tene-1 and a mixture of two isomers in the ratio of 70/30 from pentene-2. The isomers are likely to be the 2-pentyl- and 3-pentyl-silanes.

EXPERIMENTAL

Addition of trichlorosilane to pentene-1. Burkhard and Krieble[3] added trichlorosilane to pentene-1 and reported the formation of *n*-pentyltrichlorosilane. *n*-Pentyltrichlorosilane has also been made from the *n*-pentylmagnesium bromide and tetrachlorosilane.[6] The reported properties were not sufficient to indicate with certainty that the pentyltrichlorosilane we obtained was *n*-pentyltrichlorosilane free of isomers. Therefore, the product obtained as described in the discussion was carefully distilled through a column 3 ft. long and 1 inch in diameter packed with 1/16 inch "Helipak" packing. The product was *n*-pentyltrichlorosilane essentially free of isomers: b.p. 171.0° at 742 mm., n_D^{25} 1.4379, d_4^{25} 1.128; R_D 0.2327, Calc'd 0.2320.

Methylation with excess methylmagnesium bromide in ether gave an 80% yield of *n*-pentyltrimethylsilane: b.p. 139.3° at 743 mm., n_D^{25} 1.4069, d_4^{25} 0.7271; R_D 0.3385, Calc'd 0.3382.[7]

n-Pentyltrimethylsilane was prepared by adding a mixture of *n*-amyl chloride and trimethylchlorosilane to molten sodium in refluxing toluene, b.p. 138.9–139.1° at 740 mm., n_D^{25} 1.4069, d_4^{25} 0.7267; R_D 0.3387, Calc'd 0.3382.

The infrared absorption curves of the two samples were identical.

Addition of trichlorosilane to pentene-2. Under the same conditions pentene-2 yielded a pentyltrichlorosilane with properties quite easily distinguishable from those of *n*-pentyltrichlorosilane. From pentene-2 one might expect 2-pentyl- or 3-pentyl-trichlorosilane or a mixture of the two.

A gas-phase chromatographic analysis was performed on a 15 microliter sample on a six-foot Celite column impregnated with didecyl phthalate as the liquid substrate at 80°. Nitrogen was used as the carrier gas with an inlet pressure of 2 p.s.i. at a flow rate of 10 ml. per minute. Two peaks were obtained. The first had a retention time of 21.2 min. and amounted to 70% of the sample. The second at 23.1 min. contained about 30% of the sample. Because standard samples were not available it is impossible to ascertain the structures of the two components[8] at this time. The product had the properties: b.p. 165–167°, n_D^{25} 1.4455, d_4^{25} 1.145; R_D 0.2327, Calc'd 0.2320. An adduct prepared in this way has been reported[3] to boil at 164–168°.

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(6) F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **68**, 475 (1946).

(7) F. C. Whitmore, *et al.*[6] report b.p. 139° at 760 mm., n_D^{20} 1.4096, d_4^{20} 0.7313.

(8) This analysis was carried out in the Department of Research in Physical Chemistry at Mellon Institute.

Preparation of 6-Quinolyl- and 6-Quinolylmethyl-phosphonic Acids

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Although several phosphonic acids, in which the phosphono group is attached to a heterocyclic ring, have been prepared in recent years by various procedures, there is still a decided paucity of data about the phosphonic acids with the simple, more common nitrogen-bearing heterocyclic rings. In view of the fact that the classical Skraup reaction does not appear to have been applied to the readily available aminoarylphosphonic acids, it was felt that this application of the Skraup reaction should be examined. In order to avoid the separation of isomeric phosphonic acids the present synthesis was confined to amino derivatives which can give only one compound by the Skraup reaction.

EXPERIMENTAL

6-Quinolylphosphonic acid. *p*-Nitrophenylphosphonic acid was prepared according to Doak and Freedman[1] and was hydrogenated to *p*-aminophenylphosphonic acid over a palladium-charcoal catalyst in aqueous solution at room temperature and atmospheric pressure. The amino acid (3.0 g.), 13 ml. of 70% sulfuric acid, 4.0 g. of dry glycerol, and 3.5 g. of nitrobenzene were mechanically stirred and refluxed gently for 1.5 hours. The dark mixture was diluted with 20 ml. of water, steam-distilled, cooled, and filtered from tarry material. The filtrate was adjusted to the Congo Red endpoint with 20% sodium hydroxide and the crude product which precipitated was collected. The precipitate was dissolved in 15% hydrochloric acid and re-precipitated by the addition of sodium hydroxide solution. It was finally dissolved in 10% sodium hydroxide solution and precipitated by the addition of 15% hydrochloric acid. At each step of the purification the solution was treated with charcoal. There was obtained 2.0 g. (56%) of 6-quinolylphosphonic acid, in the form of colorless, stubby flat needles which melted to a bright red liquid at 303–304°. Titration of the material with 0.1 *N* sodium hydroxide yielded a curve with inflections near *p*H 5 and 10.5, the latter inflection being the more clearly defined of the two.

