tained. The solution was then concentrated to about a third of the volume and cooled. Additional crystalline material was obtained. The solution was then concentrated to 50–75 cc. and treated with three volumes of anhydrous ether. Each of the precipitates did not melt below 495°.

Acknowledgment.—The authors are grateful to Messrs. E. F. Shelberg and O. Kolsto for microanalyses, P. Helgren for vapor phase chromatographic results, and to Mr. Y. H. Ng for technical assistance.

Ortho Substitution Rearrangement of 1,1-Dimethyl-2-phenylpyrrolidinium Ion by Sodium Amide. Ring Enlargement to Form a 2-Benzazocine[1]

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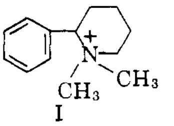
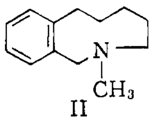
The 1,1-dimethyl-2-phenylpyrrolidinium ion (III) reacted with sodium amide in liquid ammonia to form 2-methyl-1,2,3,4,5,6-hexahydro-2-benzazocine (IV) and a polymer in about equal yields. The product IV was formed by an ortho substitution rearrangement involving the enlargement of a five-membered ring to an eight-membered ring. This reaction furnishes a new and convenient route to the synthesis of certain 2-benzazocine derivatives. The polymer evidently arose through an elimination reaction. The conformation of quaternary ion III appears to be less favorable for rearrangement than that of the earlier reported 1,1-dimethyl-2-phenylpiperidinium ion, which rearranges exclusively.

Recently[2] quaternary ammonium ion I was shown to undergo the ortho substitution rearrangement with sodium amide in liquid ammonia to form tertiary amine II in 83% yield. The rearrangement involves enlargement of a six-membered ring to a nine-membered ring. Although quaternary ion I had β-hydrogen, no appreciable elimination reaction was observed.

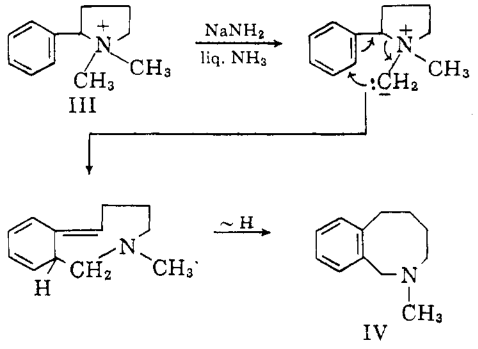


I



II

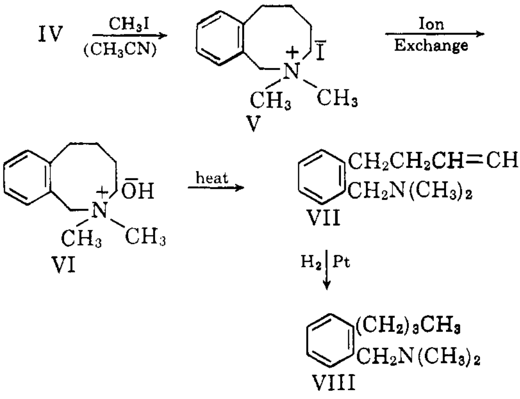
In the present investigation the related 1,1-dimethyl-2-phenylpyrrolidinium ion (III) reacted with sodium amide in liquid ammonia to afford tertiary amine IV and polymeric material in yields of 41 and 38%, respectively (see below). Amine IV arose through the ortho substitution rearrangement involving enlargement of a five-membered ring to an eight-membered ring (Scheme A).[3]



Scheme A

The distilled rearranged amine was indicated by vapor phase chromatography to consist essentially of a single substance. It was shown to be an *ortho* substitution rearrangement product by oxidation to form phthalic acid (51%). No benzoic acid was isolated; this acid should have been obtained has the original rearrangement involved a possible Stevens 1,2-shift.

Structure IV was established by a Hofmann degradation of hydroxide VI, which was prepared through methiodide V by ion exchange. The degradation afforded olefin-amine VII (not isolated), which was hydrogenated to give amine VIII (Scheme B).



