and Burg[4] on the vapor-phase dissociation of $(CH_3)_3NB(CH_3)_3$ indicate the bond energy (ΔH) to be 14 ± 1 kcal.

The contrast between $(CH_3)_3NBF_3$ and $(CH_3)_3NBF_2CH_3$ might be explained qualitatively by reference to differences of electronegativity and steric interference. The great strength of the $N \rightarrow B$ bond in the former could be attributed to the high electronegativity of fluorine, on account of which the boron atom should be unusually receptive toward electrons contributed by a base. Replacement of one fluoride by methyl should considerably decrease this effect upon the electronegativity of boron. Furthermore, the small and probably tetrahedrally-bonded F-atoms[11,12] would not exert nearly as much repulsion, against the methyl groups of the amine, as would occur if a methyl were substituted for F.

In a quantitative sense, however, this argument seems inadequate, since one would expect a second methyl substitution to have an effect nearly as large as the first. The uniform effect of the second and third substitutions is in vivid contrast to the effect of the first. The reason for this contrast might be found in the differences in the energy required to change from a planar structure[13] to tetrahedral bonding during the formation of the four different addition compounds. Since structures in which the boron atom is granted only a sextet of electrons may be regarded as improbable, the loss of resonance energy of double-bonded structures also would be a point of difference among the four compounds. These factors are at present very difficult to estimate.

Summary

The new compounds $(CH_3)_3NBF_2CH_3$ (m. p. about 35°) and $(CH_3)_3NBF(CH_3)_2$ (liquid) have been prepared and studied in regard to volatility and vapor-phase dissociation. The vapor of $(CH_3)_3NBF_3$ is considerably associated, but not dissociated below 230°. The substitution of one methyl group for fluoride in $(CH_3)_3NBF_3$ results in a large decrease in $N \rightarrow B$ bond strength, but further substitution causes relatively small decreases in the strength of that bond. Rough expressions for the free energy of dissociation of the new amine-addition compounds have been derived.

LOS ANGELES, CALIF. RECEIVED JUNE 7, 1943

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(11) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 88.

(12) Bauer, Finlay and Laubengayer, THIS JOURNAL, **65**, 892 (1943).

(13) Bauer and Hastings, *ibid.*, **64**, 2691 (1942).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Steric Factors in Quaternary Salt Formation

BY WELDON G. BROWN AND SHERMAN FRIED

The reactions of aromatic tertiary amines, in which "ortho" effects[1] appear, fall in two categories, according to whether the site of reaction is the nitrogen atom (reactions with methyl iodide, cyanogen bromide, bromoacetonitrile, etc.) or a nuclear position (coupling, nitrosation, condensations with aldehydes, etc.). The "ortho" effects in the latter type are well along toward a complete understanding, based upon the role of purely geometrical factors in a mechanism peculiar to these reactions. As yet there is no satisfactory explanation for the appearance of outwardly similar phenomena in the nucleophilic displacement reactions with alkyl halides.

As an outcome of the study[2] of a model nuclear substitution reaction showing "ortho" effects, namely, the hydrogen deuterium exchange reaction, the origin of these effects can be described with reference to the following mechanism, in which A^+ is intended to represent an electrophilic reagent.[3]

If the effective dimensions of R and R′ are such as to prevent the intermediate (I) from assuming a planar configuration, strain will arise and will be

