drous ether was added 2.5 ml. (0.0021 mole) of phenyllithium.[14] The mixture was stirred under dry nitrogen with a magnetic stirrer. Within 5 minutes, a milky solution resulted. After the solution was stirred and refluxed under dry nitrogen for 4 hours, a white precipitate settled out. As the reaction mixture was hydrolyzed with distilled water, a gas was evolved. The solid was now suspended between the ether and water layers. The material was filtered off and dried. There was obtained 0.306 g. (97.8%) of white powder melting at 361–363°. This was identified by a mixed melting point as hexaphenyldisilane.

Pentaphenylethoxydisilane and Phenyllithium.—To 0.50 g. (0.0010 mole) of pentaphenylethoxydisilane in a benzene-ether solution was quickly added 2 ml. (0.0017 mole) of phenyllithium. The solution was magnetically stirred. The reaction mixture took on a milky-white appearance in 15 minutes. After 1 hour, the suspended solids were filtered off, washed with petroleum ether (b.p. 60–70°), and dried. There was obtained 0.44 g. (83%) of material melting at 361–363°. This product was identified as hexaphenyldisilane by a mixed melting point.

Acknowledgment.—The authors are grateful to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared data.

(14) R. G. Jones and H. Gilman, in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 353–354.

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The Alkylation of Gramine and of Indole-N-methylgramine

BY ALLAN P. GRAY

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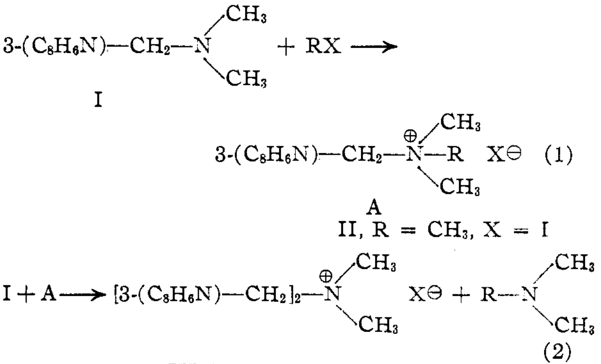
As a result of recent investigations[1] the reaction of gramine (I) with alkyl halides has been clarified. It has been shown that the product of reaction of gramine with methyl iodide (in ethanol) is not gramine methiodide (II), as reported in the literature,[2] but is actually a mixture containing tetramethylammonium iodide, bis-(3-indolemethyl)-dimethylammonium iodide (III) together with small amounts of II. The reaction may be generalized as



$$3\text{-}(C_8H_6N){-}CH_2{-}N\begin{matrix}CH_3\\CH_3\end{matrix} + RX \longrightarrow$$

I

$$3\text{-}(C_8H_6N){-}CH_2{-}\overset{\oplus}{N}\begin{matrix}CH_3\\CH_3\end{matrix}{-}R\ \ X^{\ominus}\quad(1)$$

A

II, R = CH$_3$, X = I

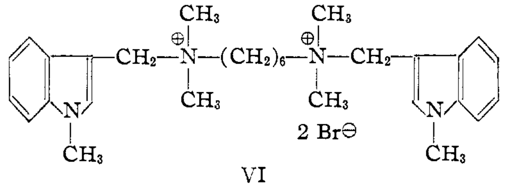
$$I + A \longrightarrow [3\text{-}(C_8H_6N){-}CH_2]_2{-}\overset{\oplus}{N}\begin{matrix}CH_3\\CH_3\end{matrix}\ \ X^{\ominus} + R{-}N\begin{matrix}CH_3\\CH_3\end{matrix}\quad(2)$$

III, X = I
IV, X = Br

The relative proportions of quaternary products are naturally dependent on the proportions of reactants used, on the relative rates of reactions 1 and 2 and on solubility of the products.

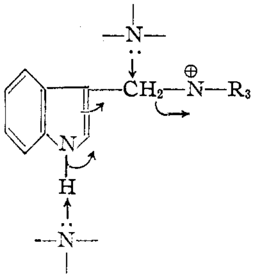
Similar results have been independently obtained in this Laboratory. In attempting to prepare a variety of quaternary derivatives, I was allowed to react with molar proportions of 1,6-dibromohexane, 1,10-dibromodecane and 1-bromohexane at room temperature in either methanol or acetonitrile. The product, which precipitated in large colorless prisms, was in each case bis-(3-indolemethyl)-dimethylammonium bromide (IV). When methanol was the solvent, IV crystallized directly from the reaction in analytically pure form.

