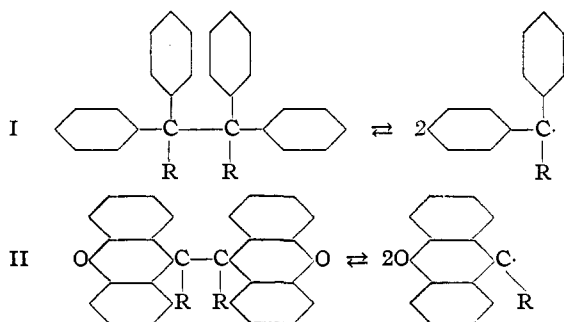


[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Studies in Stereochemistry. I. Steric Strains as a Factor in the Relative Stability of Some Coördination Compounds of Boron

BY HERBERT C. BROWN, H. I. SCHLESINGER AND SAMUEL Z. CARDON¹

The concept of free rotation about the single bond has been a basic postulate of the stereochemist. This belief is based upon the failure of



Reaction proceeds to right: $R = \text{CH}_3 < \text{C}_2\text{H}_5 < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}$.

investigators to isolate compounds, the isomerism of which is caused by restricted rotation.² Within recent years, the original concept of free rotation has required considerable modification. Not only have instances been discovered in the diphenyl³ and benzene⁴ series of isomerism caused by hindered rotation, but also entropy measurements,⁵ dipole-moment⁶ and electron-diffraction⁷ studies have indicated that rotation in ethane and its simple derivatives is not entirely "free." The actual isolation of "rotation isomers" in the simple aliphatic derivatives has probably been unsuccessful hitherto only because of the low energy barrier between the isomeric forms.

Steric interference between the two halves of an ethane derivative should reveal itself in other

(1) This paper is taken from a dissertation submitted by Samuel Z. Cardon to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Master of Science.

(2) An excellent discussion of the subject is contained in Goldschmidt, "Stereochemie," Leipzig, 1933, Vol. IV of "Hand- und Jahrbuch der chemischen Physik."

(3) Turner and Le Fèvre, *Chem. Industry*, **45**, 831 (1926); Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

(4) Mills and Kelham, *J. Chem. Soc.*, 274 (1937).

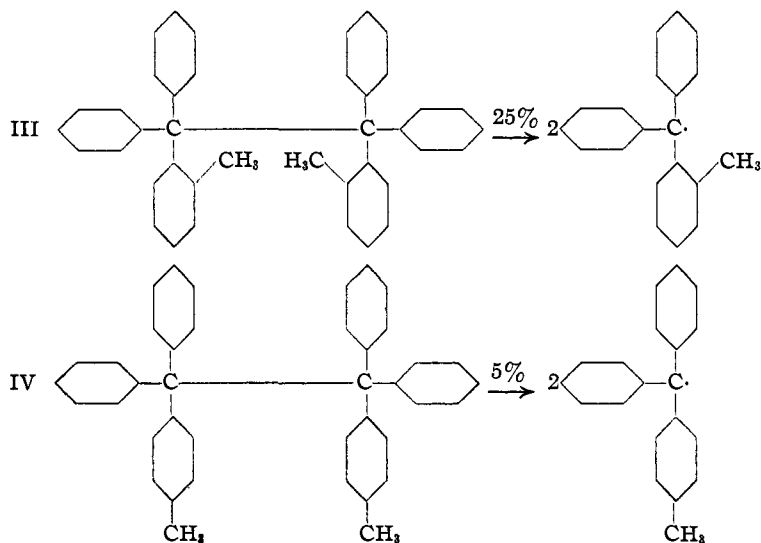
(5) Kemp and Pitzer, *THIS JOURNAL*, **59**, 276 (1937); Kistiakowsky, Lacher and Stitt, *J. Chem. Phys.*, **7**, 239 (1939).

(6) Smyth, Dornte and Wilson, *THIS JOURNAL*, **53**, 4242 (1931).