Scheme B

The hydrogenation product was shown by vapor phase chromatography to be contaminated with a small amount of higher boiling material, which arose presumably through SN2 displacement at

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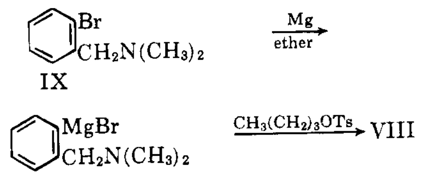
[1] Supported by the National Institutes of Health, Grant No. CY-4455(C2).

[2] D. Lednicer and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 4449 (1958).

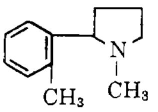
[3] The methyl carbanion in this scheme might arise through intermediate formation of a benzyl type carbanion; see ref. 7.

the benzyl carbon of VI by hydroxide ion. The structure of the main hydrogenation product was established as VIII by its independent synthesis from the Grignard reagent of *o*-bromobenzyldimethylamine (IX) and *n*-butyl *p*-toluenesulfonate (Scheme C).



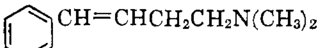
Scheme C

Incidentally the rearranged amine did not have structure X,[4] which is isomeric with IV, since the Hofmann degradation of the quaternary ammonium hydroxide corresponding to X could not have afforded olefin–amine VII. Moreover, the infrared spectrum of the rearranged amine differed from that reported for X[5], and the melting points of the picrate and methiodide of the rearranged amine were 50–60° higher than those reported for the corresponding derivatives of X.[5]



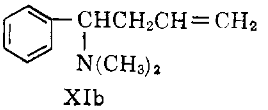
X

The polymeric material that was obtained in addition to the rearranged amine IV from the quaternary ion III with sodium amide in liquid ammonia evidently arose through elimination products XIa and/or XIb. It did not arise from rearranged amine IV on distillation, since this compound was redistilled at about the same temperature without detectable decomposition. Moreover, the infrared spectrum of the polymer showed strong bands at 755 and 700 cm.$^{-1}$ indicative of five adjacent aromatic hydrogens[6] as in the monomers XIa–b.



$C_6H_5CH=CHCH_2CH_2N(CH_3)_2$

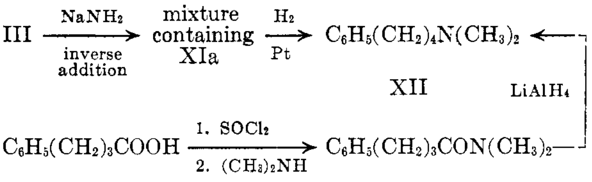
XIa



$C_6H_5CH(N(CH_3)_2)CH_2CH=CH_2$

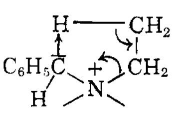
XIb

That the olefin–amine XIa was produced in the reaction of quaternary ammonium ion III with sodium amide in liquid ammonia was demonstrated by effecting the reaction by the inverse addition procedure and hydrogenating the crude product (see experimental). The hydrogenation product was shown by vapor phase chromatography to contain amine XII, a sample of which was independently synthesized (Scheme D).

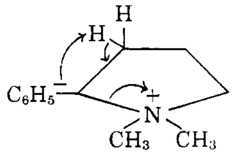


Scheme D

It should be pointed out that the α′,β-elimination mechanism which has been demonstrated to operate with straight chain benzyl type carbanions as in XIII[7] cannot apply to the formation of olefin–amine XIa from quaternary ammonium ion III. If the benzyl carbanion is involved in an intramolecular mechanism, the β-hydrogen might shift as a proton to the benzylic carbon accompanied by β-elimination as indicated in XIV. However, an intermolecular mechanism might operate. The α′,β-elimination mechanism with the benzyl carbanion of quaternary ion III might lead to the formation of XIb, but a consideration of molecular models indicates that this mechanism is unlikely. Actually we have not demonstrated whether XIb is produced.



