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

Oxygen was bubbled through a solution of 0.5 g. of the 1-($\alpha$-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-($\alpha$-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-($\alpha$-Thienyl)-$\Delta^4$-tetrahydrophthalic Anhydride (IX).**—One gram of 2-($\alpha$-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 $\alpha$-thienyl substituted butenols has been prepared, characterized, and their dehydration products studied. The product obtained by the reaction of $\alpha$-thienylmagnesium bromide with butadiene monoxide has been identified as 4-($\alpha$-thienyl)-buten-2-ol-1 formed by 1,4-addition.

NOTRE DAME, INDIANA RECEIVED JANUARY 13, 1950

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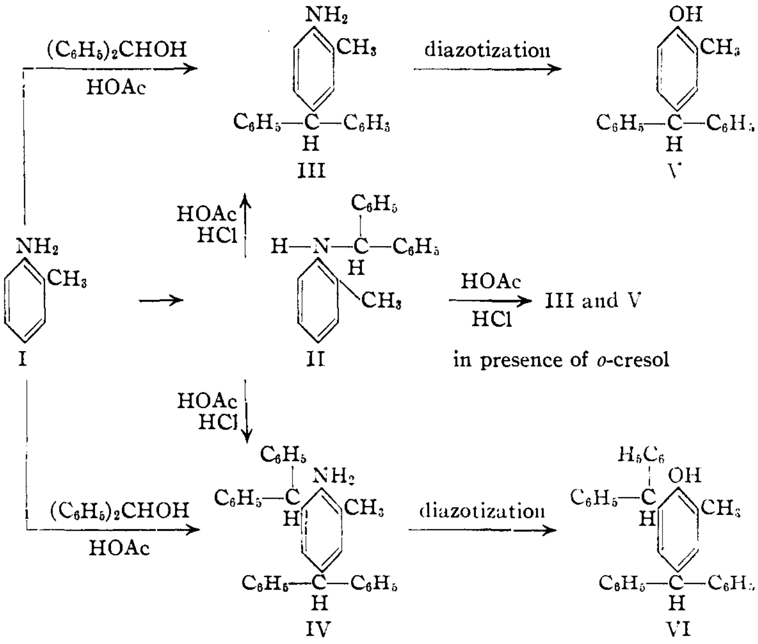
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE]

# 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).

As the next step the N-diphenylmethyl-*o*-toluidine II was rearranged by heating in an acetic acid-hydrochloric acid medium. When the reaction mixture was made alkaline and subjected to steam distillation, *o*-toluidine came over leaving the rearrangement products which were recovered as in a direct condensation and consisted of the mono and disubstituted derivatives, the latter in a molar quantity corresponding to the quantity of *o*-toluidine produced. The identity of products III and IV prepared by direct condensation or by rearrangement was demonstrated since no depression was observed in a mixed melting point comparison of the acetyl and benzoyl derivatives of each compound. A further rearrangement of compound II in the presence of *o*-cresol and in the same acid medium gave a reaction mixture from which the *p*-monosubstituted amine III and the analogous phenolic derivative V were recovered and identified.

These direct condensations and rearrangements demonstrate the possibility of introducing two diphenylmethyl radicals into the nucleus of *o*-toluidine in exact analogy to the work in the *o*-cresol series. Further the course of the reaction is shown to be intermolecular in character from three points of evidence (1) the migration of one group to the para position indicates a reaction of intermolecular type(2),[4] the production of the disubstituted derivative and an equivalent amount of *o*-toluidine from II must involve an intermolecular change, (3) the transfer of a diphenylmethyl group from compound II to a foreign molecule, *o*-cresol, offers further evidence of an intermolecular change.

## Experimental

**Direct Condensation of *o*-Toluidine and Diphenylcarbinol.**—Ten grams of *o*-toluidine hydrochloride and 19 g. of diphenylcarbinol were dissolved in 50 ml. of glacial acetic acid and refluxed for three hours. The resulting dark red solution was added to an excess of saturated sodium bicarbonate solution producing a tan spongy mass. The supernatant liquid was decanted and the residue was heated with 300 ml. of very dilute sodium hydroxide, then cooled and extracted with ether. Upon evaporation of the ether, a reddish-brown oil consisting of the disubstituted and monosubstituted products resulted. These products were separated by pouring into 3.5 liters of hot dilute sulfuric acid, made by dissolving 100 ml. of concentrated sulfuric acid in 3.5 liters of water, forming the sulfate salt of the monosubstituted product which crystallized out upon cooling while the disubstituted product remained as a brown amorphous mass. The differing character of the two solids made possible the separation of the suspended crystalline sulfate from a bottom solid layer. The sulfate salt was purified by several extractions with hot ether and these ether washings were combined with the ether-soluble brown amorphous layer. Final purification of the sulfate salt was accomplished by suspending in hot ligroin to remove trace impurities leaving the insoluble salt in a yield of 9.7 g., m. p. 151°. From the combined ether extracts 14.4 g. of a viscous brown oil was purified by distillation at 260–275° and 2 mm. pressure and recrystallized from 95% ethyl alcohol yielding 8.1 g. of the disubstituted product, m. p. 112.5–113°.

