maximum should occur in the rate of hydrogenation.

1,4-diChloroolefin

Considerable difficulty was encountered in the synthesis of 4,7-dichlor decene-5. In every attempt to prepare this compound which involved heating the reactants in the presence of acid, polymerization took place. Thus, dark resins were obtained from the reactions with thionyl chloride, phosphorus trichloride, and phosphorus pentachloride. Heating 4,7-dihydroxy decene-5 in the presence of anhydrous HCl, or even shaking in the cold with a concentrated solution of zinc chloride in aqueous hydrochloric acid, likewise produced only resins. The resins obtained by treating the glycol with phosphorus trichloride seemed to be in the form of

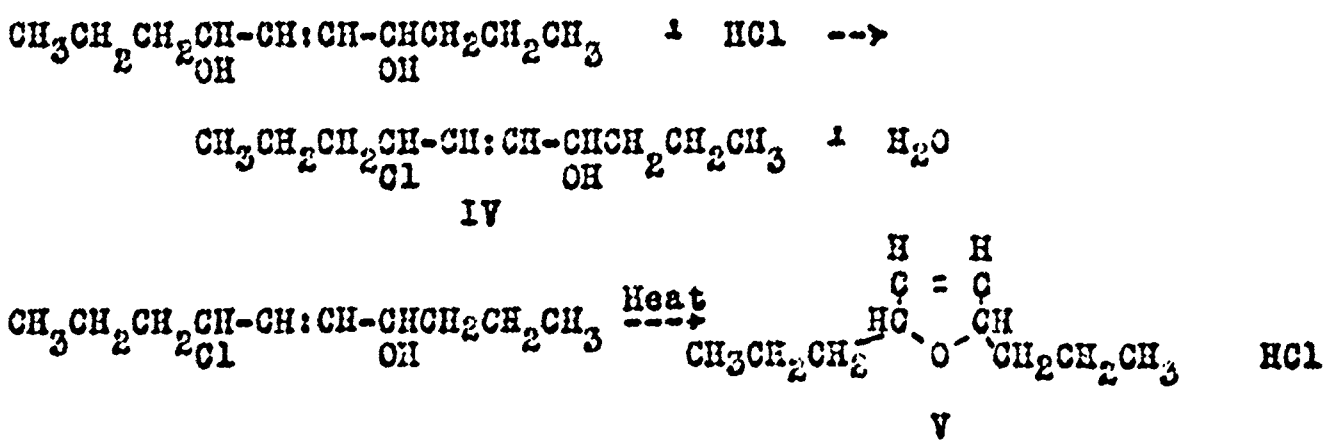
esters of phosphoric acid, for they were soluble in dilute caustic, and reprecipitated by HCl.

The synthesis was finally successfully accomplished by passing anhydrous hydrogen chloride through a petroleum ether solution of the olefin glycol at temperatures below 20°C.



In carrying out the above reaction care must be taken to insure complete reaction, since the presence of the mono-chloro compound leads to the formation of a dihydrofuran derivative during the distillation of the di-chloro compound. This product is exceedingly difficult to remove from the final triene after dehydrohalogenation. The first evidence of this difficulty was noted when an attempt was made to form the di-chloro compound by passing anhydrous HCl through an ethyl ether solution of the olefin glycol. After the reaction had been allowed to take place over a period of six hours at 5°, the product was obtained by washing once with bicarbonate and once with water. Upon distillation, hydrogen chloride was evolved in great quantity. It was at first assumed that this was due to thermal dehydrohalogenation of the di-chlor compound and that triene was being produced as a result. Later, isolation of 2,5 di-

propyl-dihydrofuran indicated that this was not the case. Instead it seems clear that the main product of the reaction as carried out above, was the mono-chlor-mono-hydroxy compound corresponding to IV, which was thermally decomposed to the dihydrofuran, V, on distillation.



The successful preparation of 4,7-dichor decene-5 was accomplished by dissolving the corresponding glycol in petroleum ether and subjecting it to the action of anhydrous HCl at about 15°C. A 40 percent yield was obtained when the reaction time was of the order of 60 hours. The product seemed quite stable to distillation at reduced pressures, but it is probable that increased yields of triene would result were the crude dichlor compound dehydrohalogenated without intermediate purification.