XIII



XIV

The fact that the yield of rearranged amine IV from quaternary ion III was only half that of rearranged amine II from quaternary ion I is in line with the apparently less favorable conformation of III than I for rearrangement. Thus a consideration of molecular models indicates that only one of the two N-methyl groups might be available for rearrangement in III, and appreciable elimination occurs. However, both of the N-methyl groups should be available for rearrangement in I, and no appreciable elimination occurs.

Since lowering of temperature is known to favor displacements over eliminations, the reaction of quaternary ion III with the alkali amide was carried out at −78° in the hope that relatively more rearrangement would be realized. The rearrangement may be regarded as an allylic type displacement (S$_N$i′). As anticipated, the ratio of rearranged amine IV to polymer appeared to be increased somewhat. From the synthetic standpoint however, the usual temperature (−33°) is probably to be preferred (see Experimental).

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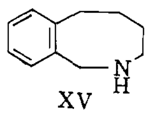
[4] This amine might have arisen by migration of a methyl group from nitrogen to the benzene ring by a mechanism that has been shown not to be operative in at least certain ortho substitution rearrangements; see S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **26**, 2979 (1961).

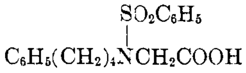
[5] L. P. A. Fery and L. van Hove, *Bull. soc. chim. Belges*, **69**, 63 (1960).

[6] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, 1958, p. 76.

[7] See F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 1542 (1962).

Although the rearrangement of III is accompanied by elimination, the reaction furnishes a new and convenient method for the synthesis of tertiary amine IV, which presumably could be obtained by methylation of the earlier reported secondary amine XV.[8] The latter amine was isolated in only 5% yield by the cyclization of XVI, which was prepared in two steps from δ-phenylbutylamine and ethyl bromoacetate.

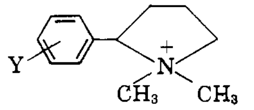

XV

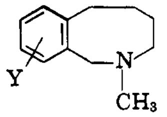

$C_6H_5(CH_2)_4\overset{SO_2C_6H_5}{\overset{|}{N}}CH_2COOH$

XVI

The starting compound III was readily prepared from N-methyl-α-pyrrolidone and phenylmagnesium bromide followed by reduction and methylation. Other convenient methods have been described previously.[9]

The present method of synthesis of IV should be applicable also to certain of its derivatives having general formula XVIII where Y is a substituent such as methoxy. These compounds, which belong to the 2-benzazocine system, could presumably be obtained through ring enlargement of XVII. Indeed, the presence of methoxy in XVII might be expected to improve the yield of XVIII, since the 2- and 4-methoxybenzylethyldimethylammonium ions have recently been observed to undergo relatively more rearrangement and relatively less elimination reaction than the unsubstituted benzylethyldimethylammonium ion.[10]


XVII


XVIII

Experimental[11]

1,1-Dimethyl-2-phenylpyrrolidinium Iodide (III).—An ethereal solution of excess phenylmagnesium bromide was treated with 99.1 g. (1.0 mole) of N-methyl-α-pyrrolidone and the product reduced with excess magnesium and hydrochloric acid, essentially as described by Craig[12] on 0.2-mole scale. There was obtained 55.3 g. (34%) of 1-methyl-2-phenylpyrrolidine, b.p. 104–106° at 20 mm., lit.[12] b.p. 106° at 20 mm. The picrate, recrystallized from 95% ethanol, melted at 146–147°, lit.[12] m.p. 146°.

A solution of 32.5 g. (0.20 mole) of 1-methyl-2-phenylpyrrolidine and 57.5 g. (0.40 mole) of methyl iodide in 200 ml. of acetonitrile was stirred for 36 hr., and 200 ml. of anhydrous ether was then added. The resulting precipitate was collected on a funnel, washed twice with anhydrous ether, and dried in a vacuum desiccator to give 52.9 g. (86%) of 1,1-dimethyl-2-phenylpyrrolidinium iodide (111), m.p. (sealed tube) 152–154° dec., lit.[13] m.p. 130°. After one recrystallization from absolute ethanol-hexane, the salt melted at 156–157°.

Anal. Calcd. for $C_{12}H_{18}IN$: C, 47.53; H, 5.98; N, 4.62. Found: C, 47.38; H, 5.95; N, 4.64.

