these compounds have been compared with those of phosphorus(III) chloride, methanol, the chlorofluorophosphines, and other similar compounds.

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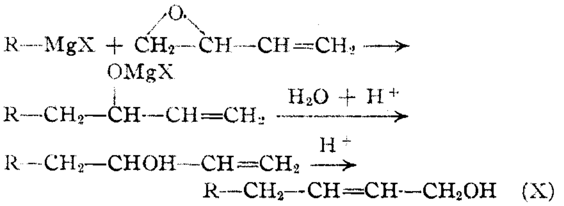
[Contribution from the Department of Chemistry, University of Notre Dame]

# The Preparation and Properties of Some Thienyl Butenols[1a]

By George T. Gmitter[1b] and F. Lee Benton

When α-thienylmagnesium bromide was allowed to react with butadiene monoxide there was obtained a butenol (I) which was tentatively assumed to be 4-(α-thienyl)-buten-2-ol-1. This assumption was based on the preparation by Semeniuk and Jenkins[2] of a series of butenols (to which was assigned the general structure of R—$CH_2$—CH=CH—$CH_2OH$ (X)) by the reaction of various Grignard reagents with butadiene monoxide. They favored the reaction course



$$\mathrm{R{-}MgX} + \overset{\diagup O \diagdown}{\mathrm{CH_2{-}CH}}\mathrm{{-}CH{=}CH_2} \longrightarrow$$

$$\mathrm{R{-}CH_2{-}\overset{\overset{OMgX}{|}}{C}H{-}CH{=}CH_2} \xrightarrow{H_2O + H^+}$$

$$\mathrm{R{-}CH_2{-}CHOH{-}CH{=}CH_2} \xrightarrow{H^+} \mathrm{R{-}CH_2{-}CH{=}CH{-}CH_2OH} \quad (X)$$

as an explanation of the formation of (X) rather than the expected R—$CH_2$—CHOH—CH=$CH_2$. They did not exclude however, the possibility of "1,4-addition" of the Grignard reagent to butadiene oxide. Evidence for assigning the general structure (X) to this series of compounds rested solely on the identification, by physical constants of the product obtained from the reaction of methylmagnesium bromide with butadiene monoxide as penten-2-ol-1. The possibility that isomeric products[3] might result from the reaction of Grignard reagents with butadiene monoxide made it desirable to confirm the tentative structure assigned to (I). Confirmation was obtained in the following manner.

1-(α-Thienyl)-buten-3-ol-2 (II) and 1-(α-thienyl)-buten-3-ol-1 (III)[4] were prepared by the reaction of α-thienylsodium with butadiene monoxide and allylmagnesium bromide with 2-thiophene aldehyde respectively. Attempts to synthesize (II) by an alternate route, the reaction of α-thienylmethylmagnesium chloride with acrolein and the Barbier modification[5] of this method yielded, as the only isolable product,[6] *sym*-di-(α-thienyl)-ethane.

A comparison of the physical constants of (I) with those of II and III indicated (I) is not identical with either compound, a fact which was further confirmed by the difference in melting points of the corresponding 3,5-dinitrobenzoates. Although the three butenols (I), (II) and (III) underwent cleavage on ozonization[7] indicating the presence of an olefinic linkage[8] in their structures, formaldehyde (isolated as a 2,4-dinitrophenylhydrazone) was obtained as an ozonization product only in the case of (II) and (III) but not in the case of (I) a fact indicating that the olefinic linkage in (I) is not terminally located. Failure to obtain acetaldehyde as an ozonization product of (I) was considered to exclude the possibility that (I) possessed the structure Th—CH(OH)—CH=CH—$CH_3$ which could conceivably result if butadiene monoxide rearranged to crotonaldehyde which then underwent a normal reaction with the Grignard reagent.