*Anal.* Calcd. for $C_{33}H_{29}N$: N, 3.17. Found: N, 3.14, 3.19.

The total yield on the basis of the *o*-toluidine hydrochloride used was 70%.

**Isolation of Product III.**—To isolate the monosubstituted product from its sulfate salt, 10 g. was heated with 15% NaOH yielding an oil which was taken up in ether, washed and dried. Upon evaporation of the ether, the residue was vacuum distilled at 196–202° and 2 mm. pressure, yielding a solid product which was recrystallized from 95% ethyl alcohol, m. p. 69–70°.

*Anal.* Calcd. for $C_{20}H_{19}N$: N, 5.12. Found: N, 5.02, 5.16.

**Preparation of N-Diphenylmethyl-*o*-toluidine.**—The N-derivative was prepared according to the directions of Busch and Rinck[3] in a 35% yield, m. p. 83–84°.

*Anal.* Calcd. for $C_{20}H_{19}N$: N, 5.12. Found: N, 5.21.

***Preparation of Rearranged Products from N-Diphenylmethyl-o-toluidine.***—To carry out a direct rearrangement, 30 g. (0.11 mole) of the N-diphenylmethyl-*o*-toluidine was refluxed in a glacial acetic acid–hydrochloric acid mixture (150 ml. and 45 ml.) for four hours, then cooled and made basic, producing the free organic bases. The mixture was steam distilled as long as any *o*-toluidine came over. By means of ether extraction of the distillate, a final recovery of 2.9 g. of *o*-toluidine, b. p. 198°, resulted. It was characterized by forming the 3,5-dinitrobenzoyl derivative, m. p. 135° and the phenyl isothiocyanate derivative, m. p. 136°, each of which corresponded with similar derivatives prepared from a known sample of *o*-toluidine. The oily residues from the steam distillation were extracted with ether, the ether distilled off and the resulting oil added to hot dilute sulfuric acid. The recovery and separation of the two rearranged products III and IV followed the procedure outlined under the direct condensation with the following results in two parallel runs:

| | Run I | | Run II | |
|---|---|---|---|---|
| | grams | moles | grams | moles |
| Monosubstituted sulfate salt | 12.9 | 0.020 | 15.0 | 0.023 |
| Disubstituted product | 11.6 | .026 | 9.5 | .022 |
| *o*-Toluidine | 2.9 | .027 | 2.6 | .024 |
| Total yield, % | 84.5 | | 83.5 | |

This isolation of both the monosubstituted product and the disubstituted product points to an intermolecular mechanism and it is further noted that for each molecule of the disubstituted product formed a molecule of *o*-toluidine was also formed.

**Rearrangement of N-Diphenylmethyl-*o*-toluidine in the Presence of *o*-Cresol.**—Twenty grams of N-diphenylmethyl-*o*-toluidine and 10 g. of *o*-cresol was refluxed for two hours in a glacial acetic acid–concd. hydrochloric acid mixture (150 ml.–45 ml.). It was then poured into 4 l. of water and the precipitated material was extracted with ether, followed by several washings with 10% sodium hydroxide to remove unreacted *o*-cresol. After drying the ether extract, the ether was distilled off and the resultant reddish-orange oil was taken up in ligroin and extracted with Claisen solution which yielded an oil upon acidification and this was distilled at 212–215° at 2 mm. pressure. To surmount difficulties in crystallization it was methylated with dimethyl sulfate producing a methyl ether which crystallized from ethyl alcohol and melted at 75.3°. A mixed melting point with a synthetic product (1a) was 75.4° proving the original phenolic product to be V.

The ligroin layer was evaporated and the residue poured into 3.5 liters of hot dilute sulfuric acid from which 1.8 g. of the sulfate salt of III was obtained. Neither the disubstituted *o*-toluidine derivative nor the analogous *o*-cresol derivative was recovered.

**Characterization of Product III.**—The acetyl derivative of the monosubstituted product III was prepared by dissolving 1 g. of material, 0.3 ml. of acetic anhydride and 0.3 g. of sodium acetate in 10 ml. of glacial acetic acid which was then refluxed for two hours. The reaction

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[4] Behagel and Freiensehner, *Ber.*, **67**, 1368 (1934); Short and Stewart, *J. Chem. Soc.*, 553 (1929); Hickinbottom, *Nature*, **142**, 630 (1938); **143**, 520 (1939).

mixture was poured into water, filtered and dissolved in a minimum of ethyl alcohol and treated with Norite. Final recrystallization from ligroin gave a fine needle-like product melting at 151–152°. *Anal.* Calcd. for $C_{22}H_{21}NO$: N, 4.45. Found: N, 4.34, 4.40. Bromination of this derivative in chloroform solution yielded a product, m. p. 184–186°. *Anal.* Calcd. for $C_{22}H_{20}ONBr$: N, 3.55. Found: N, 3.84.