Rearrangement of Salt III to Form Amine IV.—To a stirred suspension of 0.20 mole of sodium amide in 500 ml. of commercial anhydrous liquid ammonia[14] (Dry Ice–acetone condenser) was added, during 10 min. 30.3 g. (0.10 mole) of quaternary ammonium iodide III. The resulting red-brown reaction mixture became gray during 3 hr., after which time 10.7 g. (0.20 mole) of solid ammonium chloride was added. Anhydrous ether (500 ml.) was added and the ammonia was allowed to evaporate. The resulting ethereal suspension was filtered to remove salts and the filtrate was dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was distilled affording 7.20 g. (41%) of 2-methyl-1,2,3,4,5,6-hexahydro-2-benzazocine (IV) b.p. 120–122° at 9.0 mm., and leaving 6.61 g. (38% calculated as XIa–b) of polymeric residue.

Vapor phase chromatography of the distilled amine IV indicated that it consisted almost entirely of a single substance (IV) with only a slight trace of an impurity.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.30; H, 9.66; N, 7.95.

The picrate of IV, recrystallized from absolute ethanol, melted at 212.0–212.5°.

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.99; N, 13.86. Found: C, 53.49; H, 4.93; N, 13.65.

The infrared spectrum of the polymeric residue left on distilling IV showed strong bands at 755 and 700 cm.$^{-1}$ indicative of five adjacent aromatic hydrogens[6] as in XIa–b.

In a similar experiment, the crude rearranged amine IV was indicated by vapor phase chromatography to be contaminated with about 1–2% of impurity. A solution of the crude product in absolute ethanol was shaken for 1 hr. with Adams catalyst under 3.6 atm. of hydrogen at 33°. After removing the solvent, the residue was distilled to give amine IV, b.p. 114–116.5° at 4.5–5.4 mm., and leaving polymer. The distilled product was indicated by vapor phase chromatography to be contaminated with 1–2% impurity, which differed from that observed in the original crude reaction product. Apparently the original impurity consisted of olefin–amine XIa and/or XIb which then underwent hydrogenation. Support for this conclusion is described below under Evidence for the elimination reaction.

In another experiment the reaction was carried out as described above with the exception that the reaction mixture was kept at Dry Ice–acetone temperature (−78°) for 12 hr. There was obtained 4.40 g. (25%) of rearranged amine IV, b.p. 120–122° at 9.0 mm., and 2.90 g. (17% based on XIa–b) of polymeric material.

Proof of Structure of Rearranged Amine IV. A. Oxidation.—A mixture of 2.28 g. of amine IV, 100 ml. of 0.5 *N* potassium hydroxide, and 6.25 g. of potassium permanganate was stirred for 3 hr., then three more 6.25-g. portions of the permanganate were added at 1-hr. intervals. After refluxing for 36 hr., the reaction mixture was treated with Norit and filtered. The filtrate was evaporated to a volume of about 30 ml., and acidified with hydrochloric acid to give 1.10 g. (51%) of phthalic acid, m.p. 202–204° after one re-

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[8] J. von Braun and O. Bayer, *Ber.*, **60**, 1257 (1927).

[9] J. H. Burckhalter and J. H. Short, *J. Org. Chem.*, **23**, 1281 (1958).

[10] F. N. Jones and C. R. Hauser, unpublished results.

[11] Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. *All melting points and boiling points are uncorrected.* All vapor phase chromatography, unless otherwise indicated, was carried out on several columns, the best of which seemed to be one packed with one part polyethylene glycol on four parts Johns-Manville Chromasorb W (30–60 mesh) by weight, using a Perkin-Elmer Model 154-C Vapor Fractometer. Infrared spectra were produced on a Perkin-Elmer Infracord.

[12] L. C. Craig, *J. Am. Chem. Soc.*, **55**, 2543 (1933).

[13] R. A. Robinson, *J. Org. Chem.*, **16**, 1911 (1951).

[14] See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **VIII** 122 (1954).

crystallization from water. The product was identified by comparison of its infrared spectrum with that of an authentic sample of phthalic acid and by conversion to fluorescein and *o*-phthalanil, m.p. and mixed m.p. 209–210°, lit.[15] m.p. 210°.