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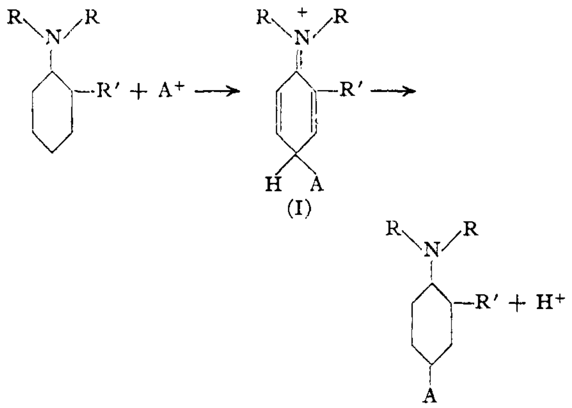
(1) (a) v. Braun and Kruber, *Ber.*, **46**, 3470 (1913); (b) v. Braun, **49**, 1101 (1916); (c) v. Braun and Mintz, **50**, 1651 (1917); (d) v. Braun, Arkuszewski and Kohler, **51**, 282 (1918). While there are numerous isolated observations, relating to abnormal behavior of ortho substituted tertiary amines, in the earlier literature, v. Braun seems to have been the first to recognize the generality of the phenomenon and to study it *per se*.

(2) Brown, Widiger and Letang, THIS JOURNAL, **61**, 2597 (1939).

(3) In the hydrogen–deuterium exchange reaction, A^+ is a deutero-acid. As applied to the coupling reaction, A^+ is diazonium ion, and the mechanism becomes identical with that written by Dilthey and Blankenburg [*Ann.*, **142**, 185 (1935)], which has been supported recently by Wistar and Bartlett [THIS JOURNAL, **63**, 413 (1941)] and by Hauser and Breslow [*ibid.*, **63**, 418 (1941)].



reflected in a lower rate of formation of the intermediate. A decrease in reactivity is the normal result of introducing an ortho substituent, but if R and R′ are suitably bridged, so as to constrain R to a position in the plane of the ring, an opposite effect may be produced. This is observed in certain bicyclic amines.

Although there is no obvious extension of the ideas underlying this interpretation to the reactions with alkyl halides, which proceed by an entirely different mechanism, there is evidence to suggest that here, too, the effects produced by ortho substituents (measured by comparison with the para isomers) are primarily steric. Evans, Watson and Williams,[4] who have made a careful kinetic study of "ortho" effects in quaternary salt formation, conclude that "the relative magnitudes of the effects are quite unconnected with the weights, volumes, or chemical characters of the groups." They find the order of effectiveness of ortho substituents, in suppressing quaternary salt formation, to be as follows: $F < OPh < OMe$ $(NO_2) < Cl < Me < Ph$. As this order corresponds closely with the order of effectiveness of groups in preventing free rotation in the biphenyl series, we should regard these results as favoring, rather than disproving, a steric interpretation.

Electronic factors, as influenced by substituent groups, are of secondary importance in determining the magnitude of the "ortho" effects in quaternary salt formation. It is true that the amines in question are subject to steric "damping" of resonance[5] by ortho substituents, but, in comparing ortho and para substituted amines, the result of "damped" resonance should be to favor quaternary salt formation of the former. An effect of this kind is seen in the higher base strength of the ortho isomers, as the reaction with hydrogen ion is not appreciably hindered, but the observed effects in quaternary salt formation are in the opposite direction.

The present investigation has for its purpose the further elucidation of the steric aspects of the problem, with particular reference to the formation of quaternary salts from bicyclic tertiary amines.

Experimental

Experimental Procedure.—The method of determining rates of reaction was essentially that of Evans, Watson and Williams,[6] in which the reaction of the amine with methyl iodide is followed by successive determinations of iodide ion by titration with standard silver nitrate solution. Equal volumes, usually 10 cc., of 0.2 *M* solutions of the amine, and of the alkyl iodide, both in methyl alcohol, were mixed in glass stoppered Pyrex tubes. Immediately after mixing, the tubes were placed in a thermostat, the temperature of which was held to within 0.02°. Bath temperatures were checked with the aid of a thermometer calibrated by the Bureau of Standards. In order to avoid a photochemical decomposition of methyl iodide, in which small amounts of free iodine are formed, it was found necessary to coat the thermostat heater lamp with black paint.

Preparation of Reagents.—Methyl alcohol, which was used as the solvent throughout, was purified by prolonged treatment with sodium hypoiodite, after which it was distilled through an all-glass vacuum jacketed column packed with glass helices. The material thus obtained was treated with magnesium metal and allowed to reflux for several hours, and then redistilled through the same column.