(7) Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

ways than by restricted rotation. For example, the repulsion of the two parts of the molecule should result in a weakening of the bond joining them. Such strains would be expected to be comparatively small (otherwise "rotation isomers" should be easily isolated), and their effect upon the strong normal carbon-to-carbon bond is probably so slight as to be observed only with considerable difficulty. So it is not entirely surprising that no evidence of the operation of such strains in the simple derivatives of ethane has yet been brought forward.

On the other hand, the comparatively weak carbon-to-carbon bonds in tetraphenylethane, hexaphenylethane and their derivatives might be expected to reflect quite markedly the presence of even small steric strains. Some experimental



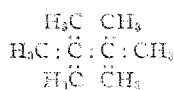
evidence that such is the case has been reported. For example, Conant and his co-workers⁸ find that the tendency of the tetraaryldialkylethanes (I) and the dixanthylalkylethanes (II) to dissociate into free radicals increases with the increasing size of the alkyl group (R).⁹

(8) Conant and Bigelow, *THIS JOURNAL*, **50**, 2041 (1928); Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

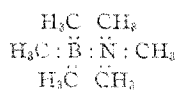
(9) Wheland [*J. Chem. Phys.*, **2**, 474 (1934)] has suggested that the increased dissociation of the derivatives containing the isopropyl and *t*-butyl groups may be due to the increased possibility of resonance in which the alkyl groups participate. At the present time, this interpretation is not generally accepted. Possibly both effects, resonance and steric, play a part in the phenomenon.

Furthermore, the methyl groups in the ortho positions of *sym*-tetraphenyl-*o*-tolylethane (III) have a much more marked effect upon dissociation into free radicals than do the methyl groups of the corresponding meta or para derivatives¹⁰ (IV).

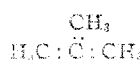
A means of investigating the presence of such effects in relatively simple molecules was suggested by an observation in an earlier investigation.¹¹ The boron-to-nitrogen bond is isosteric with the carbon-to-carbon bond (V and VI, VII and VIII).



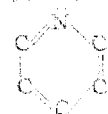
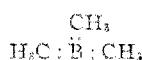
V



VI



VII

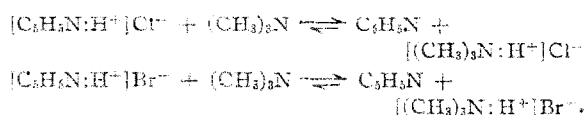


VIII

The bond distances are almost identical: 1.54 Å. for carbon-to-carbon, 1.58 Å. for boron-to-nitrogen.¹² Any strains in an organic molecule should be duplicated in the corresponding boron-nitrogen derivative, but the effect of such strains should be considerably magnified by the comparative weakness of the boron-to-nitrogen bond. Accordingly, a study was made of the relative stability of a number of coordination compounds of borine, boron fluoride and trimethylboron with trimethylamine, pyridine and lutidine (*α,α'*-dimethylpyridine).

Discussion

Trimethylamine is a considerably stronger base than pyridine.¹³ When pyridine hydrochloride or pyridine hydrobromide is treated with an equivalent quantity of trimethylamine, the greater part of the pyridine is displaced from the salt. The equilibrium may be represented as follows



(10) Marvel, Mueller, Himmel and Kaplan, *THIS JOURNAL*, **61**, 2771 (1939).

(11) Schlesinger and Brown, *ibid.*, **62**, 3429 (1940), Note 3.

(12) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 179.

(13) The basic dissociation constant for trimethylamine is 5.45×10^{-4} [Harned and Owen, *THIS JOURNAL*, **62**, 5079 (1930)] as compared with 1.7×10^{-5} for pyridine [Hahn and Klockmann, *Z. Physik. Chem.*, **A146**, 389 (1936)].

