metal acetylacetonate in initiating the autoxidation of the olefin. The most frequently proposed mechanism consists of the formation of radicals *via* some sort of "redox" reaction between the metal and the hydroperoxide and the subsequent addition of the radicals to the olefin.[7,18,20]

Table II offers a comparison of certain related reactions involving metal acetylacetonates. There seems to be some general correlation in the ability of the various metals to act as initiators; however, there is apparently no connection between this property and the ease of autoxidation of the chelates themselves.[15] The work of Arnett and co-workers[15,26,27] has shown that these compounds exhibit extraordinary catalytic and inhibiting properties toward each other in autoxidation reactions in which the ligands themselves are involved, and that small structural changes in the chelate part of the molecule have marked but unsystematic effects on these same reactions. These authors have also shown that autoxidation of these compounds is inhibited in the presence of usual free-radical sources and not affected by usual inhibitors of autoxidations.

Based on these observations and our own preliminary findings, it is difficult to predict the behavior of the metal acetylacetonate complexes under various experimental conditions. However, it is clear that the ligand itself plays a significant role[15,23,26] and reagents which are capable of altering the ligand–metal interactions will alter the transformations that are possible. For example, when the ligand portion of the molecule is varied, the catalytic properties are altered in a way which cannot be predicted by the oxidation state of the ligand itself.[25] Detailed kinetic studies are underway in this laboratory for several metal acetylacetonate–*t*-butyl hydroperoxide–olefin systems.

Experimental Section

Chemicals.—Octene-1 was Phillips research grade (99.9 mole %), distilled prior to use (bp 120–121°). *t*-Butyl hydroperoxide was obtained from Wallace and Tiernan Inc. (Lucidol Division) as *t*-butyl hydroperoxide-90 and further purified by distilling off the lighter impurities under vacuum. Iodometric titration indicated >95% hydroperoxide. The metal acetylacetonates (McKenzie Chemical Corp.) were recrystallized from acetone. Cr(III) acetylacetonate was dissolved in benzene and precipitated with petroleum ether (bp 30–60°).[28] Oxygen (Matheson) was used without further purification.

Kinetics.—Oxygen absorption measurements were carried out in jacketed Pyrex cells. Temperature was maintained at 30 ± 0.1° by running thermostated water through the jacket. Stirring was accomplished by means of a magnetic stirrer with a Teflon-coated stirring bar. A small test tube containing molecular sieve (Fisher, Type 4A) was suspended in the cell to remove heavy, gaseous products which might interfere with the measurement of oxygen uptake.[15] The volume of oxygen was read at specified times and converted to the volume at STP. Volume of oxygen absorbed was plotted against time, and the rates reported are taken from the slopes of the linear portions of these graphs. No oxygen was picked up over a period of 5.5 hr, in the absence of metal acetylacetonate, by a solution of *t*-butyl hydroperoxide in octene-1. In the absence of the *t*-butyl hydroperoxide oxygen absorption was comparatively negligible (Table I). The production of gaseous products was observed in the absence of an oxygen atmosphere. Even in the presence of oxygen for some of the experimental conditions of Table I an initial gas-producing period was detected. For the system *t*-butyl hydroperoxide–Cr(III) acetylacetonate in diphenyl ether (no octene, no oxygen) under an atmosphere of nitrogen the evolved gas was shown to be oxygen by absorption in alkaline pyrogallol.[29]

The autoxidation cell was cleaned between runs by soaking in a solution of $K_2Cr_2O_7$ plus concentrated H_2SO_4, washing successively with water, benzene, acetone, methanol, and drying in a stream of air passed through a column of molecular sieve.

t-Butyl hydroperoxide decomposition studies were carried out in the absence of oxygen. Reactants were degassed several times and sealed, *in vacuo*, in new Carius tubes. The tubes were thermostated at 30 ± 0.1° and removed at intervals. The remaining peroxide was determined iodometrically.[1]

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[26] E. M. Arnett, H. Freiser, and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 2482 (1962).