Methyl iodide, and also ethyl iodide, were washed successively with water, dilute sodium carbonate, water, dilute sodium thiosulfate and finally with water. After standing for several days over calcium chloride, the materials were distilled in an all-glass apparatus.

The sample of *o*-(*t*-butyl)-N-dimethylaniline was one which had been prepared and purified by Dr. N. Z. Fineman in this Laboratory. The bicyclic tertiary amines, as well as 1-dimethylamino-2,6-dimethylbenzene, had been prepared previously for use in hydrogen–deuterium exchange studies.[2] The two nitro compounds included in this investigation were prepared by methods not previously reported.

1-Dimethylamino-3,5-dimethyl-4-nitrobenzene.—The reaction of 1-bromo-3,5-dimethyl-4-nitrobenzene,[7] in 1-g. portions, each with 4–5 cc. of anhydrous diethylamine, in sealed tubes at 100–120° for one hundred hours, gave a product which separated, after cooling, as a mass of orange colored crystals. The product was washed out of the tubes with water and the aqueous suspension was evaporated nearly to dryness to remove excess dimethylamine. The residue was taken up in 6 *N* hydrochloric acid and, after filtering, the solution was made alkaline with dilute alkali. After recrystallization from medium boiling

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[4] Evans, Watson and Williams, *J. Chem. Soc.*, 1348 (1939).

[5] Birtles and Hampson, *ibid.*, 10 (1937).

[6] Evans, Watson and Williams, *ibid.*, 1345 (1939).

[7] We are indebted to Dr. G. W. Wheland for a supply of this compound.

ligroin, the product was obtained, in 79% yield, as dense, orange prisms—m. p. 111°.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: N, 14.43. Found: N, 14.23.

1-Dimethylamino-3-methyl-4-nitrobenzene.—This preparation was first attempted by methylation of the primary amine with methyl sulfate, as described by Vorländer and Seibert.[8] Great difficulty was encountered on purifying the product and the final yield of pure material was very small (3%). The product was obtained in 73% yield on treatment of 1-iodo-3-methyl-4-nitrobenzene[9] with anhydrous dimethylamine after the manner of the preceding preparation. After two recrystallizations from aqueous ethanol, the product was obtained as yellow platelets, m. p. 83°. A mixed melting point with an authentic specimen showed no depression.

Neither this compound nor the preceding one was sufficiently soluble in methyl alcohol at room temperature to make up a 0.2 *M* solution. However, it was possible to supercool the solutions for the short time needed to withdraw samples.

Experimental Results.—As many previous investigators have found in studying similar reactions, the rates of reaction of these amines with methyl iodide, and with ethyl iodide, are accurately described over a very considerable range by the equation for a bimolecular reaction. Only with the two nitro compounds, which approach equilibrium at an early stage, is a significant trend observed. By plotting $1/k$ against time, extrapolated rate constants were obtained but these are the least reliable of the results. Of the data for the remaining compounds, the most erratic were those for the reaction of N-methylindoline with methyl iodide at 45°, which was the fastest of the reactions studied, and for which the experimental technique was not too well adapted. These data are reproduced in full in Table I. Otherwise highly concordant results were obtained as is illustrated by the data for the reaction of 1-dimethylamino-2,6-dimethylbenzene with methyl iodide at 45° reproduced in Table I. The rate constants were calculated from the equation

$$k = 1/t \cdot x/a(a - x)$$

where x is the concentration of quaternary salt attained at time, t, and a is the initial concentration of the reacting substances (corrected for solvent expansion). The units of k are liters moles^{-1} sec.$^{-1}$.

The data are summarized in Table II, which also gives the values for the constants, *PZ* and *E*, of the Arrhenius equation, derived from the rate constants at 35 and 45°. Since the reactions were studied at only two different temperatures, no great accuracy can be claimed for the evaluation of these constants. However, the results tend to confirm the finding of Evans, Watson and Williams[4] that the terms *PZ* and *E* both increase in magnitude in going from the normal to the hindered amines.