It was of some interest to determine if indole-N-methylgramine (V) behaved in similar fashion. The possibility that it might not was supported by the fact that although prior to the recent reports[1] no complete analytical data had ever been reported for gramine methiodide,[2] a satisfactory analysis had been obtained for a sample of N-methylgramine methiodide prepared in alcohol in the ordinary way.[3] It was found that when V was allowed to react at room temperature with 1,6-dibromohexane in methanol, the main product, although somewhat difficult to separate from small amounts of impurities, was the normal 1,6-bisquaternary derivative (VI).



VI

This does not mean that products similar to III and IV might not be obtained from N-methylgramine, but only that the displacement reaction, 2, does not take place as readily with the N-methyl base. Explanation may lie in possible lowering of the activation energy for the displacement by base-catalyzed formation of an intermediate, *viz.*



Available evidence does not permit a decision as to whether the postulated base-catalyzed elimination precedes or coincides with formation of the new C to N bond. This picture of the reaction is supported by the fact that Schöpf and Thesing[1] were able to obtain pure gramine methosulfate in good yield by neutralizing the gramine with acetic acid prior to the addition of methyl sulfate.

Acknowledgment.—Many helpful and stimulating discussions with Dr. C. J. Cavallito were deeply appreciated.

Experimental[4]

Bis-(3-indolemethyl)-dimethylammonium Bromide (IV).—The following are representative experiments in which IV was the only isolated product.

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(1) T. A. Geissman and A. Armen, THIS JOURNAL, **74**, 3916 (1952); C. Schöpf and J. Thesing, *Angew. Chem.*, **63**, 377 (1951).

(2) See for example: A. Orechoff and S. Norkima, *Ber.*, **68**, 436 (1935); H. R. Snyder, C. W. Smith and J. M. Stewart, THIS JOURNAL, **66**, 200 (1944).

(3) H. R. Snyder and E. L. Eliel, *ibid.*, **70**, 1703 (1948).

(4) Microanalyses were performed by the Clark Microanalytical Laboratories, Urbana, Illinois.

A. A solution of 10 g. (0.057 mole) of gramine and 4.7 g. (0.019 mole) of 1,6-dibromohexane in 75 ml. of methanol deposited colorless prisms on standing overnight at room temperature. These were collected, washed with ethanol and then ether. After drying *in vacuo* over phosphorus pentoxide, the product melted 177–178.5° (cor.) and weighed 5.8 g. (52% yield on the basis of gramine). Additional material, which could be purified by methanol recrystallization, was recovered from the filtrates by precipitation with ether.

Anal. Calcd. for $C_{20}H_{22}N_3Br$: C, 62.50; H, 5.77; N, 10.93. Found: C, 62.78; H, 5.77.

B. Reaction of 1,10-dibromodecane with gramine in similar fashion afforded a crystalline solid which was recrystallized from methanol; m.p. alone and mixed with the product described in A was 177–178.5° (cor.).

Anal. Found: C, 62.11; H, 5.72; N, 10.80.

C. A similar reaction of 5.2 g. (0.03 mole) of gramine with 7.4 g. (0.045 mole) of 1-bromohexane in acetonitrile solution yielded 5.2 g. (92%) of crystalline precipitate after 4 days at room temperature; m.p. 178–180°, undepressed when mixed with the product from A or B. Negligible amounts of additional precipitate were obtained on addition of ether to the filtrate.

Indole-N-methylgramine (V).—N-Methylindole, b.p. 125–130° (20 mm.), n^{23}D 1.6071, was prepared from indole[5] with the exception that sodium hydride was used in place of sodium. V, b.p. 113–116° (0.5 mm.), n^{23}D 1.5734, was obtained from N-methylindole as described by Snyder and Eliel[3] who reported b.p. 94–96° (0.2 mm.), n^{20}D 1.5743.

Reaction of V with Dibromohexane (VI).—A solution of 4.8 g. (0.026 mole) of V in 50 ml. of methanol treated with 2.1 g. (0.0086 mole) of dibromohexane yielded no precipitate after 5 days at room temperature. Addition of anhydrous ether precipitated an oil which was washed with fresh ether, dissolved in ethanol and reprecipitated. The thick viscous oil was dried over phosphorus pentoxide *in vacuo* to yield 2.4 g. of white crystalline deliquescent solid (A). The material evolved gas at 144–145°, solidified at 151° and remelted 192–202°.

A was fractionally crystallized from propanol and ether. During crystallization undue heating was avoided as decomposition appeared to take place if the solution was heated much above 50°. The head fraction, after two further recrystallizations from propanol, afforded 100 mg. of white crystals (B), m.p. 220° (decomp.). B was not further investigated.