Dehydration of (I), (II) and (III) yielded an unsaturated intermediate (IV) which, without further purification[9] was converted in each case to the same maleic anhydride addition compound (V) according to the Diels–Alder method.[10]

If the possibility of migration of a thiophene ring from its original position on the butene chain during dehydration is excluded, then the dehydration product (IV) must be 1-(α-thienyl)-butadiene-1,3, the maleic anhydride addition compound (V), 3-(α-thienyl)-$\Delta^4$-tetrahydrophthalic anhydride, the carbon skeleton of (I), $\mathrm{Th{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}}$, and the original butenols must differ only in the

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(1a) Abstracted in part from the dissertation presented to the Graduate School of the University of Notre Dame by George T. Gmitter.

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(2) Semeniuk and Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 118 (1948).

(3) Since the completion of our investigation, Gaylord and Becker (*J. Org. Chem.*, **15**, 305 (1950)) have reported the formation of 1-(1-naphthyl)-buten-3-ol-2 when butadiene oxide reacted with 1-naphthylmagnesium bromide. Jenkins and Semeniuk,[2] on the other hand, report having obtained only 1-(1-naphthyl)-buten-2-ol-4 from the same reaction.

(4) Isobutylene oxide and styrene oxide have been reported by Henry (*Compt. rend.*, **145**, 21 (1907)) and Tiffeneau and Fourneau (*ibid.*, **146**, 697 (1908)) to react as isobutyraldehyde and phenylacetaldehyde, respectively, with Grignard reagents. (III) was synthesized to exclude the possibility that butadiene monoxide had reacted with α-thienylmagnesium bromide in a similar fashion.

(5) Barbier, *Compt. rend.*, **128**, 110 (1899).

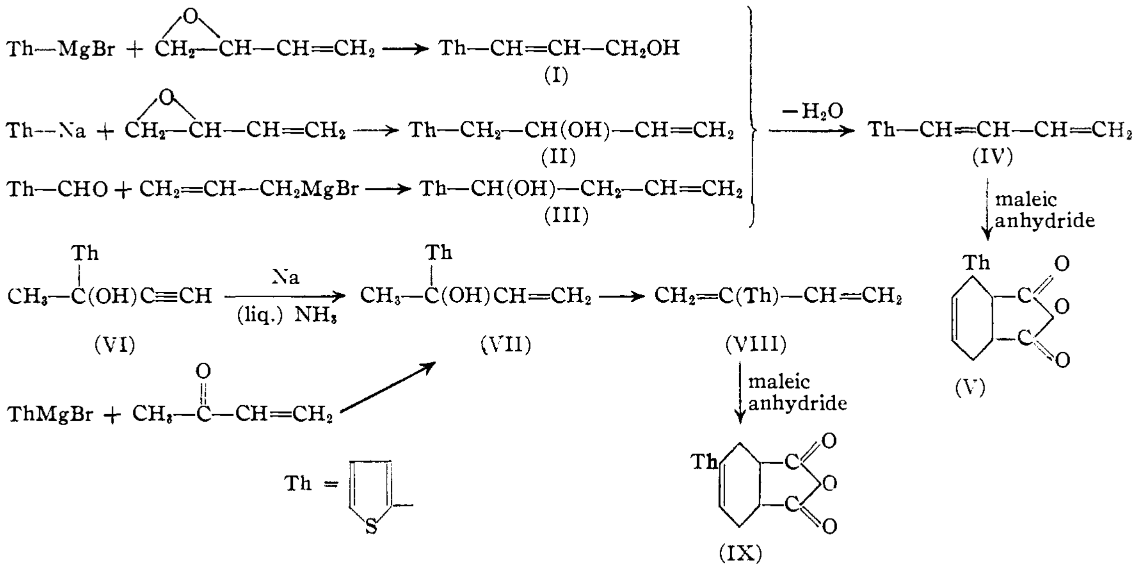
(6) Delaby (*Compt. rend.*, **194**, 1248 (1932)) reported that the reaction of benzylmagnesium bromide with acrolein gave only a 6% yield of benzylvinylcarbinol.

(7) Thiophene under identical conditions was not oxidized.

(8) Attempts to establish the presence of an olefinic linkage in compounds (I), (II) and (III) by catalytic hydrogenation were unsuccessful. The compounds failed to add hydrogen.