B. **Hofmann Degradation and Hydrogenation.**—A solution of 3.06 g. (0.017 mole) of amine IV and 4.8 g. (0.034 mole) of methyl iodide in 10 ml. of acetonitrile was stirred overnight. The resulting white precipitate was collected on a funnel and washed with several portions of dry ether to give 5.22 g. (97%) of methiodide V (dried in a vacuum desiccator), m.p. (sealed tube) 242° dec., which was not raised by two recrystallizations from acetonitrile; lit.[8] m.p. 250°.

Anal. Calcd. for $C_{13}H_{20}IN$: N, 4.42. Found: N, 4.31.

A solution of 5.22 g. (0.017 mole) of methiodide V in about 250 ml. of distilled water was passed over an ion exchange column (Amberlite IRA-401), which had previously been treated with aqueous sodium hydroxide solution. The eluate was combined with several aqueous washings of the column and the water was evaporated *in vacuo*. The resulting residue, which contained quaternary ammonium hydroxide VI, was heated until decomposition appeared to be complete. After a little sodium hydroxide solution was added, the resulting mixture was extracted three times with ether. The combined ethereal extract was dried over anhydrous magnesium sulfate, and the solvent was removed to leave crude olefin-amine VII. The infrared spectrum of the crude product showed strong bands at 990 and 910 cm.$^{-1}$ indicative of a vinyl type double bond.[16] Vapor phase chromatography showed that VII was contaminated with a small amount of a higher boiling compound.

An ethanol solution of the crude product was hydrogenated over Adams catalyst under 1 atm. pressure until the hydrogen uptake seemed complete (8 hr.). The solvent was removed under reduced pressure to leave 1.50 g. (48%) of crude *o*-(*n*-butyl)benzyldimethylamine (VIII). Vapor phase chromatography indicated that this product was contaminated with a small amount of the same high boiling compound present before hydrogenation and with a trace of olefin–amine VII (infrared spectrum showed a very slight absorption at 990 and 910 cm.$^{-1}$). The main compound in the crude product was indicated to be VIII by enhancement of the main peak in a vapor phase chromatogram on addition of a sample of pure, independently synthesized VIII, prepared as described below.

Treatment of the crude product with methyl iodide in acetonitrile afforded, after four recrystallizations from absolute ethanol–hexane, the methiodide of amine VIII, m.p. 190–191.5° dec.

Anal. Calcd. for $C_{14}H_{24}IN$: C, 50.45; H, 7.26; N, 4.20. Found: C, 50.46; H, 7.36; N, 4.27.

The melting point of this product was not depressed on admixture with a sample of the independently synthesized methiodide of VIII (see below).

Independent synthesis of amine VIII was accomplished by treatment of an ethereal solution of the Grignard reagent of *o*-bromobenzyldimethylamine[17] (10.7 g., 0.05 mole) with 22.8 g. (0.10 mole) of *n*-butyl *p*-toluenesulfonate[18] in ether. After refluxing 2 hr. and stirring overnight, the reaction mixture was poured slowly with stirring onto crushed ice. The two layers were separated, and the ethereal layer was extracted three times with 6 *N* hydrochloric acid. The combined acid extract was made strongly basic with concentrated sodium hydroxide solution, and the resulting mixture was steam distilled. The distillate was extracted three times with ether, and the combined ethereal extract was dried over anhydrous magnesium sulfate. The solvent was removed, and the crude residue (5.53 g.) was distilled to give, after a small forerun, 3.56 g. (38%) of *o*-(*n*-butyl)-benzyldimethylamine (VIII), b.p. 101–104° at 5.3 mm. Vapor phase chromatography using a column packed with one part polypropylene glycol on four parts by weight of Johns-Mannville Chromasorb (30–60 mesh) indicated that the crude residue VIII was contaminated with a small amount of benzyldimethylamine, but that the distilled product (sample b.p. 103.5° at 5.3 mm.) was pure.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.61; H, 11.07; N, 7.32. Found: C, 81.48; H, 10.96; N, 7.42.