Anal. Calc'd for $C_9H_8NO_3P$: P, 14.85; Equiv. wt. 209. Found: P, 14.7, 14.8; Equiv. wt. 210.

6-Quinolylmethylphosphonic acid. The procedure described above was followed, with 6.0 g. of *p*-aminobenzylphosphonic acid,[2] 26 ml. of 70% sulfuric acid, 8.0 g. of glycerol, and 7.0 g. of nitrobenzene. There was obtained, after three acid-base re-precipitations, 3.9 g. (54%) of 6-quinolylmethylphosphonic acid, in the form of light-tan colored, fine plates which decomposed to a red liquid at 328–329°.

Anal. Calc'd for $C_{10}H_{10}NO_3P$: P, 13.9; Equiv. wt., 223. Found: P, 13.8, 13.75; Equiv. wt., 219, 220 (inflection points on the titration curve occurred at approximately *p*H 5.8 and 11).

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(1) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(2) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **69**, 2112 (1947).

The Geminal Alkyl Effect on the Rates of Ring Closure of Bromobutylamines

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In view of the temporary interruption of an investigation[1] of the profound effect which geminal

(1) R. F. Brown and N. van Gulick, *J. Am. Chem. Soc* **77**, 1079, 1083, 1089 (1955).

alkyl substitution exerts upon ring closure, it seems advisable to present our preliminary kinetic data as well as some interesting conclusions to be drawn therefrom.

It is a well known rule that geminal alkyl substitution strikingly enhances the tendency of a suitably chosen bifunctional compound to cyclize.[2] The cyclization of substituted 4-bromobutylamines to the corresponding pyrrolidines with elimination of hydrogen bromide was selected as being conveniently amenable to kinetic investigation and because it would afford adequate information as to the effect of the nature and position of substitution. Furthermore, as demonstrated by Freundlich[3] for the parent compound, 4-bromobutylamine, the reaction is virtually quantitative, being free from side reactions, and is completely irreversible. The short half-life of approximately one second which Freundlich established for 4-bromobutylamine suggested that the reaction should be run in a buffered acidic medium, as the concentration of the reactive free base could be controlled to afford observed rates in an easily measurable region.

The kinetics may be set up on the basis of a fast equilibrium between the salt of the bromoamine and the free base, followed by the irreversible rate determining S_N2 displacement of bromide ion by the free amino group. Employing the steady state convention, the kinetic expression for a strongly buffered system is

$$k_{obs.} = \frac{k K_a}{(H^+)} = \frac{2.303}{t} \log \left[\frac{(A)}{(2(A) - (Br^-)_t)}\right], \quad (1)$$

where k is the *p*H-invariant cyclization rate constant for the free base, K_a is the dissociation constant for the 4-bromobutylammonium ion, (A) is the initial concentration of bromobutylamine hydrobromide, and $(Br^-)_t$ is the bromide ion concentration at time t. Formulated in terms of the analytical method, this becomes

$$k_{obs.} = \frac{k K_a}{(H^+)} = \frac{2.303}{t} \log \left(\frac{V_o - V_\infty}{V_t - V_\infty}\right), \quad (2)$$

where V_o, V_t, and V_∞ represent the volumes of potassium thiocyanate titrant required in the Volhard determination of bromide ion at the times indicated by the subscripts. Precise determination of rate constants in unbuffered systems is difficult as the corresponding kinetic expression,

$$k'_{obs.} = \frac{k K_a}{(Br^-)_0} = \frac{2.303}{t} \log \left(\frac{V_o - V_\infty}{V_t - V_\infty}\right) - \frac{1}{t}\left(\frac{V_o - V_t}{V_o - V_\infty}\right), \quad (3)$$

involves a small difference between large terms. Results for runs at 30.00 ± 0.01°C. with acetate-acetic acid and formate-formic acid buffers are summarized in Table I.