(9) The tendency for α-thienyl butadienes to polymerize was so pronounced that attempts to purify these compounds by distillation *in vacuo* and at temperatures as low as 40–50° led to their extensive polymerization.

(10) Diels, Alder and Pries, *Ber.*, **62**, 2081 (1929).



position of the hydroxyl group and the olefinic linkage.

To establish the fact that no migration of the thiophene ring had occurred during dehydration α-thienylmethylethynylcarbinol(VI) was prepared by the reaction of sodium acetylide with 2-acetylthiophene in liquid ammonia. Compound (VI) was then reduced by a solution of sodium in liquid ammonia to 2-(α-thienyl)-buten-3-ol-2 (VII). Confirmation of the structure of (VII) was afforded by its alternate synthesis from α-thienylmagnesium bromide and methyl vinyl ketone. The butenol (VII) was dehydrated to an intermediate (VIII) which, without further purification, was converted to a maleic addition compound (IX). This addition compound (IX) on the basis of mixed melting point and analysis, proved to be isomeric with 3-(α-thienyl)-$\Delta^4$-tetrahydrophthalic anhydride (V). Compound (IX) must, therefore, be 4-(α-thienyl)-$\Delta^4$-tetrahydrophthalic anhydride and the dehydration product (VIII) from which it was obtained, 2-(α-thienyl)-butadiene-1,3.

The principal product obtained by the reaction of α-thienylmagnesium bromide with butadiene monoxide is, therefore, 4-(α-thienyl)-buten-2-ol-1, a conclusion in conformity with the observations of Semeniuk and Jenkins.[2] According to the mechanism favored by these authors, 1-(α-thienyl)-buten-3-ol-2 (II) should be an intermediate which undergoes allylic rearrangement in the formation of (I). Compound (II), however, was found to be stable during hydrolysis of the reaction mixture. Compound (I), therefore, must have resulted from 1,4-addition of the Grignard reagent to butadiene monoxide rather than from rearrangement of (II).

## Experimental

**4-(α-Thienyl)-buten-2-ol-1 (I).**—To a solution of α-thienylmagnesium bromide prepared from 135 g. (0.83 mole) of α-bromothiophene and 20 g. (0.83 gram-atom) of magnesium in 200 ml. of anhydrous ether (cooled in an ice-bath) was added with vigorous stirring, over a period of one and one-half hours, 52 g. (0.75 mole) of butadiene monoxide dissolved in an equal volume of anhydrous ether. After standing for seven hours under an atmosphere of dry nitrogen the reaction mixture was hydrolyzed by pouring it into a mixture of ice and water made slightly acidic with dilute hydrochloric acid. The aqueous portion of the hydrolysate was extracted with ether, the extract added to the organic portion of the hydrolysate and the combined solutions washed first with aqueous bicarbonate, then with saturated brine, and finally dried over anhydrous magnesium sulfate.

The ether was removed by distillation and the residue on careful fractionation under reduced pressure yielded 40 g. (26%) of (I), b. p. 85–86° (2 mm.),[11] $n^{25}\text{D}$ 1.5561, $d^{25}_4$ 1.117.

*Anal.*[12] Calcd. for $C_8H_{10}OS$: C, 62.34; H, 6.49; S, 20.77. Found: C, 61.77; H, 6.46; S, 21.42.

The 3,5-dinitrobenzoate of (I) was prepared in the following manner. To a mixture of 1.0 ml. of (I) and 3.0 ml. of anhydrous pyridine was added 0.5 g. of 3,5-dinitrobenzoyl chloride and the mixture then heated on a steam-bath for ten minutes. After cooling the reaction mixture was poured with stirring into cold water, the resulting precipitate allowed to settle, and the supernatant liquid decanted. The residue was washed with a few milliliters of 5% sodium bicarbonate solution, filtered and, on recrystallization from absolute methanol, melted at 74.5–75°.

