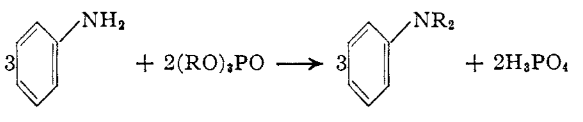
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

# Alkylation of Amines. II. N,N-Dialkylation of Nuclear Substituted Anilines

BY DONALD G. THOMAS, JOHN H. BILLMAN AND CHESTER E. DAVIS

A method for the preparation of N,N-dialkylanilines by the reaction of aniline with alkyl phosphates according to the equation has been described previously.[1]



This method has been extended successfully to the alkylation of nuclear substituted anilines and has afforded a simple and convenient means for the preparation of the nuclear substituted N,N-dialkylanilines listed in Table I.

TABLE I

N,N-DIALKYLANILINES, $R'C_6H_4NR_2''$

| R′ | R″ | B. p., 740 mm. °C. | Yield, % |
|---|---|---|---|
| *o*-Cl | $CH_3$ | 205-206 | 90 |
| *m*-Cl | $CH_3$ | 231-232 | 75 |
| *p*-Cl[a] | $CH_3$ | 233-236 | 72 |
| *m*-$CH_3$ | $CH_3$ | 205-206 | 60 |
| *p*-$CH_3$ | $CH_3$ | 204-206 | 53 |
| *p*-$CH_3O$[a] | $CH_3$ | 233-234 | 55 |
| *o*-Cl[b] | $C_2H_5$ | 219-221 | 91 |
| *m*-Cl | $C_2H_5$ | 248-250 | 95 |
| *p*-Cl[a] | $C_2H_5$ | 251-253 | 95 |
| *p*-$CH_3O$ | $C_2H_5$ | 246-247 | 74 |

[a] Samples of these compounds, when recrystallized from 30-60° petroleum ether, gave melting points of 32-33.5° for the *p*-Cl, $CH_3$; 37-38.5° for the *p*-$CH_3O$, $CH_3$; and 45.5-46.5° for the *p*-Cl, $C_2H_5$ compound. [b] This compound, *o*-chloro-N,N-diethylaniline, does not appear to have been described in the literature. *Anal.* Calcd. for $C_{10}H_{14}NCl$: N, 7.63. Found: N, 7.65. Its picrate crystallized as bright yellow plates from alcohol, m. p. 163-164°. *Anal.* Calcd. for $C_{16}H_{17}N_4O_7Cl$: N, 13.58. Found: N, 13.96.

The yields ranged from 53-95%. Samples of each of the alkylation products were treated with acetic anhydride to test for any primary and secondary amines present. Recovery of the desired tertiary amine in very high yields indicated the presence of little, if any, unalkylated or partially alkylated amines. Thus it appears that this treatment generally may be omitted.

In comparable cases diethylanilines were usually obtained in better yields than the corresponding dimethylanilines. This perhaps may be related to the fact that the reaction with triethyl phosphate was always less vigorous than that with trimethyl phosphate. In alkylations with trimethyl phosphate an extremely vigorous reaction occurred as the refluxing temperature was approached, and, after the reaction had subsided, two layers were invariably present. On the other hand, in alkylations with triethyl phosphate refluxing began smoothly and from thirty to ninety minutes were required before two layers appeared.

Methyl and ethyl alcohols were obtained from the condensed vapors returning to the reaction mixture and were identified as the *p*-nitrobenzoates. The formation of these alcohols may indicate the existence of a competing reaction tending to lower the yield of N,N-dialkylation product. Instead of the reaction proceeding entirely according to the above equation, some cleavage of the alkyl phosphate between the oxygen-phosphorus bond may occur. In this connection it may be noted that hydrolysis studies of trimethyl phosphate with water containing oxygen eighteen have shown the rupture of the phosphate to occur at the oxygen-phosphorus bond.[2]

The extension of the alkylation with trialkyl phosphates to the examples described in this paper suggests that the method may be quite general and capable of still further application. Work in this direction is being continued.

The authors wish to thank Messrs. Charles E. Mumaw and Emmit W. Archer for carrying out preliminary experiments.

## Experimental

**Alkylations.**—The alkylations were carried out essentially as described previously.[1] Equimolar amounts (0.5 mole) of amine and trialkyl phosphate were heated in a 3-liter flask equipped with an air condenser surmounted by a water condenser.

In the methylations this heating was very gentle until a fine mist was observed in the flask. At this point the flame was removed and the exothermic reaction was allowed to proceed; it was extremely vigorous as refluxing began. When the reaction had subsided, two layers were present and the color had lightened considerably; gentle refluxing was then continued for two hours. After hydrolysis for one and one-half hours of the reaction mixture with 66 g. of sodium hydroxide in 500 cc. of water, 500-800 cc. of water was added to prevent solidification of sodium phosphate and the amine was extracted with ether. After drying over sodium hydroxide and removing the ether, the tertiary amine was distilled at atmospheric pressure; practically no fore-run was ever obtained. In the case of the *o*- and *p*-chloroanilines, fourfold the above quantities were methylated and the yields stated in the table were obtained.

In the ethylations the mixture was refluxed gently for three to four hours; refluxing began smoothly and did not become nearly as vigorous as was the case with trimethyl phosphate. Separation into two layers occurred in thirty to ninety minutes.