Similar results are obtained with borine or boron fluoride. In each case, the pyridine is preferentially displaced from the coordination compound. The reactions which occur are



On the other hand, the result obtained by studying the relative base strength of these bases with trimethylboron stands in contradiction to these facts. Pyridine displaces trimethylamine from trimethylamine-trimethylboron^{13a}—apparently indicating that pyridine is the stronger base. $\text{C}_5\text{H}_5\text{N}:\text{B}(\text{CH}_3)_3 + (\text{CH}_3)_3\text{N} \rightleftharpoons \text{C}_5\text{H}_5\text{N} + (\text{CH}_3)_3\text{N}:\text{B}(\text{CH}_3)_3$

This "anomalous" result is, in all probability, the result of steric strains such as are discussed in the first part of this paper. Examination of molecular models indicates that considerable steric strains are to be expected in trimethylamine-trimethylboron, but only small strains in pyridine-trimethylboron (Figs. 2a, 2b). These strains are apparently sufficiently large to reverse the relative strength of the boron-to-nitrogen bonds which would ordinarily be expected in the boron coordination derivatives of trimethylamine and pyridine. The considerably smaller groups attached to boron in borine and boron fluoride¹⁴ reduce the strain to a point where it is insufficient to cause a reversal in the relative stability of their derivatives with the two amines (Figs. 1a, 1b).

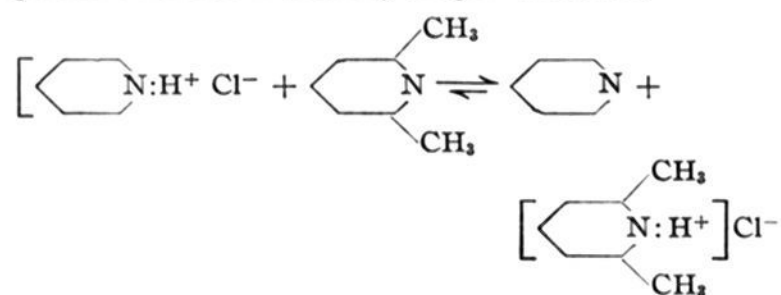
Some support for this explanation was furnished by a study of the compound triethylamine-trimethylboron. Triethylamine is a somewhat stronger base than trimethylamine¹⁵ and it would be expected that the addition compound of triethylamine with trimethylboron would be more stable than the corresponding derivative of trimethylamine. On the other hand, the ethyl group occupies a considerably greater volume than the methyl groups—the additional strains introduced should lessen the stability of the ethyl derivative. As a matter of fact, triethylamine-trimethylboron is stable only at low temperatures. At room temperature, within the limitations of the experimental method ($\approx 1\%$), it is dissociated into its components.

(13a) For a discussion of the nomenclature used in this paper, see Davidson and Brown, *THIS JOURNAL*, **64**, 316 (1942), footnote 11.

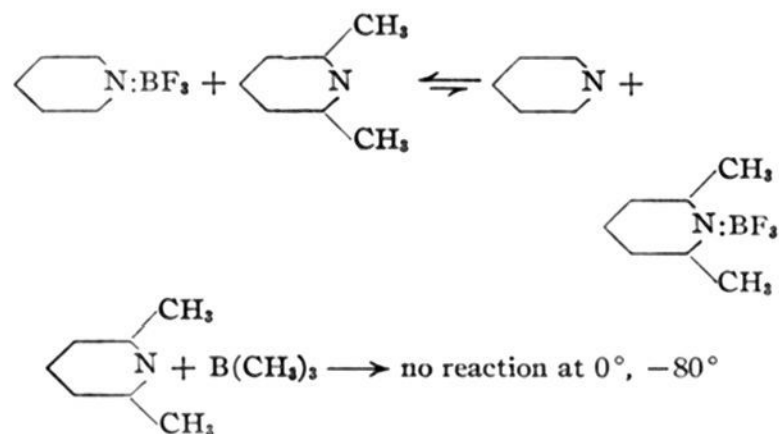
(14) The van der Waals radii of hydrogen and fluorine are 1.2 Å. and 1.35 Å., respectively, as compared with roughly 2.0 Å. for the methyl group (Pauling, *op. cit.*, p. 189).

(15) The basic dissociation constant for triethylamine is 5.64×10^{-4} [Hall and Conant, *THIS JOURNAL*, **49**, 3047 (1927)] as compared with 5.45×10^{-4} for trimethylamine.

