

The trimethylethylene was distilled with the ether and titrated with bromine by the method of Stanerson and Levin³⁹ which indicated that a 41% yield was formed (based on nitrosourethan). Addition of excess bromine to the solution, washing with bisulfite and two successive distillations gave a 25% yield of 2-methyl-2,3-dibromobutane, b.p. (16 mm.) 57–59°, n_D^{20} 1.5091 (lit.⁴⁰ b.p. (19 mm.) 63°, n_D^{20} 1.5090). The residue from the distillation of the trimethylethylene consisted of 1.7 g. of a mixture of dinitrobenzoate esters. From 1.35 g. of such a mixture obtained in a similar experiment, was isolated by fractional crystallization 0.52 g. of *t*-amyl 3,5-dinitrobenzoate, m.p. and mixed m.p. with an authentic sample described below, 115.5–116°, and 0.12 g. of neopentyl 3,5-dinitrobenzoate, m.p. and mixed m.p. 91.5–92.5°.

(b) In Ligroin.—When the ether in the above experiment was replaced by ligroin the yield of trimethylethylene by titration was 33% and the yield of esters, 0.69 g., m.p. 113–115°, and 1.2 g., m.p. 57–72°.

Reaction of III with Dilute Sulfuric Acid.—III was prepared as above from 50 g. of nitrosourethan and collected in 100 cc. of 0.045 *N* sulfuric acid cooled in an ice-salt-bath. A second trap cooled by acetone and Dry Ice was attached to the first. When the reaction was finished the aqueous solution was warmed to drive the trimethylethylene formed

into the Dry Ice-acetone traps. The trimethylethylene was distilled to give 2.75 g. (14% yield), b.p. 37–39.5°, n_D^{20} 1.3800. From the aqueous solution was obtained 7.6 g. (32% yield) of *t*-amyl alcohol, b.p. 101–106°, n_D^{20} 1.4028. These yields are based on the nitroso compound. Each fraction obtained in the distillation was treated with 3,5-dinitrobenzoyl chloride according to Reichstein⁴¹ and found to give *t*-amyl 3,5-dinitrobenzoate. No neopentyl derivative could be obtained.

Neopentyl 3,5-Dinitrobenzoate.—Neopentyl alcohol, b.p. 113°, m.p. 51–55°, was prepared by the reduction of pivalic acid in 83% yield with lithium aluminum hydride⁴² and converted to the 3,5-dinitrobenzoate 93–93.5° by the method of Reichstein.⁴² Since the previous workers have reported no analysis, that of our product is included.

Anal. Calcd. for $C_{12}H_{14}N_2O_6$: C, 51.1; H, 5.0; N, 9.9. Found: C, 51.4; H, 5.0; N, 10.0.

t-Amyl 3,5-dinitrobenzoate has been prepared previously a number of times but without elementary analysis. For this reason, the analysis of our product, m.p. 115.5–116.5°, is included.

Anal. Calcd. for $C_{12}H_{14}N_2O_6$: C, 51.1; H, 5.0; N, 9.9. Found: C, 51.4; H, 5.0; N, 10.0.

(39) B. R. Stanerson and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **14**, 782 (1942).

(40) C. M. Suter and H. D. Zook, *THIS JOURNAL*, **66**, 738 (1944).

(41) T. Reichstein, *Helv. Chim. Acta*, **9**, 802 (1926).

(42) R. F. Nystrom and W. Brown, *THIS JOURNAL*, **69**, 2548 (1947).
NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXII. Dissociation and the Cation Influence in Amylsodium and Similar Organosodium Reagents¹

BY AVERY A. MORTON AND EDWARD F. CLUFF

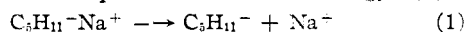
RECEIVED FEBRUARY 1, 1952

Potassium and sodium *t*-pentoxides, in the order given, accelerate the pyrolysis of amylsodium at 50°. These alkoxides similarly accelerate the chemical reaction of amylsodium. From these results and earlier work the formation of radicals during the reactions of amylsodium appears likely. Interpretations based on such an assumption are shown and the energy contributed from the formation of sodium chloride in the reaction of the sodium reagent with an alkyl chloride is discussed. Associated salts may affect the reactions of amylsodium either by accelerating the dissociation to radicals or by providing appropriate positions for adsorption of a reacting molecule. Several reactions of organoalkali metal reagents are interpreted from the electrophilic viewpoint.