**Treatment with Acetic Anhydride.**—To 25 g. of the tertiary amine was added 10 cc. of acetic anhydride and the mixture was allowed to stand overnight at room temperature. Ether was then added and the ethereal solution was extracted with three 50-cc. portions of 1:1 hydrochloric acid. The acid extract was neutralized with sodium hydroxide solution and the liberated amine was extracted with ether. After drying over sodium hydroxide, the ether was

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(1) Billman, Radike and Mundy, THIS JOURNAL, **64**, 2977 (1942).

(2) Herbert and Blumenthal, *Nature*, **144**, 248 (1939).

removed and the residual amine was distilled at atmospheric pressure; recovery ranged from 87–98%.

## Summary

1. The preparation of ten nuclear substituted N,N-dialkylanilines in yields of 53–95% by the use of trialkyl phosphates is described.

2. The procedure is simple, convenient and adaptable to moderately large amounts.

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# Ultraviolet Absorption Spectra of Organic Molecules. III. Mechanical Interference of Substituent Groups with Resonance Configurations

BY WORTH H. RODEBUSH AND ISAAC FELDMAN

Studies of the ultraviolet absorption of the substituted biphenyls[1,2,3,4] have demonstrated beyond question the effect of mechanical interference between substituent groups in the *ortho* positions of biphenyl. If the group is larger than hydrogen the departure from coplanarity is so great that most of the resonance between the rings is lost and the absorption may not be greatly different from that of two moles of the corresponding benzene derivative.

Recently Brockway[5] has suggested that the coplanar configuration is improbable even in the case of the unsubstituted biphenyls because the accepted van der Waals radius of the hydrogen atom indicates interference between the hydrogens in the *o,o'*-positions. The results obtained from the ultraviolet absorption studies are, of course, not incompatible with Brockway's conclusion. All that can be stated with certainty from the spectrographic studies is that in the unsubstituted biphenyls the configuration is near enough to coplanarity to allow a resonance energy amounting to several large calories.

Likewise, the results of Adams[6] and his coworkers proved that it is impossible to resolve the optically active biphenyls when the *o,o'*-positions are occupied by hydrogen but this does not prove coplanarity or even free rotation since there might be a considerable energy barrier to rotation such as exists in the case of ethane.

The X-ray evidence appears contradictory and inconclusive.[7] Biphenyl and *p*-terphenyl are reported to be coplanar while in 1,3,5-triphenylbenzene the substituent rings are believed to be tilted 25° from the plane of the central ring. However, a number of reservations must be made. The biphenyl configuration was determined a number of years ago. The exact crystal structure of triphenylbenzene has never been determined. The configuration in the crystal may be different from that of the free molecule in solution.

The authors have determined the ultraviolet absorption of symmetrical triphenylbenzene with the hope of obtaining additional evidence upon the question of its structure. The extinction coefficient (Fig. 1) shows a maximum at about the same wave length as biphenyl but the molar extinction is nearly four times that of biphenyl. It must be regarded as a coincidence that the resonance energy of triphenylbenzene, as calculated from thermal data, appears also to be about four times that of biphenyl. One may conclude, therefore, that triphenylbenzene has a considerable amount of resonance energy and that, if the configuration is not planar, the departure from coplanarity has not reduced the resonance to any considerable degree.

**Van der Waals Radii.**—Any estimate of the interference between the hydrogens in *o,o'*-positions in biphenyl must take account of the accepted values for the van der Waals radius of hydrogen. It must be recognized, of course, that the radii for atoms cannot have such precise values as are assigned, for example, to the covalent radii. The uncertainty is of the order of magnitude of 0.2–0.3 Å.

In ethylene the distance between hydrogens which are on different carbons is 2.4 Å. In ethane the distance between hydrogens similarly placed is 2.3 Å. yet ethane has a potential barrier to rotation of about 3000 calories. This barrier can hardly be due to interference between hydrogens. It may very well be the result of what has been termed hyperconjugation between the methyl groups. It is not known, of course, which configuration has the lower energy.

In biphenyl the distance the hydrogens in *o,o'*-positions is 1.84 Å. and here there must be a good deal of interference. (An estimate based on the calculations of Slater and Kirkwood[8] for helium indicates that the coplanar configuration might be unstable by about 3000 calories.) Since the resonance energy is not more than two or three

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[1] L. W. Pickett, G. F. Walter and H. France, THIS JOURNAL, **58**, 2182 (1936).

[2] M. Calvin, *J. Org. Chem.*, **4**, 256 (1939).

[3] M. T. O'Shaughnessy, Jr., and W. H. Rodebush, THIS JOURNAL, **62**, 2906 (1940).

[4] Barbara Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

[5] I. L. Karle and L. O. Brockway, *ibid.*, **66**, 1974 (1944).

[6] R. Adams and G. C. Finger, THIS JOURNAL, **61**, 2828 (1939).

[7] Jagattaran Dhar, *Indian J. Phys.*, **7**, 43–60 (1932); L. W. Pickett, *Proc. Roy. Soc.*, **A142**, 333 (1933); C. J. B. Clews and K. Lonsdale, *ibid.*, **A161**, 493 (1937).

[8] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).