Further support for the hypothesis was obtained by the study of the relative stability of similar coordination compounds with pyridine and α,α' -lutidine. α,α' -Lutidine is a stronger base than pyridine as shown by a study of a competitive reaction with hydrogen chloride.¹⁶



But pyridine displaces α,α' -lutidine from α,α' -lutidine-boron fluoride, and trimethylboron does not even add to this base.



Examination of the models (Figs. 1b, 1c, 2b, 2c) shows that a considerably higher order of steric interference is to be expected in the α,α' -lutidine derivatives. The strain produced is evidently so great as to reverse the relative stability of the boron fluoride addition compound, in spite of the small size of the van der Waals radius of the fluorine atom, and actually prevents the addition of the trimethylboron molecule at temperatures as low as -80° .

Experimental Part

Apparatus and Technique.—The apparatus and technical methods used in this work have been described by Stock,¹⁷ and in previous papers from this Laboratory.¹⁸ The materials used were measured as vapors in calibrated bulbs, condensed in a reaction vessel, and permitted to react at room temperature. The products were separated by fractional condensation and identified by their vapor tensions.

In all of the reactions investigated, the displacement of the amine appeared to be quite rapid. In experiments

(16) The basic dissociation constant of lutidine is 1×10^{-7} [Mündler, Diss., Heidelberg, 1901] as compared with 1.7×10^{-9} for pyridine.

(17) Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(18) Schlesinger and Walker, *THIS JOURNAL*, **57**, 622 (1935); Burg and Schlesinger, *ibid.*, **59**, 780 (1937).