*Anal.* Calcd. for $C_{15}H_{12}N_2O_6S$: C, 51.72; H, 3.45; N, 8.04; S, 9.19. Found: C, 52.11; H, 3.44; N, 7.77; S, 9.11.

**1-(α-Thienyl)-buten-3-ol-2 (II).**—α-Thienylsodium was prepared from 50 g. (2.17 gram atoms) of sodium and 118 g. (1.0 mole) of α-chlorothiophene in 600 ml. of benzene according to the procedure of Schick and Hartough.[12a] To this mixture, maintained under a nitrogen atmosphere were added, with vigorous stirring, 70 g. (1.0 mole) of butadiene monoxide in 100 ml. of anhydrous benzene at such a rate that the reaction mixture was held at gentle reflux. Stirring was continued until it had cooled to room temperature and the mixture was then poured into ice and water. The hydrolysate was acidified with dilute hydrochloric acid and the aqueous portion extracted with ben-

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[11] All boiling points and melting points uncorrected.

[12] All analyses by Micro Tech. Laboratories, Skokie, Illinois.

[12a] Schick and Hartough, THIS JOURNAL, **70**, 286 (1948).

zene. The combined benzene extract and organic portion of the hydrolyzate were washed with aqueous sodium bicarbonate, brine, and finally dried over anhydrous magnesium sulfate. After removal of the benzene by distillation under a nitrogen atmosphere, fractionation of the residue under reduced pressure yielded 25 g. (16.2%) of (II), b. p. 80–81° (2 mm.), $n^{25}\mathrm{D}$ 1.5468, $d^{25}{}_4$ 1.106.

*Anal.* Calcd. for $C_8H_{10}OS$: C, 62.34; H, 6.49; S, 20.77. Found: C, 62.08; H, 6.56; S, 18.14.

Preparation of the 3,5-dinitrobenzoate of (II) according to the method previously indicated for the 3,5-dinitrobenzoate of (I) yielded a compound which, on recrystallization from absolute methanol, melted at 89–90°.

*Anal.* Calcd. for $C_{15}H_{12}N_2O_6S$: C, 51.72; H, 3.45; N, 8.04; S, 9.19. Found: C, 52.27; H, 3.55; N, 7.82; S, 9.33.

**1-(α-Thienyl)-buten-3-ol-1 (III).**—To a liter of an ether solution of allylmagnesium bromide prepared from 96 g. (4.0 gram atoms) of magnesium and 145 g. (1.2 moles) of allyl bromide according to the method of Gilman and McGlumphy[13] was added slowly with vigorous agitation a solution of 112 g. (1.0 mole) of α-thiophenealdehyde dissolved 150 ml. of anhydrous ether. Throughout the addition of the aldehyde the reaction mixture was cooled in an ice-bath.

The reaction mixture was then hydrolyzed and treated according to the procedure outlined in the preparation of (I). After removal of ether by distillation, fractionation of the reaction product under reduced pressure yielded 95 g. (61%) of (III), b. p. 76–77° (2 mm.), $n^{25}\mathrm{D}$ 1.5441, $d^{25}{}_4$ 1.108.

*Anal.* Calcd. for $C_8H_{10}OS$: C, 62.34; H, 6.49; S, 20.77. Found: C, 61.65; H, 6.40; S, 20.95.

Preparation of the 3,5-dinitrobenzoate of (III) according to the method of Marvel and Walton[14] yielded a yellow crystalline compound, m. p. 54–55°.

*Anal.* Calcd. for $C_{15}H_{12}N_2O_6S$: C, 51.72; H, 3.45; N, 8.04; S, 9.19. Found: C, 51.58; H, 3.67; N, 8.03; S, 9.06.