TABLE I

RATES OF REACTION WITH METHYL IODIDE AT 45°

t, min.	$AgNO_3$ solution,[a] ml.	x	$a - x$[b]	$k \times 10^4$
		N-Methylindoline, First Run		
78	2.86	0.02877	0.06818	9.31
123	3.86	.03883	.05812	9.34
166	4.51	.04537	.05158	9.11
190	4.82	.04849	.04846	9.05
259	5.59	.05624	.04071	9.17
308	6.06	.06096	.03599	9.45
444	6.84	.06881	.02814	9.19
604	7.36	.07404	.02991	9.20
		Second Run		
273	5.73	0.05764	0.03931	9.23
332	6.13	.06167	.03528	9.05
393	6.57	.06609	.03086	9.37
		Third Run		
100	3.38	0.03400	0.06295	9.28
144	4.20	.04225	.05470	9.22
188	4.82	.04849	.04846	9.14
231	5.38	.05412	.04283	9.40
			Mean	9.23
				$k \times 10^4$
		1-Dimethylamino-2,6-dimethylbenzene		
4,576	1.98	0.00996	0.08699	4.30
7,428	3.03	.01524	.08171	4.31
8,755	3.48	.01750	.07945	4.32
9,962	3.85	.01936	.07759	4.31
11,722	4.36	.02192	.07502	4.29
13,481	4.86	.02445	.07250	4.30
14,874	5.24	.02636	.07509	4.32

[a] Normality of silver nitrate solution, 0.01006; sample of reaction mixture taken for titration, 2 ml. [b] a = 0.09695 mole per liter.

Discussion of Results

In the series of bicyclic amines, $C_6H_4(CH_2)_nNCH_3$, no hindrance to quaternary salt formation is observed when n is 2, or 3, but, when n is 4 (7-membered ring), the rate of reaction falls abruptly to a value comparable with those of dimethyl-*o*-toluidine and similar hindered amines. These results strongly suggest that the important factor is the configuration of the nitrogen valences in relation to the benzene ring, as it is in this respect that the 7-membered ring compound differs decisively from the other two. The configuration

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(8) Vorländer and Seibert, *Ber.*, **52**, 303 (1909).

(9) Artman, *Monatsh.*, **26**, 1096 (1905).

TABLE II

	With CH_3I		With C_2H_5I		E for react. with CH_3I	Log PZ with CH_3I	E for react. with C_2H_5I	Log PZ with C_2H_5I
	10^4k_{35}	10^4k_{45}	10^4k_{35}	10^4k_{45}				
Dimethylaniline	1.31	2.38	0.0662	0.171	15,200	6.9	18,340	7.90
N-Methylindoline	4.47	9.22	.198	.529	14,090	6.65	19,190	8.91
N-Methyltetrahydroquinoline	0.883	1.95	.0298	.0952	15,310	6.92	20,480	9.00
N-Methyltetrahydro-*homo*-quinoline	.0245	0.0718	.00686	.0220	20,910	9.23	22,680	9.93
o-*t*-Butyldimethylaniline	.00952	.0287	...	...	21,500	9.24	...	..
1-Dimethylamino-2,6-dimethyl-benzene	.0109	.0431	...	...	25,590	12.91	...	..
1-Dimethylamino-3,5-dimethyl-4-nitrobenzene	0666	.125	...	...	12,600	3.32	...	..
1-Dimethylamino-3-methyl-4-nitrobenzene	.0258	.0555	...	...	14,910	4.53	...	..

most favorable for quaternary salt formation is evidently one in which the dialkylamino group and the benzene ring are coplanar[10] or nearly so.