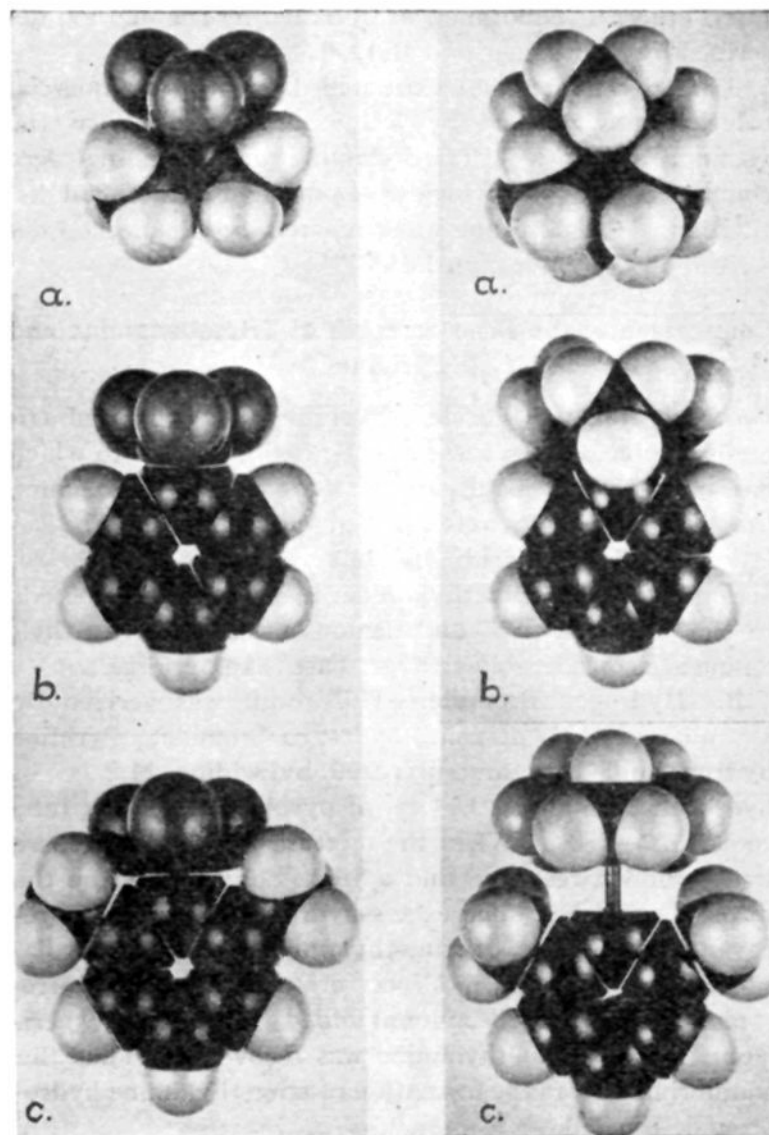


Fig. 1.—Molecular models of the coordination compounds of boron fluoride with (a) trimethylamine, (b) pyridine and (c) α,α' -lutidine.

Fig. 2.—Molecular models of the coordination compounds of trimethylboron with (a) trimethylamine, (b) pyridine and (c) α,α' -lutidine.

with the trimethylboron-trimethylamine-pyridine system, designed to test the rapidity of the approach to equilibrium, the reaction appeared complete in less than two minutes at room temperature. However, to eliminate any possibility of error from this cause, all reaction mixtures were permitted to stand two to four hours at room temperature and, in a number of instances, the equilibrium was approached from both directions.

All volumes refer to vapors corrected to standard conditions. The data are probably accurate to within 5% as indicated by experiments in which the equilibrium was approached from both directions, and each of the components of the volatile products was isolated and measured.

Materials.—Hydrogen chloride and hydrogen bromide were prepared by the dehydration of aqueous solutions of the corresponding acid with suitable agents: concentrated sulfuric acid for hydrogen chloride and sirupy phosphoric acid for hydrogen bromide. Boron fluoride was prepared by the action of sulfuric acid on sodium fluoborate and boric oxide.¹⁹ Trimethylboron was prepared by the action of methylmagnesium bromide on methyl borate in *n*-

(19) "Inorganic Syntheses," **1**, 21 (1939).

butyl ether.²⁰ Diborane was obtained by the method described by Schlesinger and Burg.²¹

Trimethylamine was extracted from the commercial solution and purified by fractional distillation in the vacuum apparatus. Triethylamine and pyridine were commercial products which were purified by fractional distillation. α, α' -Lutidine was prepared by the method described in "Organic Syntheses."²²

Comparison of the Base Strength of Trimethylamine and Pyridine

A. Hydrogen Chloride.—Pyridine, 8.98 cc., and trimethylamine, 8.99 cc., were condensed in a tube to which 8.99 cc. of hydrogen chloride was added. After two hours, the volatile products were distilled and analyzed. The isolation of 1.1 cc. of trimethylamine indicated that the reaction to form trimethylamine hydrochloride proceeds to the extent of 88% and demonstrates that trimethylamine is a considerably stronger base than pyridine.

B. Hydrogen Bromide.—This result was verified by a similar experiment using hydrogen bromide. Pyridine hydrobromide was first prepared by adding 11.2 cc. of hydrogen bromide to 9.14 cc. of pyridine in a small tube cooled to -180° . When the mixture was warmed, there was a sudden reaction, and a white solid formed on the walls of the tube. The excess hydrogen bromide was recovered and 9.18 cc. of trimethylamine added. The volatile products contained 1.7 cc. of trimethylamine corresponding to 19% of the amount added. In another experiment, 16% of trimethylamine was recovered. Thus the equilibrium favors the formation of trimethylamine hydrobromide (85-15).

C. Boron Fluoride.—Trimethylamine-boron fluoride was prepared by condensing equimolar quantities of boron fluoride and trimethylamine in the reaction vessel. When the mixture was warmed, a reaction took place with the formation of a white crystalline solid which melts at $133-135^\circ$ and does not exert any appreciable vapor pressure at room temperature. It appears to be stable to air and dissolves in water to form a clear colorless solution which was not investigated further.

To 8.50 cc. of the preceding compound, 8.48 cc. of pyridine was added and the mixture permitted to stand overnight. The volatile products consisted of 0.87 cc. of trimethylamine and 6.96 cc. of pyridine. Thus 11% of the trimethylamine had been displaced. In other experiments pyridine-boron fluoride was prepared and treated with trimethylamine. The results were essentially the same: the equilibrium in all cases was 85-90% in favor of the formation of trimethylamine-boron fluoride.