**2-(α-Thienyl)-butyn-3-ol-2 (VI).**—Three gram atoms (117.3 g.) of potassium was converted[15] to potassium amide in 1500 ml. of liquid ammonia contained in a three-liter three-necked flask equipped with a mechanical stirrer, liquid ammonia condenser, and protected from atmospheric moisture and carbon dioxide by a soda lime filled drying tower. The mixture, cooled to −50°, was then saturated with dry acetylene for a period of forty minutes after which ether were added 107 g. (0.85 mole) of 2-acetylthiophene dissolved in 100 ml. of anhydrous ether. The reaction mixture was stirred vigorously, held at −50°, and kept saturated with acetylene throughout the addition of the ketone and for five hours thereafter. It was then neutralized by addition of excess ammonium chloride, the ammonia removed by evaporation, and the residue hydrolyzed. The aqueous portion of the acidified hydrolyzate was extracted with ether and the ether extract, combined with the organic portion of the hydrolyzate was washed with aqueous sodium bicarbonate, brine, and dried over anhydrous magnesium sulfate. Removal of the ether by distillation followed by fractionation of the residue under reduced pressure yielded 38.8 g. (30%) of (VI),[16] b. p. 70–71.5° (2 mm.); $n^{20}\mathrm{D}$ 1.5556; $d^{20}{}_4$ 1.1518.

*Anal.* Calcd. for $C_8H_8OS$: C, 63.15; H, 5.27; S, 21.08. Found: C, 62.03; H, 5.44; S, 21.35.

**2-(α-Thienyl)-buten-3-ol-2 (VII).**—A. Methyl-α-thienylethynylcarbinol (VI), 20 g. (0.13 mole), was reduced by sodium in liquid ammonia according to the method of Campbell and Eby.[17] The crude product was freed from traces of the unreduced acetylenic carbinol by extracting its ether solution with Tollens reagent, after which it was washed with brine and dried. The ether was removed by evaporation under reduced pressure and the residue on fractionation, likewise under reduced pressure, yielded 4 g. (20%) of (VII), b. p. 66–67° (2 mm.), $n^{25}\mathrm{D}$ 1.5431.

B.—To a solution of α-thienylmagnesium bromide in 400 ml. of ether prepared from 163 g. (1.0 mole) of α-bromothiophene and 24.3 g. (1 gram atom) of magnesium were added slowly and in dropwise fashion a solution of 54.5 g. (0.79 mole) of methyl vinyl ketone in 200 ml. of anhydrous ether. During this addition the reaction mixture was vigorously stirred and cooled. The reaction mixture was then hydrolyzed and treated according to the procedure outlined in the preparation of (I). After removal of ether by distillation under reduced pressure, fractionation of the reaction product under reduced pressure yielded 7.0 g. (4.5%) of (VII), b. p. 66–68° (2 mm.); $n^{25}\mathrm{D}$ 1.5428. The portions of (VII) obtained from procedures (A) and (B) were combined and redistilled under reduced pressure, b. p. 66–67° (2 mm.); $n^{25}\mathrm{D}$ 1.5430, $d^{25}{}_4$ 1.074.

*Anal.* Calcd. for $C_8H_{10}OS$: C, 62.34; H, 6.49; S, 20.77. Found: C, 62.50; H, 6.45; S, 20.65.

**Ozonization.**—Three-gram samples of (I), (II) and (III) dissolved in 50 ml. of low-boiling ligroin were ozonized at 0° and the ozonide decomposed according to the method of Whitmore and Church.[18] Decomposition of the ozonides of (II) and (III) yielded as one of the products formaldehyde, isolated as 2,4-dinitrophenylhydrazone, m. p. 165°. The identity of this compound was further confirmed by mixed melting point with an authentic sample, the 2,4-dinitrophenylhydrazone of formaldehyde. No formation of formaldehyde 2,4-dinitrophenylhydrazone was observed when the ozonide of (I) was decomposed.

**Dehydration of Butenols.**—A 10-g. sample of the butenol to be dehydrated was mixed with an equal weight of anhydrous potassium acid sulfate together with a trace of hydroquinone and introduced into a 50-ml. Claisen flask attached to a receiver cooled in a bath of Dry Ice–acetone. The flask was then heated to 80° over a period of one-half hour and kept at 80–90° for one hour in the case of (VII) or heated to 100° over one-half hour and kept at 100–110° in the cases of (II) and (III). A pressure of 2 mm. was maintained in the apparatus throughout the period of heating and the material collected in the receiver consisted of a mixture of ice and approximately 1–2 g. of an organic substance which was immediately separated from the ice, dried over anhydrous magnesium sulfate, and without further purification[8] converted to the corresponding tetrahydrophthalic anhydride derivative.