The extent to which a coplanar configuration favors the reaction is further illustrated by the observation of v. Braun[1b] that the introduction of a methyl group in the one remaining ortho position of N-methyltetrahydroquinoline does not give rise to hindrance in reactions with methyl iodide. This observation would offer some difficulty in any theory of "ortho" effects based on proximity relationships or general steric effects.

The retarding effects of ortho substituents in monocyclic amines are to be correlated with the hindered rotation of the dialkylamino group. As suggested earlier, this appears to be the real significance of the order of effectiveness of groups which was observed by Evans, Watson and Williams.[4] We find, in further substantiation of this view, that the tertiary butyl group is more effective than a methyl group in suppressing quaternary salt formation. Also, confirming v. Braun's qualitative observations,[1d] we find that the introduction of a second ortho methyl group produces a further diminution of reactivity over that produced by one such group although the effect produced by the second methyl group, as measured by the change in rate constants, is relatively small.

The configurational requirements are thus apparently the same for the nuclear substitution and the quaternarization reactions, thereby accounting for the parallel occurrence of "ortho" effects. However, the reasons for these configurational requirements must be quite different as the coplanar configuration cannot have the same significance in the reaction of quaternary salt formation as it has in nuclear substitution reactions.

We visualize the reaction of an amine with methyl iodide as occurring in an oriented collision in which the alkyl group approaches the exposed face of the nitrogen atom along a line at right angles to the plane of the three groups to which it is attached.[11] In planar bicyclic amines and the unhindered monocyclic amines, the line of approach would be at right angles to the plane of the ring and would be relatively unobstructed. In the hindered amines, as can be shown clearly with scale models, the nitrogen atom is shielded from approach along a normal line. Obviously, this picture is an oversimplification as the divergent variations of the terms in the Arrhenius equation are not accounted for, but it will perhaps serve to illustrate how two different types of reactions might be subject to similar configurational requirements.

The experimental data given in Table II for the two nitro substituted amines are somewhat inconclusive in so far as a demonstration of the effect of damped resonance is concerned. The observed difference is in the expected direction, as a nitro group which is flanked by two methyl groups should have less of a mesomeric deactivating effect than a nitro group which is not thus hindered. However, the magnitude of the difference is hardly greater than could be ascribed to the methyl groups as such.

Summary

N-Methylindoline and N-methyltetrahydroquinoline react normally with methyl and ethyl iodides, but N-methyl-*homo*-tetrahydroquinoline

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[10] Although normally pyramidal in configuration, the three valences of nitrogen probably tend toward a planar configuration in aromatic amines because of resonance effects.

[11] This mechanism gives rise to inversion on the carbon atom involved (*cf.* Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 166), but does not necessitate inversion on the nitrogen atom, as is shown by the remarkable ease with which cage-type tertiary amines, having nitrogen in the bridgehead position, react with alkyl halides (*cf.* Meisenheimer, *Ann.*, **420**, 218 (1920)).

reacts very slowly and is thus a typically hindered amine. This observation, together with other evidence cited, leads to the conclusion that the "ortho" effects in quaternary salt formation are steric effects and are not secondary valence effects as has been supposed.

Rates of quaternary salt formation have also been determined for 1-dimethylamino-2,6-dimethylbenzene, 1-dimethylamino-3-methyl-4-nitrobenzene, and 1-dimethylamino-3,5-dimethyl-4-nitrobenzene.

CHICAGO, ILLINOIS RECEIVED MAY 17, 1943

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Photochemical Dimerization of *trans*-Cinnamic Acid[1]

BY HERBERT I. BERNSTEIN[2] AND WILLIAM C. QUIMBY

Moderately large amounts of α-truxillic acid (III) were needed for studies of configurational changes during molecular rearrangements.[3] The simplest method of preparation according to most textbooks,[4] should be the irradiation of *trans*-cinnamic acid (I) with sunlight.