After several recrystallizations of the mother liquor material from propanol and ether 900 mg. of white hygroscopic solid (C), which softened and evolved gas at 100°, turned red at 125° and fused at 140°, was obtained.

Anal. Calcd. for bis-(indole-N-methylgramine)quaternary salt, VI, $C_{30}H_{44}Br_2N_4$: C, 58.06; H, 7.15. Found: A: C, 57.18; H, 7.20. C: C, 57.72; H, 7.58. *Anal.* of B: C, 38.08; H, 7.83.

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[5] R. Weissgerber, *Ber.*, **43**, 3520 (1910).

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The Mechanism of the Acid-catalyzed Hydration of Olefins[1]

BY JOSEPH B. LEVY, ROBERT W. TAFT, JR., AND LOUIS P. HAMMETT

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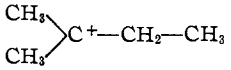
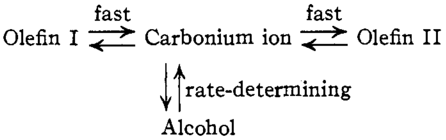
In a study of the rates of the acid-catalyzed hydration of the two isomeric olefins trimethylethylene (I) and *asym*-methylethylethylene (II) by methods whose application to other olefins has been described[2] we have had occasion to observe that at 50% reaction neither olefin has been measurably converted to the isomer. The result is of importance in connection with the mechanism of the hydration because an identical carbonium ion (III) is obtained by the addition of a proton to



$$(CH_3)_2C^{+}—CH_2—CH_3$$

either of these olefins. Consequently, the reaction scheme consisting in the rapid and reversible addi-



tion of a proton to the olefin followed by a rate-determining reaction of the ion with a water molecule is definitely excluded as the mechanism of the hydration reaction.

The two olefins would be expected to hydrate to a single product *t*-amyl alcohol and this has been reported[3] to be the case. A further careful test on our part shows that the most probable alternative, methylisopropylcarbinol, does not constitute as much as 2% of the product of the hydration of I.

Experimental

Test for Interconversion of the Olefins.—Gaseous olefin I was shaken at 35° with 0.973 *M* nitric acid under the conditions of a rate measurement[2] until the pressure had dropped to about half of the initial value and olefin II was treated similarly at 20°. The residual olefin was then removed in each case and its infrared absorption observed in the gaseous state with a path length of 10 cm. and at a pressure equal to the vapor pressure of the olefin at 20° (*ca.* 380 mm. for I and 450 mm. for II). Under these conditions I has an absorption band with a peak at 1120 cm.$^{-1}$ for which log I_0/I was 1.2 both for the pure substance and for the partially reacted sample. At this frequency log I_0/I for II was about 0.1, both for the pure substance and for the partially reacted sample. II has a band at 1660 cm.$^{-1}$, for which log I_0/I was found to be 0.9 both for the pure substance and for the partially hydrated sample. At this frequency log I_0/I was about 0.2 both for pure I and for the partially hydrated sample.

Reaction Product.—A sample of several ml. of trimethylethylene was allowed to react at 35° for several days with 0.973 *M* nitric acid under conditions essentially identical with those prevailing during a rate measurement. The resulting solution was filtered, saturated with ammonium sulfate, and extracted with ether. The ether solution was dried and the ether evaporated through a small column. All of the residue (1.4 g.) was then distilled through the column at 99 to 102° (uncor.), n^{25}D 1.4017. Under the same conditions a purified known sample of *t*-amyl alcohol boiled at 100.8 to 101.3° and had n^{25}D 1.4028, and a purified known sample of methylisopropylcarbinol boiled at 110.0 to 111.0° and had n^{25}D 1.4069. These values are consistent with data in the literature.

A 15% solution of the hydration product in carbon tetrachloride absorbed strongly in the infrared at 1190 cm.$^{-1}$ but not detectably at 1110 cm.$^{-1}$. *t*-Amyl alcohol has a strong broad absorption band at 1190 ± 10 cm.$^{-1}$ and methylisopropylcarbinol has a similar one at 1100 ± 10 cm.$^{-1}$. On the basis of the absorption shown at 1110 cm.$^{-1}$ by a solution containing the tertiary and secondary alcohols in the ratio of 9:1 we estimate that the hydration product cannot contain as much as 2% of the methylisopropylcar-

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[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951); (b) R. W. Taft, Jr., B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952).

[3] (a) H. J. Lucas and Yun-Pu Liu, *ibid.*, **56**, 2138 (1934); (b) Yun-Pu Liu and Tien-Chi Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).