[27] E. M. Arnett and M. A. Mendelsohn, *ibid.*, **84**, 3821, 3824 (1962).

[28] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 444 (1958).

[29] A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 186.

Rearrangement of 1,1,1,2-Tetraphenylethane to 1,1,2,2-Tetraphenylethane by Means of Phenylsodium[1]

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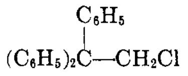
Received August 1, 1966

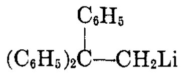
1,1,1,2-Tetraphenylethane underwent a 1,2 shift of a phenyl group to form 1,1,2,2-tetraphenylethane on treatment with phenylsodium in decane–heptane at 90–100°. This appears to be the first example of such a rearrangement in which the initial carbanion was generated by an acid–base reaction.

Although a few anionic 1,2-phenyl migrations from carbon to carbon within a saturated system to form a saturated product have been reported,[2] the initial carbanion has previously been generated only by the action of an alkali metal on a halide; for example, halide I converted by means of lithium metal to initial carbanion I′, which rearranged to form the more stable carbanion II.



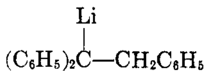
$(C_6H_5)_2\overset{C_6H_5}{\overset{|}{C}}\text{—}CH_2Cl$

I



$(C_6H_5)_2\overset{C_6H_5}{\overset{|}{C}}\text{—}CH_2Li$

I′



$(C_6H_5)_2\overset{Li}{\overset{|}{C}}\text{—}CH_2C_6H_5$

II

Such a rearrangement has now been realized in which the initial carbanion was generated by an acid–base reaction. Thus, 1,1,1,2-tetraphenylethane (III) was rearranged by phenylsodium in decane–heptane at 90–100° to form 1,1,2,2-tetraphenylethane (IV); presumably hydrocarbon III was converted initially to carbanion III′, which rearranged to carbanion IV′ (Scheme I).

Interestingly, this rearrangement was facilitated by the presence of sodium *t*-butoxide which appeared to enhance the activity of the organosodium compounds. This observation is similar to that of Benkeser and Crimmins who found that sodium *t*-butoxide greatly enhances the reactivity of *n*-amylsodium toward metalation of *t*-butylbenzene.[3]

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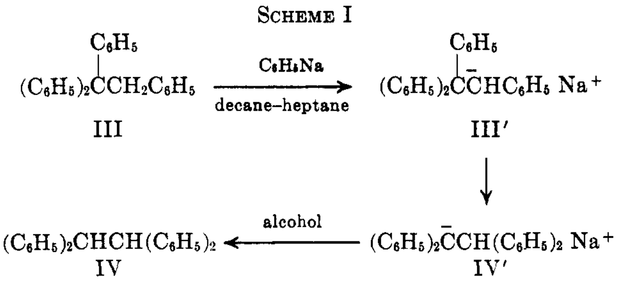
[1] This research was supported by the National Science Foundation, Research Grant GP 2274.

[2] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 233–238.

[3] T. F. Crimmins, Ph.D. Thesis, Purdue University, 1965. We are indebted to Professor R. A. Benkeser for permission to mention this result prior to publication; private communication.

Scheme I



In Table I are summarized the results obtained from the rearrangement of III with phenylsodium in the absence of sodium *t*-butoxide and in the presence of approximately 1 molar equiv of this alkoxide. This table shows that although the rearrangement was less than one-half complete in the absence of alkoxide after 24 hr (expt 1), complete rearrangement was realized in 10 hr in the presence of alkoxide (expt 4). However, even in the presence of the alkoxide less than one-half rearrangement was observed within 3 hr (expt 3). In general, good material balances were obtained.

Table I

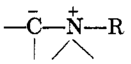
Rearrangement of 1,1,1,2-Tetraphenylethane by Means of Phenylsodium

Expt no.	$(CH_3)_3CONa$	Time, hr	Material balance, %	Isomer distribution, % III	IV
1	Absent	24	81	66	44
2	Present	10	91		100
3 .	Present	3	99	54	46
4	Present	24	74		100

The product from these reactions was shown to be the rearranged hydrocarbon IV by comparison of its vpc retention time and infrared spectrum with those of an authentic sample. Also, hydrocarbon IV gave an undepressed melting point upon admixture with a sample of IV.