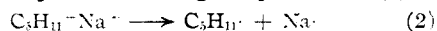
From time to time during the extensive study of organosodium compounds which is being made in this Laboratory some insight into the manner by which these reagents function has been possible. For example, in the Wurtz reaction of an alkyl chloride with sodium all products were observed to pass through an organosodium intermediate² and the facts which previously seemed to demand a free radical were found inconclusive and fully explained as the behavior of an organosodium compound. Later the reagents were thought to have cation as well as anion activity and a classification as electrophilic^{3–5} appeared useful for interpreting and predicting reactions. An attempt to modify the cation influence in the polymerization of butadiene by amylsodium led to the accidental discovery of the Alfin catalyst⁶ with its unique property of pro-

ducing, at extreme rapidity, a polybutadiene of around 7,000,000 weight average molecular weight⁷ with no cross-linking. The present work, which began with the supposition that the ion-pair in amylsodium acts solely as ions, has uncovered the idea that this reagent probably functions also as a radical or radical pair whose activities are restricted to the spot where the electron attracting influence of the cation acts.

The arguments which led to this idea are as follows: (a) a dissociation of solid amylsodium into separated ions, as in equation (1), might under some circumstances require considerable energy, (b) an



alternative dissociation to radicals, as in equation (2), would require no charge separation, (c) de-



composition of amylsodium to radicals was found in an earlier study⁸ to occur at room temperature and probably also at zero degrees and the common experience in this Laboratory is for all preparations of amylsodium to suffer some reversion to metallic sodium and hydrocarbon while standing overnight,

(1) The authors are indebted to the Office of Rubber Reserve, Reconstruction Finance Corporation, for financial assistance of this and other work.

(2) A. A. Morton, J. B. Davidson and H. A. Newey, *THIS JOURNAL*, **64**, 2240 (1942); A. A. Morton, J. B. Davidson and B. L. Hakon, *ibid.*, **64**, 2242 (1942).

(3) A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., *ibid.*, **65**, 1339 (1943).

(4) A. A. Morton, *Chem. Revs.*, **35**, 1 (1944).

(5) A. A. Morton, *THIS JOURNAL*, **69**, 969 (1947).

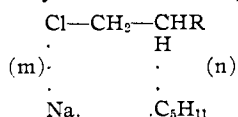
(6) A. A. Morton, E. E. Magat and R. L. Letsinger, *ibid.*, **69**, 960 (1947); A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

(7) Unpublished results by R. L. Cleland.

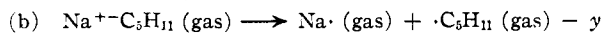
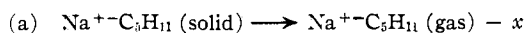
(8) A. A. Morton and H. A. Newey, *THIS JOURNAL*, **64**, 2247 (1942).

(d) alkoxides which accelerate the chemical reactions of amylsodium are now found to accelerate also its decomposition and the potassium alkoxide causes more rupture than the corresponding sodium salt, even as it affects chemical reactions.⁹ These decompositions were at 50° which is a common temperature for this reagent. The reversion to metal was extensive and pieces of sodium as large as marbles were formed.

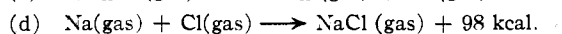
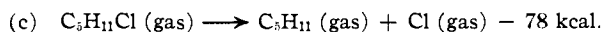
The evidence shows that radicals are present under conditions where amylsodium is used. A metal thus formed *in situ* would be unusually active toward any organic compound that might be present. The manner of reaction should therefore be considered. If we assume a process by this course the radical pair and an alkyl halide could next yield disproportionation products through the complex shown below. The dotted lines "m" and "n" represent paths by which the respective radicals