This unanimity, however, is lacking in the original literature. Stoermer and co-workers[5] and Stobbe and his co-workers[6] reported that the *trans*-cinnamic acid yielded principally α-truxillic acid upon irradiation in the dry state, while the *cis*-acid was converted into a mixture of α-truxillic (III) and β-truxinic acid (II). DeJong,[7] on the other hand, obtained β-truxinic acid from freshly precipitated *trans*-cinnamic acid. The longer the cinnamic acid stood before irradiation, the smaller was the yield of β-truxinic, while that of α-truxillic acid increased.

We have found that irradiation of the commercial *trans*-cinnamic yielded only β-truxinic acid. The same was true of a rapidly precipitated cinnamic acid. If the commercial acid was allowed to stand for four months, β-truxinic acid was still the only dimerization product. However, if the *trans*-cinnamic acid were slowly recrystallized from aqueous alcohol, dried and irradiated, the sole product was α-truxillic acid. Addition of the peroxide, ascaridole, to this recrystallized cinnamic acid exerted no influence upon the reaction products. The irradiation of an aqueous suspension of freshly precipitated *trans*-cinnamic acid is the best known method for preparing β-truxinic acid.

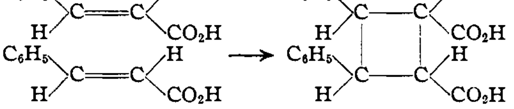
Stobbe[6] sought to explain his data by means of the following transitions:

$$\begin{tikzcd} \textit{cis}\text{-Cinnamic acid} \arrow[r, shift left] \arrow[d] & \textit{trans}\text{-Cinnamic acid (I)} \arrow[l, shift left] \arrow[d] \\ \beta\text{-Truxinic acid (II)} & \alpha\text{-Truxillic acid (III)} \end{tikzcd}$$

The assumption that only the *cis* acid yields β-truxinic, while only the *trans*-cinnamic gives α-truxillic acid probably accounts for the textbook over-simplification.

DeJong[7] made use of the reported existence of two polymorphic forms of *trans*-cinnamic acid, the metastable *beta* and the stable *alpha*.[8,9] Both have the same melting point. He assumed that the *beta* form isomerized to the *cis*-cinnamic acid, which then combined with a molecule of *trans*-cinnamic to yield β-truxinic acid. The α-truxillic comes from two molecules of *trans*-cinnamic acid.

However, these assumptions seem unnecessary. It is possible that in the metastable *beta* form of *trans*-cinnamic acid resulting from rapid precipitation, the phenyl groups lie next to each other in the crystal, while they are opposite in the stable *alpha* form.



trans-Cinnamic acid quickly precipitated β-Truxinic acid

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[1] Presented before the Organic Division of the American Chemical Society, Memphis, April 20–21, 1942.

[2] National Research Fellow, Princeton University, 1940–1941. Present address: Illinois Institute of Technology, Chicago, Illinois.

[3] Bernstein and Wallis, *J. Org. Chem.*, **7**, 261 (1942).

[4] (a) Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1925, Vol. II, p. 1309; (b) Richter, "The Chemistry of the Carbon Compounds," "Elsevier," Amsterdam, 1939, Ed. III, Vol. II, p. 40; (c) Hans Meyer, "Synthese der Kohlenstoffverbindingen," Julius Springer, Vienna, 1938, Part 1, Vol. II, pp. 1173 and 1182; (d) Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 634; (e) Karrer, "Organic Chemistry," "Elsevier," Amsterdam, 1938, p. 602.

[5] (a) Stoermer and Foerster, *Ber.*, **52**, 1263 (1919); (b) Stoermer and Laage, *ibid.*, **54**, 77 (1921).

[6] (a) Stobbe, *ibid.*, **52**, 666 (1919); (b) Stobbe and Steinberger, *ibid.*, **55**, 2225 (1922); (c) Stobbe and Lehfeldt, *ibid.*, **58**, 2415 (1925).

[7] DeJong, *ibid.*, **55**, 463 (1922).

[8] Erlenmeyer, Brakow and Hery, *ibid.*, **40**, 653 (1907).

[9] Lehmann, *Z. Krist.*, **10**, 329 (1885).