3,5,7 Decatriene

Dehydrohalogenation of the dichlor olefin according to the following equation was the final step of the synthesis.

$$CH_3CH_2CH_2CH\text{-}CH{:}CH\text{-}CHCH_2CH_2CH_3 \xrightarrow[\text{pyridine}]{-\ 2\ HCl} CH_3CH_2CH{:}CH\text{-}CH{:}CH\text{-}CH{:}CHCH_2CH_3$$

VI

Pyridine was selected as the dehydrohalogenating agent because it might be expected to have some polymerization inhibiting properties, and because hydroquinone, an excellent inhibitor, would be more stable in it than in alcoholic alkali. Pure 3,5,7 decatriene was obtained by distilling the crude product under reduced pressure in an atmosphere of nitrogen to prevent oxygen catalized polymerization or air drying in the course of purification.

Drying properties of 3,5,7 decatriene.

Evaluation of 3,5,7 decatriene as a drying oil in the presence of suitable catalysts indicated that the molecular weight of the monomer was not sufficiently high. While reaction set in rapidly and a tack free film was formed within 45 minutes, further oxidation caused the film to break down once more to a tacky oil. Additions of the monomer in the extent of 50 percent and 10 percent to a heat bodied linseed oil had little effect on its properties.

When 3,5,7 decatriene was prepolymerized in the presence of 0.5 percent benzoyl peroxide for 70 hours at 70°C, the material resulting had considerably improved drying characteristics even though polymerization had not gone far enough to increase its viscosity appreciably. Instead of an initial loss

of weight, there was a small, but definite gain accompanied by tack free film formation within one hour. This film was stable for a longer period of time than that formed from the monomer, but it, too, broke down, becoming tacky once more after 24 hours. After one week this film was again practically tack free, but soft. It had lost weight from its maximum until it now weighed less than the original sample.

It is evident that the oxidation of either the monomer or pre-polymerized 3,5,7 decatriene yields volatile products causing an eventual loss in weight. It seems evident that this same oxidation lowers the molecular weight of the film which has been formed, causing it to become tacky after it has once dried to a non-tacky surface. Higher initial polymerization of the monomer should correct these difficulties.

Resins from acetylene di-Grignard

The di-functionality of acetylene di-magnesiumbromide suggested that it might yield interesting resins when condensed with di-functional aldehydes, ketones, or esters.

$$n\ BrMgC{\equiv}CMgBr + n\ CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow \xrightarrow{H_2O}$$

$$\left(\begin{matrix} OH & & OH \\ | & & | \\ -C-CH_2CH_2-C-C{\equiv}C- \\ | & & | \\ CH_3 & & CH_3 \end{matrix} \right)_n$$

Such resins were made with 0.25 moles of each reagent. Resins

prepared from acetonyl acetone ethyl acetate, and benzil were all dark, brittle materials which formed poor films.

Experimental Part

Acetylene di-magnesiumbromide

This was prepared according to the method of Jozitsch[37,38] by passing acetylene for five hours at 150cc/min. through a well stirred solution of 3 moles of ethyl magnesiumbromide in 1500cc of absolute ether contained in a 3 liter, 3 necked flask equipped with a mercury sealed stirrer, reflux condenser, dropping funnel and gas inlet tube.

4,7-dihydroxy decyne-5[42]

After the acetylene di-Grignard had been allowed to stand overnight, 255cc (217 gm, 3 moles) of freshly distilled butyraldehyde was added slowly from the dropping funnel with good agitation over the course of 1½ hours. After the butyraldehyde was completely added, stirring was continued for another hour and the mixture allowed to stand for twenty-four hours before hydrolyzing. Hydrolysis was accomplished by pouring the reaction mixture into 1500cc of 20 percent H_2SO_4 made from 150cc of concentrated acid and 1350 gm of cracked ice. The layers were separated and the aqueous layer extracted once with 200cc of ether, which was then added to the organic layer. The combined organic

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42. Marvel and Williams, J.Am.Chem.Soc., 61, 2714 (1939)

layer was washed once with 100cc of water, once with 100cc of 10 percent sodium carbonate, and finally once again with water. The ether solution was dried over sodium sulphate in the refrigerator overnight, and then the bulk of the ether removed. Distillation at reduced pressure through a glass helices packed column (20mm x 150cm) gave 130 gm (51 percent) of 4,7-dihydroxy decyne-5, BP/1.5mm 116-119°C. Yields of 65 percent have been obtained from larger batches.

4,7-dihydroxy,5,6-dibromodecene-5

A sample of 4,7-dihydroxy decyne-5 was brominated in carbon tetrachloride by adding a carbon tetrachloride solution of Bromine until the color no longer disappeared. Crystalization of the product was induced by cooling while shaking. After two more crystalizations from CCl_4 and one from alcohol-water, the white plates melted at 118.4-118.9 corr.