D. Diborane.—Pyridine-borine was prepared from 2.2 cc. of pyridine and 1.1 cc. of diborane at 30° . It is a white crystalline solid of low volatility which melts at $10-11^\circ$. The following vapor tensions were noted:

Vapor tension, mm.	0.1	0.15	0.35	0.5	0.9	1.8
Temperature, $^\circ\text{C}$.	25	45	60	70	85	99

It appears to be stable toward dry air and is but slowly attacked by water.

(20) Unpublished procedure developed by Professor A. B. Burg.

(21) Schlesinger and Burg, *THIS JOURNAL*, **53**, 4321 (1931).

(22) "Organic Syntheses," **14**, 30 (1934).

Pyridine-borine was treated with an equimolar quantity of trimethylamine. Of the 31.6 cc. of trimethylamine added, 27.5 cc. reacted. The equilibrium point thus lies toward the formation of trimethylamine-borine (85:15). The equilibrium point was approached from the opposite direction with corresponding results.

E. Trimethylboron.—Pyridine-trimethylboron was prepared by adding an excess of pyridine to 7.94 cc. of trimethylboron. After the excess had been distilled away, 8.68 cc. of trimethylamine was added. The mixture was allowed to stand for several hours at room temperature, following which the volatile products were removed and fractionated. Trimethylamine, 7.09 cc., was recovered. This corresponds to 80% of that added.

In other similar experiments, the quantities of trimethylamine recovered varied between 80 and 84%. Experiments in which trimethylamine-trimethylboron was treated with pyridine gave corresponding results. Several experiments were carried out in which both the pyridine and trimethylamine in the volatile products were measured. Since the results checked with those already described, they need not be described in detail.

Comparison of Base Strength of Triethylamine and Trimethylamine

Trimethylboron.—Triethylamine-trimethylboron could not be isolated at room temperature. When 7.84 cc. of triethylamine was introduced in the same bulb with 7.87 cc. of trimethylboron, the resulting volume was 15.7 cc., which corresponds to a dissociation of over 99%. In another experiment, equimolar quantities of the two substances were allowed to warm up from -180° . The formation of a white solid which melted with decomposition between -15 and -13° , was observed.

Comparison of Base Strength of Pyridine and α, α' -Lutidine

A. Hydrogen Chloride.—Hydrogen chloride, 12.41 cc., was added to a mixture of 12.90 cc. of pyridine and 13.04 cc. of α, α' -lutidine. From the volatile products, 58% of the pyridine was recovered. This indicates that α, α' -lutidine is a slightly stronger base toward hydrogen chloride than is pyridine.

B. Boron Fluoride.— α, α' -Lutidine-boron fluoride was prepared by direct combination of the two substances. It is a white crystalline solid which exhibits the following vapor pressures:

Temp., $^\circ\text{C}$.	100	123	136	159	194
Pressure, mm.	3.1	11.5	25.8	49.0	66.0
Vol., cc.		3.29	7.14	12.82	15.99

The calculated volume was 11.5 cc. It is apparent that there is appreciable dissociation above 150° .²³ It melted over a considerable range (roughly from 100 to 130°),

(23) The fact that dissociation occurs at so low a temperature corroborates the conclusion that the boron-to-nitrogen bond in α, α' -lutidine-boron fluoride is considerably weaker than the corresponding bond in pyridine-boron fluoride. The latter compound exhibits no appreciable dissociation at temperatures below 300° . We are undertaking a careful study of the dissociation of these compounds in order to obtain quantitative data on the magnitude of these steric strains. This method of attack should eliminate the small inaccuracies which may have been introduced in the data obtained in the present experiments as a result of the assumption that crystal energy effects are small and could be neglected.

probably because of accompanying dissociation into its components.