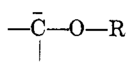
Apparently an intramolecular mechanism operated since the possible intermolecular elimination of phenide ion from carbanion III′ and readdition of this anion to the resulting 1,1,2-triphenylethene to form IV seemed not to occur. Thus, not only was none of this olefin detected by vpc in the reaction product, but treatment of this olefin with phenylsodium under similar conditions afforded less than 1% (by vpc) of a compound which has an identical retention time with IV.[4] From a study employing labeled phenyllithium, Grovenstein and Wentworth[5] concluded that the similar rearrangement of a phenyl group within carbanion I′ occurred intermolecularly. However, the related rearrangement of 2,2,3-triphenylpropyllithium evidently involved elimination of benzyllithium and its readdition to the resulting olefin.[5]

The present 1,2 shift of an R group from carbon to carbon within initial carbanion III′ compliments the Stevens and Wittig 1,2 shifts involving initial carbanions V and VI, respectively, where these initial carbanions are likewise generated by acid–base reactions. However, the mechanism of the three rearrangements are not necessarily the same.



$-\underset{|}{\overset{-}{C}}-\overset{+}{N}-R$

V



$-\underset{|}{\overset{-}{C}}-O-R$

VI

Experimental Section

Melting points were obtained on a Uni-Melt capillary melting point apparatus and are uncorrected. Gas chromatograms were obtained on an F and M Model 700 gas chromatograph instrument equipped with a 6 ft × 1/8 in. stainless steel Se-30 column. The analyses were performed with an oven temperature of 250° and a helium flow of 60 ml/min. Peak areas were obtained by the triangulation method of integration. Infrared spectra were obtained with a Perkin-Elmer 237 spectrophotometer; the samples were run as Nujol mulls.

1,1,1,2-Tetraphenylethane (III), mp 142.5–144.5° (lit.[6] mp 144°), was prepared by alkylation of sodium triphenylmethide with benzyl chloride in liquid ammonia. Decane (99 mole %) was purchased from Phillips Petroleum Co. and was used without further purification. Eastman White Label heptane was washed with sulfuric acid and stored over sodium ribbon before use. All rearrangements were run in a Morton-type flask with a "Stir-O-VAC" stirring apparatus. The reactions were run in a predried flask under a positive nitrogen pressure.

Phenylsodium.—A sodium dispersion was prepared in 75 ml of decane; the mixture was then diluted with 100 ml of heptane. Bromobenzene in 25 ml of heptane was added dropwise to the sodium dispersion over 1 hr. If the reaction between the sodium and bromobenzene did not commence after a few milliliters of the bromobenzene solution was added to the flask, the reaction mixture was heated to 80° until the reaction started. In some cases, *t*-butyl alcohol was used to initiate reaction.[7] Once the reaction commenced, the temperature of the mixture was kept between 50 and 60° until the bromobenzene solution was added. The phenylsodium suspension was stirred for 1 hr before use. The quantities of sodium and bromobenzene used in each experiment are given below.

Rearrangement of 1,1,1,2-Tetraphenylethane by Phenylsodium.—Phenylsodium was prepared from 6.9 g (0.30 g-atom) of sodium and 15.7 g (0.10 mole) of bromobenzene as described above. To the phenylsodium suspension was added 11.7 g (0.05 mole) of 1,1,1,2-tetraphenylethane. The contents of the flask were heated to 90–100° and stirred at this temperature for 1 day. Excess isopropyl alcohol was then added to the mixture to protonate the organosodium compounds and destroy excess sodium. Water was added. The organic and aqueous layers were filtered to remove the III and IV (crop 1) which precipitated from the organic layer prior to work-up. The organic and aqueous layers were then separated. The aqueous layer was extracted several times with diethyl ether. The combined ethereal extracts and organic layer were dried over Drierite and condensed on a rotary evaporator. After the solution was cooled, a second crop (crop 2) of crude product precipitated. Crops 1 and 2 were combined and dried over Drierite under vacuum to give 9.5 g (81% material balance) of crude product. Vpc analysis of a chloroform solution of crops 1 and 2 showed that the product contained 34% IV and 66% III.