TABLE I

SUMMARY OF RATE STUDIES AT 30°

Run No.	Substances as Hydrobromides	Buffer, Moles per liter NaAc	HAc	NaFo	HFo	KNO_3	$k_{obs} \times 10^6$ (sec.$^{-1}$)	k_{rel}
5[a]	4-Bromobutylamine	2.0	0.5				6.7	
12	4-Bromobutylamine	0.5	.25				2.66 ± 0.05	1.00
13[a]	4-Bromo-1,1-dimethylbutylamine	.5	.25				5.5	
17	4-Bromo-1,1-dimethylbutylamine	.5	.25				5.84 ± .25	2.19
1	4-Bromo-2,2-dimethylbutylamine	1.0	1.0				204 ± 6	
7	4-Bromo-2,2-dimethylbutylamine	1.0	1.0				204 ± 2	
3	4-Bromo-2,2-dimethylbutylamine	1.0	1.0			1.0	203 ± 2	
6	4-Bromo-2,2-dimethylbutylamine	0.5	0.5			0.5	180 ± 1	
9	4-Bromo-2,2-dimethylbutylamine	.25	.25			.75	171 ± 3	
11	4-Bromo-2,2-dimethylbutylamine	.25	.25				210 ± 5	158
2	4-Bromo-2,2-dimethylbutylamine	.5	1.0			.5	96.3 ± 1.4	
10	4-Bromo-2,2-dimethylbutylamine	.25	0.5			.75	87.8 ± 1.0	
16	4-Bromo-2,2-dimethylbutylamine			0.5	1.0		7.96 ± 0.08	
8	4-Bromo-2,2-dimethylbutylamine	None					0.47 ± .05[b]	
19	4-Bromo-2,2-diethylbutylamine			.5	1.0		29.9 ± 1.7	594
4[a]	4-Bromo-2,2-diisopropylbutylamine	0.5	1.0			.5	56	9190
18[a]	4-Bromo-2,2-diphenylbutylamine	.5	0.25				140	5250
14[a]	4-Bromo-3,3-dimethylbutylamine	.5	.25				0.42	0.158

[a] These runs should be regarded as preliminary results. [b] This is k'_{obs} in which $(Br^-)_0 = 9.59 \times 10^{-3}$ *M*.

Comparison of runs 1 and 7 illustrates the excellent reproducibility of the system. Inspection of run 3 shows that, at an acetate concentration of 1 *M*, addition of an inert salt, potassium nitrate, has no further effect upon the rate. However, by maintaining a constant buffer ratio of 1 and using potassium nitrate to maintain constant ionic strength, runs 7, 6, and 9 demonstrate a definite trend of increasing rate with increasing buffer concentration. The same phenomenon is evident in runs 2 and 10 at the same ionic strength but with a buffer ratio of ½. Offhand, this would appear to result from oper-

(2) See, for example, G. W. Wheland, *Advanced Organic Chemistry*, 2nd ed., J. Wiley and Sons, Inc., New York, N. Y., 1949, pp. 373–374.

(3) H. Freundlich, *et al.*, *Z. physik. Chem.*, **122**, 29 (1926).

ation of a mild Brønsted general acid catalysis. However, comparison of runs 9 and 11 shows that removal of the inert salt allows $k_{obs.}$ to increase. Also, since runs 9 and 11 show a faint tendency to slow down as the reaction proceeds, 0.25 *M* acetate was considered to be the lower limit of successful buffer action.

A rate *versus* buffer concentration plot at the two buffer ratios gives two lines with different slopes. These facts fail to support general catalysis as the only explanation. An understanding is rather to be sought in the complex *p*H–composition behavior of the acetate-acetic acid buffer system.[4] The rates of runs 2 and 10 would be $^1/_2$ those of runs 6 and 9 if hydrogen ion concentration were determined only by the buffer ratio. Such discrepancies preclude using buffer ratios to determine relative *p*H's among runs. In extending the work, it will be necessary to determine *p*H's to three places in the mantissa, a bothersome task it was originally hoped to avoid. Until this is done, it will be impossible to ascertain the magnitude of the primary and secondary salt effects on the reaction *per se*. On the other hand, once standardized, a very sensitive method would be available for the determination of *p*H.