Analysis	Calc. for $C_{10}H_{18}O_2Br_2$	Found
% Br	48.5	48.3

Tetramethyl Butyne diol[38]

220cc (174 gm, 3 moles) of freshly distilled acetone dissolved in 500cc of absolute ether, was added slowly to 1.5 moles of acetylene di-Grignard dissolved in 1.5 liters of ether. The solution was stirred throughout the addition and for an additional four hours, after which the complex

was decomposed by pouring into a saturated ammonium chloride solution made from 250gm of technical grade NH_4Cl. The layers were separated; the aqueous extracted once with 100cc of ether, and the combined organic washed with water. After the ether was removed, the solid which separated was recrystallized twice from CCl_4 and found to melt at 94.8-95.3°C uncorr. A yield of 71gm (50 percent) of pure material was obtained.

4,7-dihydroxy decene-5

4,7-dihydroxy decyne-5 was hydrogenated in 0.2 mole batches under 15 psi of hydrogen with Raney nickel as the catalyst. The batches were composed of 34.0gm (0.2 mole) of the acetylene, 6cc of a Raney nickel catalyst suspended in alcohol (corresponding to 1.6gm of dry Ni powder), and 150cc of 95 percent ethyl alcohol. This was shaken under hydrogen until 0.2 mole was absorbed, as indicated by the pressure drop. 32.9gm of acetylene glycol after hydrogenation, filtration, and solvent removal, gave 25.0gm (76 percent) of 4,7-dihydroxy decene-5, BP/3mm 126-128.8, $n_{20}^{D} = 1.4640$, $d_{20}^{20} = .9354$.

Analysis	Calc. for $C_{10}H_{20}O_2$	Found
%C	69.8	69.6
%H	11.7	11.3

17.2gm of 4,7-dihydroxy decene-2 absorbed 0.1 mole of hydrogen when dissolved in 150cc of alcohol and treated with an additional

6cc of Raney nickel suspension under 45 psi of hydrogen. The saturated glycol, 4,7-dihydroxydecane MP 79.0-79.5, previously prepared by Marvel and Williams[42] was isolated as the reaction product.

Tetramethyl butene diol[40]

28.4gm (0.2 mole) of tetramethylbutyne diol was dissolved in 150cc of 95 percent ethyl alcohol, and 6cc of Raney nickel catalyst suspension (equivalent to 1.6gm of dry powder) added. This was shaken under 15 psi of hydrogen until 0.2 moles were absorbed. The catalyst was removed by filtration, alcohol stripped off, and the residue recrystalized from petroleum ether. 18.9gms (65.5 percent) of tetramethyl butene diol, MP 69.5-70.8°C uncorr., were obtained.

4,7-dichlorodecene-5

1. Thionyl chloride reaction

7.3cc (12gm, 0.1 mole) of cold thionyl chloride was added slowly to 8.5gm (0.06 mole) of 4,7-dihydroxy decene-5 in 8.05cc (7.9gm, 0.1 mole) of pyridine in a cooling bath. After the addition was complete, the mixture was heated to reflux till fumes of SO_2 were no longer evolved. The reaction was worked up by stirring in 300cc of cold 6 normal sulphuric acid for ½ hour, separating layers, extracting the water layer with ether, washing the organic layer with water and 10 percent

Na_2CO_3, drying over Na_2SO_4, and removing the ether. The residue was a resinous material which gave a strong test for sulphur and chlorine.

2. Phosphorus trichloride reaction

All attempts to use this reagent, whether in solution (pyridine, ether) or undiluted, hot or cold, led only to esters of phosphoric acid, characterized by solubility in alkali and precipitability with acids.

3. Hydrogen chloride reactions

a. 8.5gm (0.05 mole) of 4,7-dihydroxy decene-5 were heated for eight hours over a steam bath, while anhydrous HCl was passed through it at about 75cc/min. The reaction mixture was then dissolved in petroleum ether, washed with water and 10 percent Na_2CO_3, and dried over Na_2SO_4. Distillation of this material at 40mm after the solvent was removed, gave 4.6gm of material boiling below 140° with no indication of any pure cut, and 3gm of resinous still residue.

b. 106gm (0.615 moles) of 4,7-dihydroxy decene-5 were dissolved in 150cc of anhydrous ether and then cooled below 5° in an ice bath. Anhydrous HCl was passed through for 13 hours at 50-75cc/min. while the solution was vigorously stirred. After storing in the refrigerator overnight, the reaction mixture was poured on ice, washed with water, and