Rearrangement of 1,1,1,2-Tetraphenylethane by Phenylsodium and Sodium *t*-Butoxide.—Phenylsodium was prepared from 13.8 g (0.60 g-atom) of sodium and 31.4 g (0.20 mole) of bromobenzene according to the above method. To the phenylsodium suspension was added 5.9 g (0.08 mole) of *t*-butyl alcohol to prepare the phenylsodium–sodium *t*-butoxide mixture *in situ* followed by the addition of 11.7 g (0.05 mole) of III. The rearrangement was run under the same reaction conditions which are described in the preceding section. After the appropriate time (see Table I), the reaction mixture was hydrolyzed and worked up as described above. The crude product which was obtained from the reaction mixture was dried over Drierite under vacuum and weighed crude to obtain the material balance; vpc analysis of

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[4] The intramolecular nature of the rearrangement, however, cannot be considered established. The phenylsodium that might be eliminated from carbanion III′ could possibly be in a more reactive form in the rearrangement reactions than the phenylsodium employed in our experiment with triphenylethene.

[5] E. Grovenstein, Jr., and G. Wentworth, *J. Am. Chem. Soc.*, **85**, 3305 (1963).

[6] "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965, p 3033.

[7] *t*-Butyl alcohol was not used in the preparation of phenylsodium in expt 1 (see Table I).

a chloroform solution of the product gave the isomeric composition. These results are summarized in Table I.

Attempted Addition of Phenylsodium to Triphenylethene.—Phenylsodium was prepared according to the above method from 8.75 g (0.38 g-atom) of sodium and 31.4 g (0.20 mole) of bromobenzene. To the phenylsodium suspension was added 5.9 g (0.08 mole) of *t*-butyl alcohol to prepare the phenylsodium–sodium *t*-butoxide complex *in situ* followed by the addition of 12.8 g (0.05 mole) of triphenylethene. The reaction was run under the same conditions which are described in the preceding section. After 10 hr, the reaction was hydrolyzed and the organic layer was separated from the aqueous layer. Vpc analysis of the organic layer showed that triphenylethene was recovered and that a trace (*ca.* 1%) of a compound formed which had an identical vpc retention time with an authentic sample of IV. It was found that sodium could not be in excess in this system since the sodium added across the double bond of triphenylethene to give, after hydrolysis, triphenylethane. A slight deficiency of sodium was therefore used in this experiment.

Two Types of Rearrangement of Benzhydryltrimethylammonium Ion by Sodium Amide in Liquid Ammonia[1]

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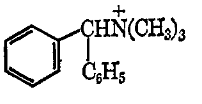
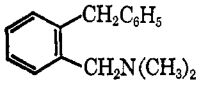
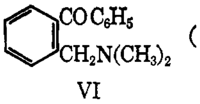
Previously,[2] the product from the reaction of the benzhydryltrimethylammonium ion (I) with sodium amide in liquid ammonia was thought to consist exclusively of the tertiary amine II, which arose through the *ortho*-substitution rearrangement.