Dehydration of (I) was carried out in the manner just described for (VII) except that pulverized potassium hydroxide pellets were used instead of anhydrous potassium acid sulfate.

**3-(α-Thienyl)-Δ⁴-tetrahydrophthalic Anhydride (V).**—A solution of 2 g. of maleic anhydride and 3 g. of 1-(α-thienyl)-butadiene-1,3 (IV), obtained by the dehydration of (I) and dissolved in 20 ml. of anhydrous benzene, was heated for three hours at 90°. The product which crystallized from the reaction mixture on cooling, was filtered, and after four recrystallizations from a mixture of benzene and low-boiling ligroin, yielded 0.17 g. of a colorless compound (V), m. p. 100–101°.

*Anal.* Calcd. for $C_{12}H_{10}O_3S$: C, 61.53; H, 4.27; S, 13.63. Found: C, 61.06; H, 4.44; S, 13.80.

When the products obtained by the dehydration of (II) and (III) were derivatized according to the same procedure, crystalline compounds were obtained whose identity with (V) was established by absence of depression in their mixed melting points with (V).

**1-(α-Thienyl)-1,4,4a,9a-tetrahydroanthraquinone and 1-(α-Thienyl)-anthraquinone.**—A mixture of 2 g. of 1,4-naphthoquinone and 2 g. of 1-(α-thienyl)-butadiene-1,3-(IV) was heated in a steam-bath for two hours. The

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(13) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

(14) Marvel and Walton, *J. Org. Chem.*, **1**, 88 (1942).

(15) Vaughn, Vogt and Nieuwland, This Journal, **56**, 2120 (1934).

(16) This acetylenic carbinol which darkens rather rapidly on exposure to light and air may be stabilized by addition of a trace of hydroquinone.

(17) Campbell and Eby, This Journal, **63**, 216 (1941).

(18) Whitmore and Church, *ibid.*, **54**, 3710 (1932).

product after six recrystallizations from 95% ethanol yielded 0.6 g. of 1-(α-thienyl)-1,4,4a,9a-tetrahydroanthraquinone, m.p. 159–160°.

Oxygen was bubbled through a solution of 0.5 g. of the 1-(α-thienyl)-tetrahydroanthraquinone dissolved in 25 ml. of 0.2 *N* alcoholic sodium hydroxide until the solution changed from red to colorless and an almost quantitative yield of 1-(α-thienyl)-anthraquinone had precipitated therefrom. It crystallized from 95% ethanol as yellow needles, m. p. 175.5–176.5°.

*Anal.* Calcd. for $C_{18}H_{10}O_2S$: C, 74.48; H, 2.90; S, 11.03. Found: C, 74.22; H, 3.78; S, 11.08.

**4-(α-Thienyl)-Δ⁴-tetrahydrophthalic Anhydride (IX).**—One gram of 2-(α-thienyl)-butadiene-1,3 (VIII) obtained by the dehydration of (VII) was converted to (IX) according to the method previously indicated, yielding a colorless crystalline compound which after four recrystallizations from a benzene–low boiling ligroin mixture melted at 112–113°.

*Anal.* Calcd. for $C_{12}H_{10}O_3S$: C, 61.53; H, 4.27; S, 13.63. Found: C, 61.52; H, 4.25; S, 13.71.

Depression of the melting point of a mixture of (V) and (IX) confirmed the lack of identity between them.

**Acknowledgment.**—The authors wish to acknowledge the assistance of Dr. K. N. Campbell during the portions of the investigation concerned with ozonization and to Drs. C. C. Price, Ernest Eliel and G. F. Hennion for their advice and interest.