10 percent Na_2CO_3, and dried over Na_2SO_4. When the ether was removed, distillation furnished 49cc of material boiling below 80°C at 3mm (with copious evolution of HCl), and 35gm of recovered starting material. Redistillation of the low boiling cut through a micro-column (Vigreux, 10mm x 50cm) at 10mm indicated a boiling range of 65-100° for 43cc of the material. The 20cc boiling from 68-78°C were distilled once more through the micro-column at 13.5mm and the 13cc (10gm, 15.7% yield) boiling at 67.7-69.0°C analized as 2,5-dipropyl-dihydrofuran, $n_{20}^{D} = 1.4412$, $d_{20}^{20} = .8822$

Analysis	Calc. for $C_{10}H_{18}O$	Found
%C	78.0	78.2
%H	11.7	12.0

c. 116gm (0.675 moles) of 4,7-dihydroxy decene-5 were dissolved in one liter of petroleum ether contained in a 2 liter flask equipped with a stirring bubbler, such as that later described by Russel and Vanderwerf[43], and a gas trap to absorb excess HCl. While maintaining the solution at 17°C, and stirring effeciently, anhydrous HCl, saturated with petroleum ether at 17°C, was passed through for 51 hours at 75cc/min. At the end of this period, the solution, treated in two portions, was washed twice with water, twice with 10 percent Na_2CO_3, twice with distilled water, and then dried over Na_2SO_4. After stripping the petroleum ether, the

43. Russel and Vanderwerf, Ind.Chem.Anal. Ed., 17, 269 (1945)

residue distilled 73cc through the large column from 75 to 88°C at 2mm. Redistillation of this fraction through the micro-column gave 48cc (46.5gm, 33 percent yield) which boiled at 64.0-66.5/1.0mm, n_{20}^{D} = 1.4704, d_{20}^{20} = .9986.

Analysis	Calc. for $C_{10}H_{18}Cl_2$	Found
%C	57.4	57.6
%H	8.7	8.6
%Cl	33.9	33.8

Another run of the same type but a 60 hour reaction period gave a 40 percent yield.

3,5,7-decatriene

51gm (0.349 mole) of 4,7-dichlor decene-5, together with 0.1gm of hydroquinone, were dissolved in 200cc of pyridine contained in a 500cc, 3 necked flask equipped with a reflux condenser and mercury sealed stirrer. This was refluxed with stirring for 15 hours, after which it was worked up by pouring into a solution made from 65cc of conc. H_2SO_4 and 1 Kg of cracked ice. The organic layer was washed once with distilled water, and immediately distilled through the micro-column under nitrogen in the presence of 0.1gm of hydroquinone. 13cc (11.9gm, 35.1% yield) distilled from 78.1-79.6°C at 14.8mm, n_{20}^{D} = 1.5274, d_{20}^{20} = .7938

Analysis	Calc. for $C_{10}H_{16}$	Found
%C	88.3	88.1
%H	11.8	11.6

2,5-dimethyl-hexatriene-1,3,5

92.2gm of crude 2,5-dimethyl-2,5-dihydroxyhexene-3 were suspended in one liter of petroleum ether and stirred well at 18° while HCl gas was passed through at 75cc/min. The solid phase disappeared within an hour. After 5 hours, the water layer was separated, the ether washed once with water and once with saturated bicarbonate. It was then cooled to dry ice temperature and 17 gm of crystals which proved to be 2,5-dimethyl-2,5-dichlorhexane (from completely saturated impurity) were removed. The oil was then stripped of solvent, dissolved in 100cc of pyridine and refluxed overnight. After the pyridi was removed through solution in dilute H_2SO_4, the oil was distilled through the small column at 110mm in the presence of hydroquinone. Th first 8cc boiled from 45-45.5°u.c. and proved to be 2,5-tetramethyl-dihydrofuran in 10% yield. The second fraction, 3.5cc, boiled from 45.5-70°, while the 4cc distilling at 70-74° was shown to be the desired triene through formation of the maleic anhydride adduct[17] m.p. 114-5°u.c. The yield of triene was 6%. A considerable amount of polymer was formed in the column and left in the stillpot. An increase in the HCl reaction time is indicated by the appreciable amount of dihydrofuran formed.