The benzoyl derivative was prepared by warming 2.0 g. of the product with 4 ml. of benzoyl chloride. Upon crystallization from a ligroin–acetone mixture a colorless product was obtained, m. p. 188.0–188.4°. *Anal.* Calcd. for $C_{27}H_{20}ON$: N, 3.71. Found: N, 3.65.

For further characterization, 5 g. of the diphenylmethyl-*o*-toluidine sulfate was dissolved in 50 ml. of glacial acetic acid and 3 ml. of sulfuric acid, cooled to 30° and diazotized by the slow addition of 4 ml. of amyl nitrite. A portion of the diazotized solution was poured into boiling water, then allowed to cool and extracted with two 50-ml. portions of ether. Upon evaporation of the ether the resulting oil was converted to its methyl ether, 2 methyl-4-diphenylmethylanisole, m. p. 75.8°. This gave a mixed m. p. of 75° with the identical material m. p. 74–76° previously prepared in the *o*-cresol series.[2] A second portion of the diazotized solution was treated with zinc dust in ethyl alcohol, replacing the original amino group with hydrogen. The product melted at 61.5° and was shown to agree by mixed melting point with the product made by direct syntheses.[1b]

**Characterization of Product IV.**—The acetyl derivative of the disubstituted product IV was prepared in a manner analogous to the preparation of the monosubstituted product. The colorless crystals melted at 189–189.5°. *Anal.* Calcd. for $C_{35}H_{31}ON$: N, 2.91. Found: N, 3.27.

The benzoyl derivative was prepared as described above and melted at 232–233°. *Anal.* Calcd. for $C_{40}H_{33}ON$: N, 2.58. Found: N, 2.85.

The disubstituted product IV was diazotized as above and poured into boiling water. Upon cooling, 2 g. of the dark brown solid was acetylated by warming with 10 ml. of acetic anhydride and a trace of sulfuric acid. After reaction, a yellow tarry mass was obtained which was recrystallized from alcohol yielding a colorless crystalline product, m. p. 142–143°. No melting point depression was observed when this material was mixed with O-acetyl-2-methyl-4,6-bis-(diphenylmethyl)-phenol as previously prepared.[2]

## Summary

1. The rearrangement of N-diphenylmethyl-*o*-toluidine or the direct reaction of diphenylcarbinol with *o*-toluidine yields products with one and two diphenylmethyl radicals in the nucleus which is analogous to comparable reactions in the *o*-cresol series.

2. An intermolecular mechanism is demonstrated, since a para rearrangement takes place; equal amounts of the disubstituted product and *o*-toluidine are produced and an actual migration of the diphenylmethyl radical from the nitrogen to an *o*-cresol nucleus was observed.

DURHAM, N. H. RECEIVED MARCH 9, 1950

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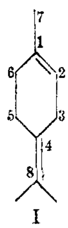
[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

# Oxidation of Terpenes with Molecular Oxygen. I. Oxidation of Terpinolene in Aqueous Dispersion[1]

BY J. N. BORGLIN, D. A. LISTER,[2] E. J. LORAND AND J. E. REESE

The autoxidation of terpenes has been the subject of numerous investigations, some of which date back almost a century; however, there have been no data available on the oxidation of terpinolene with molecular oxygen. This is surprising in view of the considerable interest in 1,4-diene systems (*e. g.*, linoleic acid) and the easy oxidizability of this terpene. The only oxidation studies published on terpinolene deal with the action of dilute potassium permanganate,[3] chromic acid,[4] and lead tetraacetate.[5] This neglect might have been due to the fact that terpinolene of satisfactory purity was not readily available. Recently this situation has changed, inasmuch as terpinolene of 85–90% purity can now be obtained by efficient fractionation of the higher boiling constituents of wood turpentine or of the monocyclic terpene by-products formed in the hydration of wood or gum turpentine. The main impurities remaining with terpinolene are 2,4(8)-*p*-menthadiene (isoterpinolene) and fenchone. By further fractionation in a high-efficiency column, the fenchone–terpinolene azeotrope can be eliminated to obtain a terpinolene of 95% or higher purity (b. p., 100 mm., 120.6°, $d^{20}_4$ 0.8620, $n^{20}$D 1.4900).

**Oxidation of Terpinolene with Molecular Oxygen in a Single-phase System.**—Since terpinolene has a methylene group (position 3 in Formula I) activated by two double bonds, oxidative attack should readily start here. Indeed,



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we have found at the outset that oxygen reacts with terpinolene more readily than with any of the other common terpenes, and that the oxidation does not require a catalyst, initiator, stronger than diffuse light. The reaction is not inhibited by the presence of other terpenes. At room temperature about one mole of oxygen per mole of terpinolene may thus be absorbed rather rapidly,

[1] Presented before the Philadelphia Meeting of the American Chemical Society, April, 1950.

[2] Deceased.

[3] Wallach, *Ann.*, **362**, 292 (1908); **368**, 10 (1909).

[4] Henry and Paget, *J. Chem. Soc.*, **134**, 25 (1931).

[5] Ward, THIS JOURNAL, **60**, 325 (1938).