The effect of change of position of geminal methyl substitution is seen to be large. For substitution at the first carbon, the rate is only doubled as compared to the parent molecule, but, at the second carbon, the maximum effect appears, the rate being 158 times faster. Substitution at the third carbon decreases the rate which is only about $^1/_6$ as fast as the parent. However, the bromine occupies a neopentyl position in this case and the observed rate represents a marked acceleration for such a hindered displacement reaction.

The remarkable effect of size of the geminally substituted group at the 2-position is shown by the observation that ethyl is 594 times better than the parent, isopropyl is 9190 times better, and phenyl is 5250 times better in promoting ring closure. This would seem to exclude electronic effects of the substituents as exerting anything other than a minor influence on the rates, as phenyl and isopropyl have opposite electronic effects but similar steric requirements. A consideration of the intimate cyclization process suggests that geminal alkyl substitution profoundly affects the distribution of rotational configurations by reason of nonbonded interactions with the chain, favoring coiled configurations over what would be the energetically preferred extended configuration of the parent molecule. While it is difficult to predict how this would affect activation energies *a priori*, the effect upon activation entropies is more clearly evident. The decrease in entropy for a rotationally restricted coiled molecule upon going into the transition state would be less than that for the parent molecule, thus increasing the cyclization probability. It is expected that activation energies and entropies made available from rate data at other temperatures will provide valuable quantitative information concerning rotational conformations which would otherwise be difficultly accessible for such relatively complex molecules.

With these preliminary data in hand, it is possible to advance an explanation for the puzzling behavior of 4-phenoxy-2,2-diarylbutylamines and 4-methoxy-2,2-diisopropylbutylamine in boiling concentrated hydrobromic acid.[1] The expected 4-bromobutylamine hydrobromides were formed in yields of 3% (48 hour reflux period) and 47% (*ca.* 30 min. reflux period), respectively. Surprisingly, the corresponding pyrrolidine hydrobromides accounted for the remainder of the starting material. That the pyrrolidine salts were formed by cyclization of the bromoamine hydrobromides produced by hydrolysis of the amino ethers was considered completely untenable at the time as the concentration of the reactive free bromoamine must be negligible in such a highly acidic reaction medium. However, it now appears that such negligible concentrations are sufficient to explain the results.

It is reasonable to assume that $K_{a(BrRNH_3^+)} \simeq K_{a(BuNH_3^+)}$ and $\Delta H_{(BrRNH_3^+)} \simeq \Delta H_{(NH_4^+)}$, where ΔH refers to the heat of dissociation of the corresponding aqueous ammonium ions, and it can be seen that for a one *molar* solution in boiling 48% hydrobromic acid, the concentration of the free bromoamine is on the order of 10^{-9} *M*, if K_a is still reasonably valid under these conditions. Despite this tiny concentration, ring closure will occur at an easily measurable rate by virtue of the inordinate cyclization tendency conferred by geminal or isopropyl substitution. This is easily shown by a simple approximate calculation. Using the observed cyclization rate of 4-bromo-2,2-diphenylbutylamine hydrobromide at 30°, and, assuming that the heat of dissociation of this salt in aqueous solution is 12 kcal., the value for the aqueous ammonium ion, and that $\Delta H^{\mp}$ is 20 kcal., a reasonable value for most organic reactions, then $(k\ K_a)_{126°} \simeq 10^{-1}$ sec^{-1}. The observed value from the preparative data[1] is on the order of 10^{-4} sec^{-1}. The main reason for the discrepancy is to be found in the implicit assumption that hydrolysis of the phenoxyamine is rapid compared to cyclization of the bromoamine so produced. This condition is not actually fulfilled as the insolubility of the phenoxyamine in the reaction medium precludes rapid hydrolysis. If this could be taken into account, the correction would be in the right direction. On the other hand, 4-methoxy-2,2-diisopropylbutylamine is quite soluble in concentrated hydrobromic acid and hydrolysis does appear to be rapid. Consequently, the observed and calculated values agree more closely. Thus, $(k\ K_a)_{126°}$ is calculated to be on the order of 10^{-1} sec^{-1}

(4) W. M. Clark, *The Determination of Hydrogen Ions*, 3rd ed., The Williams and Wilkins Co., Baltimore, Md., 1928, pp. 21, 219.

and the observed value is on the order of 10^{-2} sec^{-1}. Considering the drastic approximations, this agreement is excellent and substantiates the proposed explanation. Further supporting evidence is available in the fact that the 4-bromo-2,2-disubstituted-butylamine hydrobromides melt with dissociative decomposition in the range 170–195°, freely evolving hydrogen bromide with concomitant formation of the corresponding pyrrolidine hydrobromides. In fact, the isopropyl compound is so predisposed to cyclize that solutions of the pure bromoamine salt in carbon tetrachloride begin visibly to evolve hydrogen bromide at 50°. Rate studies of cyclization in 48% hydrobromic acid are planned for the future in order to throw additional light on this unexpected phenomenon.