I


II

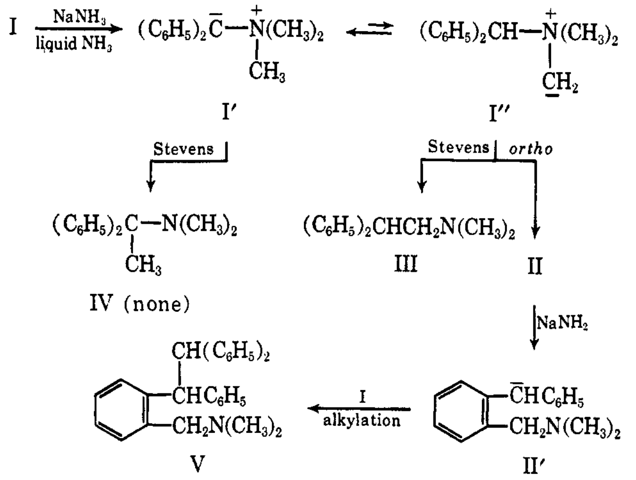
We have now found by vapor phase chromatography that the distilled reaction product from I, obtained in 85–88% yield, boiling over 2°, consists not only of II (80–85%), but also of the isomeric amine III (15–20%), which presumably arose through a Stevens 1,2 shift; none of the isomeric amine IV, which also would have been a Stevens 1,2-shift product, was detected. Similar results were obtained with the crude reaction product. Also, some of solid amine V, which arose through alkylation of II with unchanged quaternary ion I, was isolated from the crude product. These reactions may be represented by Scheme I; the conversion of I′ to I″ might occur intra- or intermolecularly.

Authentic samples of isomeric amines II, III, and IV employed in the vpc determinations were prepared by Wolff–Kishner reduction of amino ketone VI,[3] by lithium aluminum hydride reduction of amide VII,[4] and by addition of methylmagnesium iodide to imminium iodide VIII,[5] respectively.


VI

$(C_6H_5)_2CHCON(CH_3)_2$ VII $\quad (C_6H_5)_2C{=}\overset{+}{N}(CH_3)_2I^-$ VIII

SCHEME I

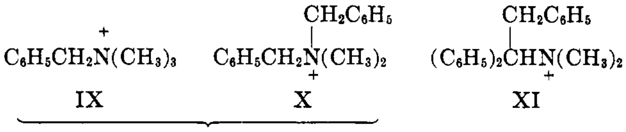


I′ I″ IV (none) III II V II′

The formation of Stevens product III from the less predominant ylid I″, rather than Stevens product IV from the more predominant ylid I′, may be rationalized by equilibration of I′ with I″ (see Scheme I) and migration of the benzhydryl group of I″ rather than a methyl group of I′. This more facile 1,2 shift of the benzhydryl group should be expected whether the SNi[6] or an elimination–readdition[7] mechanism operates.

The formation of some of amine V is not surprising since, not only is the *ortho*-rearrangement product II probably converted to its sodio salt II′ in the reaction mixture (see Scheme I), but quaternary ion I should be capable of alkylating II′.

Interestingly, the observance of both the *ortho* rearrangement and the Stevens 1,2 shift with quaternary ion I places it in an intermediate position between quaternary ions IX (or X) and XI in their reactions with sodium amide in liquid ammonia, since IX and X undergo exclusively the *ortho*-substitution rearrangement,[2] whereas XI exhibits exclusively the Stevens 1,2 shift (two types).[8]


$C_6H_5CH_2\overset{+}{N}(CH_3)_3$ IX $\quad C_6H_5CH_2\overset{+}{N}(CH_3)_2CH_2C_6H_5$ X $\quad (C_6H_5)_2CH\overset{+}{N}(CH_3)_2CH_2C_6H_5$ XI

exclusive *ortho* rearrangement exclusive 1,2 shift

Since consideration of molecular models indicates that the relative ease of the *ortho* rearrangement by the originally proposed cyclic mechanism (SNi′)[2a] should decrease in the order, IX > X > I > XI, the occurrence of the Stevens 1,2 shift with sodium amide in liquid ammonia appears to be dependent on retardation of the *ortho* rearrangement.

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(1) Supported by the Army Research Office (Durham).

(2) (a) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); (b) W. R. Brasen and C. R. Hauser, *ibid.*, **77**, 4157 (1955).

(3) R. L. Vaulx and C. R. Hauser, unpublished results.

(4) T. Morikawa, *Yakugaku Zasshi*, **80**, 475 (1960); *Chem. Abstr.*, **54**, 19589c (1960).

(5) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **24**, 46 (1959).

(6) See C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).

(7) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 229.

(8) C. R. Hauser, R. L. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955).