A mixture of 13.4 cc. of α,α' -lutidine, 13.13 cc. of pyridine, was treated with 13.3 cc. of boron fluoride. A white solid formed. The supernatant liquid was distilled out and identified as α,α' -lutidine by its vapor pressure (6 mm. at 23°). In several trials the recovery corresponded to 77% of the α,α' -lutidine added. The presence of an appreciable amount of pyridine in the volatile product could not be demonstrated. Thus, toward boron fluoride, α,α' -lutidine acts as a weaker base than pyridine.

Summary

1. Trimethylamine forms more stable addition compounds than does pyridine with hydrogen

chloride, hydrogen bromide, borine, and boron trifluoride, whereas with trimethylboron, pyridine forms the more stable compounds.

2. α,α' -Lutidine acts as a stronger base than pyridine toward hydrogen chloride, whereas toward boron trifluoride, pyridine acts as a stronger base.

3. These reactions are explained on the basis of steric strains produced by steric hindrance of the groups about the coordinating central atoms.

4. The significance of the results to the concept of free rotation is discussed.

CHICAGO, ILLINOIS

RECEIVED OCTOBER 25, 1941

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

Carboxylation.¹ I. The Photochemical and Peroxide-catalyzed Reactions of Oxalyl Chloride with Paraffin Hydrocarbons²

BY M. S. KHARASCH AND HERBERT C. BROWN³

The chemical inertness of the paraffinic hydrocarbons as compared with those of the aromatic series has long been a cherished conviction of the organic chemist. The availability and widespread utilization of nitric and sulfuric acids as laboratory reagents probably accounts for this belief. Because these acids react differently toward the two classes of hydrocarbons (under ordinary laboratory conditions), it was natural for the early workers to conclude that the aromatic hydrocarbons were reactive and the aliphatic hydrocarbons inert. That this classification has persisted can be attested by examination of a number of textbooks of organic chemistry. But it is now becoming evident that the term "reactivity" must be carefully defined if it is to have any significant meaning. Reactivity or lack of it as broad terms applying to classes of substances must be abandoned, unless the reactions which are used as the criteria of reactivity are carefully specified. Thus, recent studies of the paraffin hydrocarbons have brought forth abundant evidence that they can be isomerized,

halogenated, sulfonated, and (as will be shown in this paper) carboxylated with the aid of reagents which have little or no effect on aromatic hydrocarbons.

This apparent anomaly is probably due to the fact that substitution reactions in the two series tend to take place by reactions which, in general, follow mechanisms of two distinct types. Substitution reactions in the aromatic series indicate that the mechanism is one involving ionic or polar intermediates. On the other hand, substitution into paraffin hydrocarbons appears to occur most readily by means of chain reactions operating through atom and free radical intermediates.

In the course of the work under way in this Laboratory on chain reactions in solution involving atoms and free radicals, it appeared desirable to investigate means of introducing the carboxyl group directly into aliphatic hydrocarbons. A possible approach to the problem was suggested by the postulated occurrence of the $\cdot\text{COCl}$ free radical as an intermediate in certain photochemical reactions, notably in the formation of phosgene⁴ and in the photochemical decomposition of both phosgene⁵ and oxalyl chloride.⁶ Accordingly, a study of the reaction of phosgene and oxalyl chloride with paraffin hydrocarbons under appropriate experimental conditions was under-

(1) No convenient expression is available for referring to the direct introduction of the chloroformyl group ($-\text{COCl}$) into organic compounds. Rather than coin a new word, the term "carboxylation" has been extended to include this reaction.

(2) Preliminary communication: Kharasch and Brown, *THIS JOURNAL*, **62**, 454 (1940).

(3) Part of the work described in this paper was carried out while H. C. B. was the holder of an Eli Lilly Post-Doctorate Fellowship (1938-1939). The authors wish to express their appreciation to the Eli Lilly Company for the support which made this investigation possible.

(4) Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B2**, 459 (1929).

(5) Montgomery and Rollefson, *THIS JOURNAL*, **56**, 1089 (1934).

(6) Krauskopf and Rollefson, *ibid.*, **58**, 443 (1936).