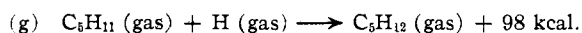
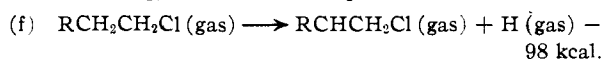
could attack the alkyl halide. One can use thermochemical data¹⁰ to observe what energies might exist if each stage were separate. For the initial dissociation of amylsodium the typical representation would be



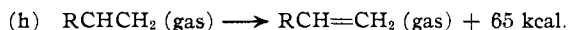
The values for x and y are unknown but would be small because the reagent is falling apart even at room temperature. The equations for the (m) path which involves the metal radical in the formation of sodium chloride would be



Here the net change evolves 77 kcal. An action by path (n) involving the non-metal radical in disproportionation shows a thermal balance of zero (equations f and g). The final step would be the formation of the double bond, equation (h), with evolution of heat. The total heat liberated by step (m) and formation of the double bond is 142 kcal. The



tion of the double bond, equation (h), with evolution of heat. The total heat liberated by step (m) and formation of the double bond is 142 kcal. The

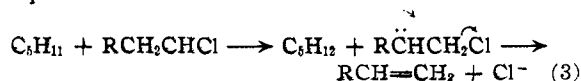


sum of x and y in equations (a) and (b) cannot exceed this amount because the process is exothermic and a conservative estimate is that the sum does not exceed 25 kcal. This energy is readily supplied by the formation of sodium chloride which, barring steric or other influence, should occur early and before exchange if any preference is given and certainly should not come at the end of all action, as

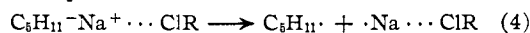
(9) A. A. Morton and A. E. Brachman, *THIS JOURNAL*, **73**, 4363 (1951).

(10) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936; K. S. Pitzer, *THIS JOURNAL*, **70**, 2140 (1948).

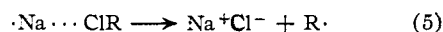
postulated in the nucleophilic picture shown by equation 3



Such distinct steps are extreme conditions not realized in practice where certainly the phases must overlap and the ions may even act simultaneously. This situation was recognized in 1943, when the reagents were called electrophilic, and has been mentioned ever since.⁴⁻⁶ However some initiating role on the part of the cation seems unavoidable even should it happen to be small from an energy viewpoint. For dissolved alkyl chloride to react with solid amylsodium adsorption must occur at the surface. The cation with its known coördinating power and the halogen atom of the alkyl chloride with its exposed electrons seem more favored to function in this way than other parts of the reactants. If so, a simple product of this phase might be written as $\text{C}_5\text{H}_{11}^- \text{Na}^+ \dots \text{ClR}$. This adsorption (dotted line) can then be looked upon as preformation of sodium chloride and the decomposition to two radicals could be written as in equation (4). The complex radical in turn would dissociate fur-



ther to sodium chloride and an alkyl radical, as in (5), if breakdown were complete.



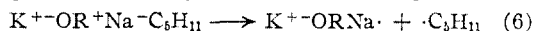
It is only one more step to assume that under some conditions or by a rapid transition the sodium cation might never lose its character as an ion but might serve practically as a point about which all processes pivot with bond stretching to permit rearrangements and with minimum dissociation to radicals. An intermediate could then be pictured as $\overset{\delta-}{\text{C}_5\text{H}_{11}} \dots \overset{\delta+}{\text{Na}} \dots \overset{\delta-}{\text{ClR}}$, in accord with the statement often made³⁻⁵ that the old anion is released as the new one is formed. The radicals, even if the breakdown goes the extreme distance to give $\text{R} \cdot$, NaCl and $\cdot \text{C}_5\text{H}_{11}$ must act in the vicinity of the cation and their relative times of formation and position would determine the course of disproportionation or the amount of coupling.

The steps here illustrated are regarded as general. The reactions with olefins and other systems would be written in a similar way. The facility of breakdown of the adsorbate-ion-pair complex may be greater or less than the ion-pair itself, depending on the adsorbed molecule.