## Summary

A series of α-thienyl substituted butenols has been prepared, characterized, and their dehydration products studied. The product obtained by the reaction of α-thienylmagnesium bromide with butadiene monoxide has been identified as 4-(α-thienyl)-buten-2-ol-1 formed by 1,4-addition.

NOTRE DAME, INDIANA RECEIVED JANUARY 13, 1950

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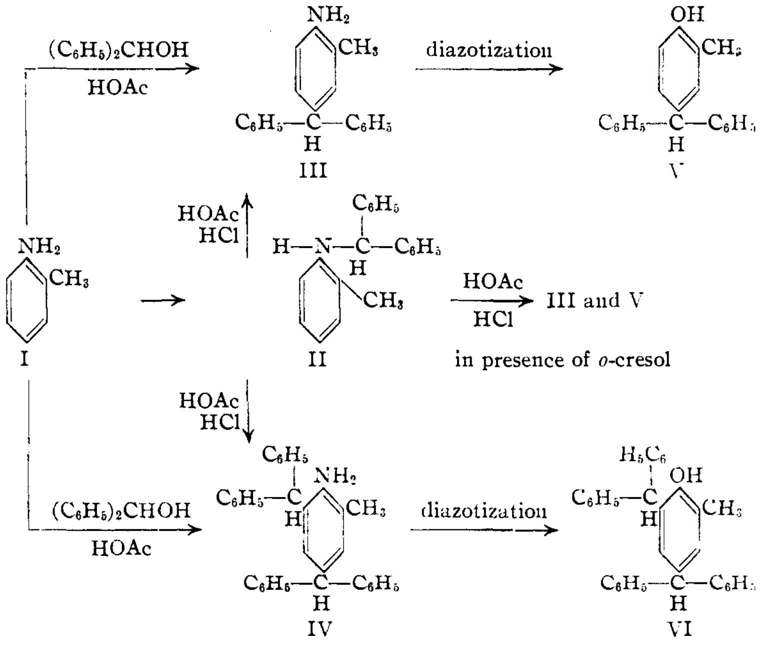
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE]

# Rearrangement of N-Diphenylmethyl-*o*-toluidine

BY H. A. IDDLES AND W. L. HARTOP, JR.

In earlier studies concerning the rearrangement of the triphenylmethyl ether of *o*-cresol and of N-triphenylmethyl-*o*-toluidine, as well as in the related direct introduction of the triphenylmethyl radical into the para position of either *o*-cresol or of *o*-toluidine, the entrance of only one triphenylmethyl radical has been observed.[1] In extending these observations, the less highly substituted diphenylmethyl ether of *o*-cresol was rearranged; the conditions were determined leading to the direct introduction of one and two radicals into the nucleus and the orientation of the products was established by direct syntheses.[2]

The elucidation of these structures has now been utilized in interpreting the analogous introduction of the diphenylmethyl radical into *o*-toluidine and in extending the earlier work of Busch and Rinck[3] who prepared N-diphenylmethyl-*o*-toluidine II from benzylidene-*o*-toluidine and phenylmagnesium bromide and found that this material, when heated with *o*-toluidine hydrochloride in a sealed tube at 210°, rearranged to give a product which they postulated to be 2-methyl-4-diphenylmethyl aniline III.



In this study a direct condensation of *o*-toluidine with diphenylcarbinol in acetic acid medium led to the production of a mixture of products. These could be separated by the precipitation of the sulfate salt of a mono-substituted product III and the recovery of an ether-soluble fraction which was proved to be the disubstituted product IV. Each of these free amines was diazotized and converted to the corresponding phenols V and VI, whose derivatives proved to be identical with the analogous products previously characterized in the *o*-cresol series.[2]

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(1) (a) Iddles and Minckler, THIS JOURNAL, **62**, 2757 (1940); (b) Iddles and Hussey, *ibid.*, **63**, 2768 (1941).

(2) Iddles, Chadwick, Clapp and Hart, *ibid.*, **64**, 2154 (1942).

(3) Busch and Rinck, *Ber.*, **38**, 1761 (1905).