Evidence for Elimination Product XIa from Quaternary Ammonium Ion III.—To a stirred solution of 30.3 g. (0.10 mole) of quaternary salt III in 400 ml. of liquid ammonia was added through a stopcock attached to the bottom of a flask a suspension of 0.087 mole of sodium amide in 300 ml. of liquid ammonia (inverse addition procedure). An immediate red-brown color was produced and was discharged to gray during the 1-hr. reaction period. The crude product, which was obtained using the work up described above, was hydrogenated in ethanol for 1 hr. with Adams catalyst under about 4 atm. of hydrogen. After the solvent was removed, vapor phase chromatography using a polypropylene glycol column indicated that there was present in addition to rearranged amine IV and polymer a small amount of δ-phenylbutyldimethylamine (XII) and a much smaller amount of a second compound with almost the same retention time.

Independent Synthesis of XII.—The acid chloride of γ-phenylbutyric acid was prepared from 10.8 g. (0.066 mole) of the acid and 21.0 g. of thionyl chloride by a method previously described.[19]

The acid chloride was cooled in an ice bath as 200 ml. of 25% aqueous dimethylamine was added very slowly. After the completion of the addition, the reaction mixture was stirred for 10 hr. at room temperature. The basic solution was extracted in a liquid–liquid extractor with ether for 3 days. The ether extract was dried over anhydrous magnesium sulfate, and the solvent removed. Vapor phase chromatography using a polypropylene glycol column on the crude product indicated the presence of one main compound and a small amount of a second compound (1–2%). The infrared spectrum of the crude material showed strong absorption at 1644 cm.$^{-1}$ indicative of an amide carbonyl.[20] The spectrum also indicated the presence of a small amount of a carboxylic acid.

The crude product was refluxed overnight with 2.70 g. (0.07 mole) of 95% lithium aluminum hydride in dry ether. The complex was then destroyed with wet ether and the salts were removed by filtration. Since the vapor phase chromatography indicated the presence of a small amount of impurity in the product (probably δ-phenylbutanol), the ether solution was extracted with 3 *N* hydrochloric acid. After the acid extracts were made basic with concentrated sodium hydroxide solution, the basic mixture was extracted with three 100-ml. portions of ether. The ether extracts were dried over anhydrous magnesium sulfate, the solvent was removed, and the residue was distilled yielding 2.69 g. (23%) of δ-phenylbutyldimethylamine (XII), b.p. 70–71° at 0.85–0.90 mm. The infrared spectrum of the product showed no absorption at 1644 cm.$^{-1}$. V.p.c. using a propyl-

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(15) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, 1953, p. 191.

(16) See ref. 6, p. 49.

(17) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 701 (1962).

(18) S. H. Gilman and J. Robinson, "Organic Syntheses," Coll. Vol. 2, John Wiley & Sons, New York, 1948, p. 47.

(19) E. L. Martin and L. F. Fieser, "Organic Syntheses," Coll. Vol. 2, John Wiley & Sons, New York, p. 569.

(20) See ref. 6, p. 212.

ene glycol column indicated the product to be a single compound.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.27; H, 10.69; N, 7.85.

The picrate, after two recrystallizations from absolute ethanol, melted at 131.5–132.5°.

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.26; H, 5.49; N, 13.94.

The Reaction between Dialkyl Phosphonates and Their Sodium Salts

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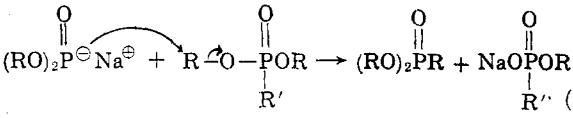
Received April 30, 1962

Sodium dialkylphosphonates having primary alkyl groups react with the parent dialkyl phosphonate *via* P-alkylation, to yield dialkyl alkylphosphonates and sodium alkyl phosphonates. The analogous reaction with *sec*-butyl esters is much slower and proceeds *via* O-alkylation, to yield tri-*sec*-butyl phosphite and sodium *sec*-butyl phosphonate.