Another important feature disclosed by our studies is that associated salts influence the reactions of organosodium reagents. No better example can be cited than the Alfin catalyst⁶ where sodium isopropoxide and sodium chloride cause allylsodium to polymerize butadiene to an unusually large polymer which has over 70% of 1,4-structure. Also secondary alkoxides cause greatly increased yields of *n*-hexylbenzene⁹ in the alkylation of toluene, and *t*-alkoxides promote the metalation of *t*-butylbenzene.¹¹ The present work on the pyrolysis in the presence of *t*-pentoxides shows that these added

(11) A. A. Morton and C. E. Claff, *Am. Chem. Soc., Boston Meeting 1950 and unpublished work.*

salts accelerate the dissociation of amylsodium. Hence a portion of an ionic aggregate falls apart in the sense shown in equation (6) and this radical complex in turn may act as if it were in part $\cdot K-OR$



Na^+ . To the extent that ion interchange occurs the ion aggregate could, indeed, act as if it were $Na^+ - OR K^+ - C_5H_{11}$ and dissociation could accordingly be easier.

Another important way in which associated salts may affect reactions is by providing more and better points for adsorption of molecules with which reaction is to occur. Figure 1 shows how an alkyl chloride or olefin can be adsorbed by its polar or

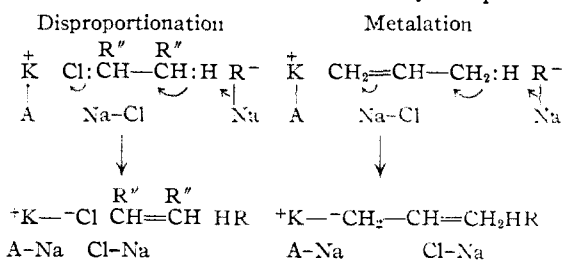


Fig. 1.—Disproportionation and metalation in an aggregate of ions.

electron-rich end on the cation of one of the associated salts and yet participate in the reaction. KA is a potassium alkoxide and $NaCl$ is the sodium chloride that is always present with the organosodium reagent, RNa , commonly prepared in this Laboratory. Curved arrows give a direction for electronic flow but are not intended to designate ionic steps. The inorganic products from left to right are theoretically potassium chloride, sodium alkoxide and sodium chloride but separate salts in this system would be indistinguishable. The processes are essentially the same as on a single ion-pair but back-side approaches and highly specific effects, both favorable and unfavorable, are possible. A longer ionic bridge between two reactive points can be realized. Size and position of ions are important.

This discussion is intended to point out how easily radicals may be present in the reactions of amylsodium but is not intended to claim that the amyl ion never acts as a base. Also the idea that radicals are probably present does not alter the conclusion originally made concerning free radicals in the Wurtz reaction.² The viewpoint then was that "decisive evidence of any free radical phase which may be present in this common reaction is a goal yet to be reached." At that time free radicals were supposed to originate from the reaction of sodium with alkyl halide or from alkylsodium with alkyl chloride. The present evidence is that radicals do arise from dissociation of amylsodium.

The classification of this type of reagent as electrophilic has been misunderstood, and complete similarity with the action of a mineral acid has been expected. By no means is this analogy so. The initial role is supposed to be the attraction of the cation for electrons. Attachment at the metal ion takes place and subsequent changes are then anchored to that spot. If an aromatic compound contains a hydrocarbon substituent such as the iso-

propyl group in cumene¹² the attachment is at the para position and the sodium remains there after transfer of hydrogen. If the group is methoxy, as in anisole, the attachment is at the oxygen and the final product is the result of the entrance of the sodium ion into the adjacent ortho position. The positions taken in these cases accord with the attack by other electrophilic agents, such as nitric acid. But when the group is meta-directing, as is the nitro or aldehyde or ammonoaldehyde group, the anchoring takes place at the electron-rich end of the polar group and the reagent is not free to attack as does nitric acid. Hence for 2-ethoxyquinoline the metal cation first undergoes coordination at the nitrogen—as it does⁴ in pyridine systems—or at the oxygen of the ethoxy group. The processes, thus limited, consist of the replacement of the ethoxy group with butyl to give 2-butylquinoline or metalation to a small extent in the 3-position. Actually 2-ethoxyquinoline could be regarded as an ammono ester, $-C(OEt)=N-$, and its reaction with butyllithium should give the ammono ketone, $-C-(C_4H_9)=N-$ just as with any other ester if the process were stopped midway to the tertiary carbinol. No more need exists for assuming¹³ that nitric acid and butyllithium should have similar actions on this compound than that they should act the same toward benzaldehyde or ethyl benzoate.