Drying properties of 3,5,7-decatriene

a. 0.008gm of Cobalt drier (3.23% Co), 0.008gm of Manganese dr (3.23% Mn), and 0.020gm of Lead drier (14.0% Pb) were added to 0.500g samples of:

1. monomeric 3,5,7-decatriene
2. 50%-monomeric 3,5,7-50% heat bodied linseed oil
3. 10% monomeric 3,5,7-90% heat bodied linseed oil
4. heat bodied linseed oil

Drying was followed by weight changes and visual observations.

b. The same amounts of catalysts were added to a sample

of 3,5,7 decatriene which had been pre-polymerized by treatment with 0.5 percent benzoyl peroxide for 70 hours at 70°C. The slight change in viscosity indicated that polymerization had not gone very far, but the drying properties were definitely improved as indicated by weight changes and visual observation.

Resins from acetylene di-Grignard

Each of the three resins prepared from acetonyl acetone, benzil, and ethyl acetate was obtained through the same procedure. The benzil resin will be illustrative. 0.25 moles of acetylene dimagnesium-bromide were prepared in a 500cc, 3 necked flask equipped with a mercury sealed stirrer, dropping funnel, reflux condenser, and gas inlet tube. Acetylene was passed through 0.5 moles of ethyl Grignard solution dissolved in 250cc of ether in this flask until the volume of the lower layer became approximately 150cc. The solution was then allowed to stand overnight. A solution of 52.5gm (0.25 mole) of benzil in 100cc of absolute ether was then prepared and added dropwise to the acetylene di-Grignard, with vigorous stirring. The complex was allowed to stand overnight before it was hydrolized by pouring into 500cc of cold, 10 percent sulphuric acid. The layers were separated, and the water layer extracted two times with 100cc portions of ether. After washing the combined organic layer with water and bicarbonate, the volatile fraction was removed by steam

distillation. Drying the solid from the foregoing treatment produced a thermoplastic material which was dark in color and did not form good films.

Hydrogenation rate study

a. Effect of varying catalyst amount

For convenience, the Raney nickel catalyst was used as a suspension in alcohol, the amount of catalyst formed from 150gm of alloy after the treatment of Covert and Adkins[44] being suspended in 400cc of 95 percent ethyl alcohol. This was equivalent to 0.267gm of nickel per cc of suspension after the solvent was removed under vacuum. After vigorously shaking the suspension, the indicated amounts of catalyst were measured into a graduate and added to a solution of 17.0gm (0.1 mole) of 4,7-dihydroxy decyne-5 in 95 percent alcohol. The volume of alcohol was then adjusted so that the total added was 150cc. The batch was then shaken under 15 psi of electrolytic hydrogen and the rate of hydrogenation was determined as the slope of the straight-line portion of the curve drawn from the plot of hydrogen disappearance versus time. These rates were, in turn, plotted against the amount of nickel present in the suspension.

b. Effect of varying the amount of 4,7-dihydroxy decyne-5

Each run contained 3cc of catalyst suspension (0.80gm Ni) and a total of 150cc of 95 percent ethyl alcohol, and was made

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44. Covert and Adkins, J.Am.Chem.Soc., 54, 4116 (1932)

at an initial hydrogen pressure of 15 psi. Runs were made with 0.05, 0.10, 0.20, 0.30, and 0.50 moles of 4,7-dihydroxy decyne-5. The hydrogenation curves were plotted as above, and the rates determined from them were plotted against the moles of acetylene compound.

c. Effect of varying the amount of solvent

Two sets of data were collected at an initial hydrogen pressure of 15 psi. The first of these contained 3cc of catalyst (0.80gm Ni) and 0.10 moles of 4,7-dihydroxy decyne-5, and the second 3cc of catalyst and 0.20 moles of the glycol. In each set the total amount of 95 percent ethyl alcohol was varied, rates determined from the straight-line slopes, and these plotted against solvent amount.

Summary

1. A new synthesis of potential generality has been developed for symmetrically substituted trienes. This is expected to be of special value in the preparation of high molecular weight trienes.

2. Several new compounds have been synthesized, among them 3,5,7-decatriene, 2,5-dipropyl-dihydrofuran, 4,7-dihydroxy-decene-5, 4,7-dichlor-decene-5, and 4,7-dihydroxy-5,6-dibromdecene-5.

3. A study of several of the variables in the semi-hydrogenation of 4,7-dihydroxy-decyne-5 has been made with reference to their effect upon the rate of reaction.

4. It has been shown that 3,5,7 decatriene will air dry to a solid film in the presence of the usual catalysts.