Pelchowicz[1] and co-workers have recently described the reaction of sodium dialkyl phosphonates with dialkyl phosphonates shown in equation 1. Previously Petrov[2] and co-workers had reported a related reaction wherein R′ was primary alkyl. Concurrently in this laboratory the reaction has been applied successfully to the preparation of esters of butyl- and dodecylphosphonic acids. It was then hoped to use the reaction to prepare *sec*-alkylphosphonate esters. When one equivalent of sodium was treated with two equivalents of di-*sec*-butyl phosphonate in refluxing heptane, sodium mono-*sec*-butyl phosphonate was isolated in about 50% yield. This structure was established by the splitting of the phosphorus absorption in the nuclear magnetic resonance (n.m.r.) spectrum into a doublet (due to spin-spin coupling with the attached hydrogen), by comparison of the infrared spectrum with that of an authentic sample, and by elemental analyses. Identification and isolation of the other products was not achieved because they codistilled with the solvents during work-up.



$$(RO)_2\overset{\overset{O}{\|}}{P}{}^{\ominus}Na^{\oplus} + R\text{—}O\text{—}\underset{\underset{R'}{|}}{\overset{\overset{O}{\|}}{P}}OR \longrightarrow (RO)_2\overset{\overset{O}{\|}}{P}R + NaO\underset{\underset{R''}{|}}{\overset{\overset{O}{\|}}{P}}OR \quad (1)$$

(R = primary alkyl; R′ = hydrogen)

When sodium di-*sec*-butyl phosphonate was dissolved in excess di-*sec*-butyl phosphonate and the mixture was heated at 120° for seven days, the principal ester product formed was tri-*sec*-butyl phosphite. The indicated yield (based on unrecovered di-*sec*-butyl phosphonate) was 81% by n.m.r. and infrared spectral analysis. A small amount of unidentified phosphate was also detected.[3] *No* di-*sec*-butyl *sec*-butylphosphonate was detected by either method. A small portion of the trialkyl phosphite was isolated by column chromatography and was converted to its solid cuprous chloride complex, which was identical with that prepared from authentic tri-*sec*-butyl phosphite.

Discussion

Sodium di-*n*-butylphosphonate undergoes P-alkylation by di-*n*-butyl phosphonate at elevated temperatures, yielding di-*n*-butyl *n*-butylphosphonate and sodium *n*-butyl phosphonate. Sodium di-*n*-dibutyl phosphonate also undergoes P-alkylation by *n*-butyl bromide, yielding di-*n*-butyl *n*-butylphosphonate and sodium bromide (the Nylen reaction). However, it has now been established that di-*sec*-butyl phosphonate reacts differently with its sodium salt, and much more slowly, to give tri-*sec*-butyl phosphite, the product of O-alkylation, and sodium mono-*sec*-butyl phosphonate as the principal products. A rationale for these results may be found in the work of Kornblum and co-workers on the alkylation of ambident anions, such as the nitrite ion.[4] Kornblum states that greater SN1 character (carbonium ion participation) in the transition state leads to greater amounts of the product of bond formation with the atom of greatest electronegativity, and *vice versa.* Our observations are in complete accord with this principle. The oxygen atom of the phosphonate anion is more electronegative than the phosphorus atom. Moreover, the greater stability of secondary carbonium ions as compared to primary carbonium ions should give more SN1 character to the reaction involving *sec*-butyl phosphonates.

One observation not consistent with this relatively simple interpretation is that sodium di-*sec*-butyl phosphonate was alkylated with *sec*-butyl bromide to give predominantly di-*sec*-butylphosphonate, the product of P-alkylation. This suggests that the structures of both the

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[1] Z. Pelchowicz, S. Brukson, and E. D. Bergmann, *J. Chem. Soc.*, 4348 (1961).

[2] K. A. Petrov, N. K. Bliznyuk, M. A. Korshunov, F. L. Maklyaev, and A. N. Voronkov, *Zh. Obshch. Khim.*, **29**, 3407 (1959).

[3] It was established that both di-*sec*-butyl phosphonate and tri-*sec*-butyl phosphite are oxidized to the corresponding phosphates at 120° in air.

[4] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).