Very recently¹⁴ the metalation of monobromodiphenylsulfones by *n*-butyllithium has been reported. With this meta-directing group the initial attachment would occur at the oxygen of the sulfone. Thereafter substitution in an aromatic ring is restricted to that vicinity and takes place in an ortho position. The benzene ring with the bromo group is the one attacked because the salt of the strongest acid possible will thereby be formed. All reactions described in that work are predictable on the electrophilic basis.

An earlier paper⁵ has already described the interpretation in the case of trifluoromethylbenzene where another meta-directing group is present.

The metalation of 2-ethoxynaphthalene has been credited as being nucleophilic¹⁵ rather than electrophilic, apparently because the action occurs on the 3-position rather than on the 1-position expected from the comparison with nitric acid. β -Substitution constitutes no argument against the electrophilic view. In another electrophilic process—sulfonation—the β -position is affected when the conditions are severe. The present evidence on metalation suggests a similar situation because the metalation of naphthalene by the mild-acting butyllithium¹⁶ gave both α - and β -products in the ratio of 2.5 to 1 and by the more vigorous amylsodium which gave primarily β -products. 2-Ethoxynaphthalene represents a system which is more susceptible to metalation than naphthalene and therefore possibly more prone to β -replacement. Much remains to be learned about the metalation of naphthalene systems, particularly about the steric factor,

(12) A. A. Morton, J. T. Massengale and M. L. Brown, *THIS JOURNAL*, **67**, 1620 (1945).

(13) H. Gilman and J. A. Beel, *ibid.*, **73**, 32 (1951).

(14) W. E. Truce and M. F. Amos, *ibid.*, **73**, 3013 (1951).

(15) S. V. Sunthanker and H. Gilman, *J. Org. Chem.*, **16**, 8 (1951).

(16) H. Gilman and R. L. Bebb, *THIS JOURNAL*, **61**, 100 (1939).

because in the somewhat parallel case of the methyl ether of *m*-cresol¹⁷ metalation takes place at the 6-position rather than between the methyl and methoxy groups.

The idea that these reagents are electrophilic was intended to offset the commonly held notion that they were nucleophilic and not to imply that the anion was inactive. Indeed, in all papers³⁻⁵ from this Laboratory, both ions have been credited with activity that could well be simultaneous. The search for cation activity has uncovered the large field of ionic aggregates where the reactions of the reagent are dependent on the salts with which the reagent is associated. In such a highly concentrated ionic field steric factors both favorable and unfavorable are probably more in evidence than with dissolved reagents. One example is the highly specific character of the Alfin reagent which causes an outstandingly fast polymerization of butadiene, much less polymerization of isoprene and virtually no polymerization of 2,3-dimethylbutadiene.¹⁸ Branched compounds should be very subject to steric effects on a surface. Admittedly the dissolving of the reagent in a solvent will reduce the electrophilic character, but in many cases, particularly in ether solution, a notable difference in behavior of the potassium, sodium and lithium reagents still exists even when a common anion is used. For other sodium salts which are soluble in polar solvents the electrophilic character might suffer extinction by solvation. However, Brady and Jacobovits¹⁹ have recently found evidence for cation influence even in alcoholic and aqueous solutions.

(17) Unpublished experiments with A. E. Brachman.

(18) Unpublished experiments with R. D. Coombs.

(19) O. L. Brady and J. Jacobovits, *J. Chem. Soc.*, 767 (1950).