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The Dimethylamine–1,3,5-Trinitrobenzene Complex in Dioxane

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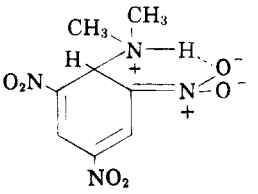
Evidence has been presented[1] that 1,3,5-trinitrobenzene reacts with four molecules of dimethylamine in dioxane solution to form a colored 4:1 complex. The particular treatment used to test this hypothesis assumed that the only species present in the solution were dimethylamine, 1,3,5-trinitrobenzene, and the 4:1 complex. We find that the color produced by dimethylamine and 1,3,5-trinitrobenzene in dioxane is formed instantaneously and is stable with time at constant temperature. It, therefore, seems to us improbable that only a 4:1 complex is formed, particularly since this would necessitate a transition state involving five molecules. Moreover, if 1:1, 2:1, or 3:1 complexes are intermediates for formation of the 4:1 complex, then it seems to us inconsistent with both the chemical nature of the reagents involved and the principle of microscopic reversibility that none of these lower complexes persist at equilibrium. Accordingly, it is our present purpose to offer an alternate hypothesis which fits the available data equally well and which appears to us to be more probable.

Studies of the acidity of aromatic nitro compounds towards amines by Lewis and Seaborg[2] suggest a possible mode of interaction of dimethylamine and 1,3,5-trinitrobenzene. These authors suggest that the attachment of the amine to the nitro compound is *via* the direct addition of the base to one of the ring carbons that is not attached to a nitro group and *via* hydrogen bonding between the amine hydrogen and an oxygen of a nitro group. To illustrate, we have represented one of the contributing structures to the resonance state of the 1:1 complex in the formula below.



Since 1,3,5-trinitrobenzene has three nitro groups and three intervening ring carbon atoms, there are possibilities for forming three complexes, a 1:1, a 2:1, and a 3:1 complex.

For this type of interaction the three equilibria involved are

$$T + A \rightleftharpoons TA$$
$$TA + A \rightleftharpoons TA_2$$
$$TA_2 + A \rightleftharpoons TA_3$$

where T is the trinitrobenzene and A is dimethylamine, and the three associated equilibrium constants are given by

$$K_1 = \frac{TA}{T \cdot A}$$

$$K_2 = \frac{TA_2}{A \cdot TA}$$

and

$$K_3 = \frac{TA_3}{A \cdot TA_2}$$

To relate these equilibrium constants to the spectroscopic data in a manageable form it is necessary to make some assumptions as to the relative amounts of the 1:1, the 2:1, and 3:1 complexes at equilibrium. The simplest assumption we can make is that the relative amounts of the three complexes are determined by purely statistical considerations; *i.e.*, $K_1 = 9\,K_3$ and $K_2 = 3\,K_3$. This assumption is probably justified, since all of the species involved are neutral molecules and no strong electrostatic forces are involved. Further, we assume that

$$A \cong Ao,$$

where A is the equilibrium concentration of amine and Ao is the initial concentration of the amine. This assumption is clearly permissible, since in all of the measurements the amine concentration is at least 200 times as great as the trinitrobenzene concentration. Finally, we assume that

$$TA_3\,\epsilon_{TA_3} \gg TA\,\epsilon_{TA} \text{ or } TA_2\,\epsilon_{TA_2},$$

where the ϵ's are extinction coefficients. This assumption is, we feel, a reasonable approximation based on the qualitative results reported by Lewis and Seaborg.[2]

The resulting equation, which relates the optical data and the equilibria is

(1) Foster, Hammick, and Wardley, *J. Chem. Soc.*, 3817 (1953).

(2) Lewis and Seaborg, *J. Am. Chem. Soc.*, **62**, 2122 (1940).