Experiments

Amylsodium was made at -10° and 5000 r.p.m. in the "standard" proportions and in the way commonly used²⁰ in this Laboratory except that *n*-heptane was used as the medium instead of pentane. After the usual time allotted for a preparation each mixture was thoroughly stirred at 10,000 r.p.m. for 1.5 hours at -10° in order to provide control conditions for subsequent tests. The mixture was then carbonated on solid carbon dioxide. Three such preparations gave yields of 89, 86 and 84% of caproic acid indicative of amylosodium. The corresponding quantities of decane were 3, 4 and 7% based on the amyl chloride used for preparing amylosodium.

Two additional preparations of the above type were then heated to 50° and held there for three hours. Carbonation showed 79 and 81% caproic acid. Decane (6%) was present in each case. From one of the experiments the water-soluble acid was determined as 4%. Earlier work⁸ had shown this material to be a pentenedicarboxylic acid probably derived, as is now understood, by dimetalation of some of the pentene obtained by disproportionation of the amyl radical formed by pyrolysis. The yield of this product is computed on the basis of one carboxyl group for every amyl chloride used in preparing amylosodium. Approximately these yields agree with those expected from the previous study on pyrolysis except that the tarry acid product obtained earlier was eliminated by the use of the high-speed stirrer.

The pyrolysis was next carried out in the presence of an equivalent amount of a *t*-pentoxide which was added just before the stirring (10,000 r.p.m.) period so that the alkoxide was intimately mixed with the amylosodium. The sodium *t*-pentoxide thus added was made by addition of the theoretical amount of *t*-amyl alcohol to a standard preparation of amylosodium and the potassium alkoxide was made by addition of the alcohol to potassium. The pyrolysis in the presence of sodium *t*-pentoxide yielded, after carbonation, 33% caproic acid, 11% of decane and 34% of water-soluble acid. From the action in the presence of the potassium alkoxide the yields were 25% caproic acid, 7% decane and 21% water-soluble acid. After each experiment lumps of metallic sodium were removed.

(20) A. A. Morton and co-workers, *THIS JOURNAL*, **72**, 3785 (1950).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE AND SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

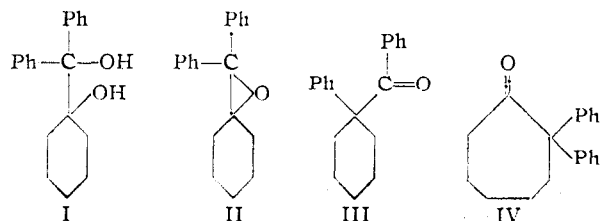
Molecular Rearrangements. I. A Study of the Pinacol Rearrangement of 1-(1-Hydroxycyclohexyl)-diphenylcarbinol¹

BY ROBERT E. LYLE² AND GLORIA G. LYLE²

RECEIVED DECEMBER 8, 1951

1-(1-Hydroxycyclohexyl)-diphenylcarbinol (I) undergoes the pinacol rearrangement on treatment with reagents such as concentrated sulfuric acid, boron trifluoride in acetic acid, or Lucas reagent forming 2,2-diphenylcycloheptanone (IV). Zinc chloride in acetic anhydride converts the glycol I to 1-(1-phenylcyclohexyl)-phenyl ketone (III). Conclusive evidence for the structures of the rearrangement products is presented and a mechanism for the selective migration of phenyl or ring methylene groups is suggested.

Meerwein,³ in a previous study of the pinacol rearrangement of 1-(1-hydroxycyclohexyl)-diphenylcarbinol (I), isolated a material from the treatment of I with sulfuric acid which he identified as the epoxide of cyclohexylidenediphenylmethane (II). Meerwein³ reported further that this compound on distillation from zinc chloride produced 1-(1-phenyl-



(1) Presented in part before the Division of Organic Chemistry at the 119th meeting of the American Chemical Society at Cleveland, Ohio, April 10, 1951.

(2) Department of Chemistry, James Hall, University of New Hampshire, Durham, New Hampshire.

(3) H. Meerwein, *Ann.*, **396**, 200 (1913); **419**, 121 (1919).

ylcyclohexyl) phenyl ketone (III). In a recent paper Cauquil and Rouzaud⁴ suggested that the product of sulfuric acid treatment of I was 2,2-diphenyl-

(4) G. Cauquil and J. Rouzaud, *Compt. rend.*, **231**, 699 (1950).