a high degree of positive charge at the benzyl carbon, and a positive entropy of activation,[19] consistent with a fragmentation step as the rate-determining process.

In summary, decarboxylative dehydration is a sequential process in which loss of water from zwitterion D to give the dipolar ion E is rate controlling in weakly acidic solution. Species E does not return to D; rapid rotation about the C_α–C_β bond of E occurs prior to fragmentation to give carbon dioxide and *trans-p*-propenyltoluene.

Acknowledgments. This investigation was supported in part by a Public Health Service Fellowship (GM-14542 to S.K.B.) from the National Institute of General Medical Sciences. Partial support was also provided by grants from the National Science Foundation (GP-1572 and GP-6133X).

Cyclopropanes. XXIV. Sodium–Liquid Ammonia Reduction of Optically Active Cyclopropyl Halides[1]

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Abstract: The reduction of (−)-(*R*)-1-halo-1-methyl-2,2-diphenylcyclopropane (**1**) leads to the formation of optically active (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane (**2**) with over-all retention of configuration, as well as two ring-opened products, 1,1-diphenyl-2-methylpropane (**3**) and 1,1-diphenylbutane (**4**). The amount of optical activity observed in **2** is dependent on the nature of the starting halogen (Cl > Br > I), the concentration of the sodium in liquid ammonia solution, and a heterogeneity factor.

Sodium in liquid ammonia solutions have been used for some time as a means of reducing organic halides to hydrocarbons; indeed, this reaction is the basis for a quantitative determination of halogen in such compounds.[2] The mechanism of such reactions has, however, been speculative. Two mechanisms have generally been considered: the displacement of halogen as an anion in a two-electron process leading to the formation of a carbanion (eq 1), and a one-electron displacement of halogen as an anion leading to a carbon radical (eq 2) which can then react with solvent or add another electron to give a carbanion intermediate. It has been fairly well established that

$$\text{R-X} + 2e^- \longrightarrow \text{R}^- + \text{X}^- \qquad (1)$$

$$\text{R-X} + e^- \longrightarrow \text{R}\cdot{}^+\text{X}^- \qquad (2)$$

radical intermediates generally lead to products which reflect loss of configurational stability whereas carbanionic intermediates often give products whose configuration is maintained. Several workers have used these observations in trying to decide between the two possible mechanisms shown above for reduction of organic halides by solutions of sodium in liquid ammonia. Thus Verkade and coworkers[3] have reduced optically active (−)-6-chloro-2,6-dimethyloctane and obtained optically active (+)-2,6-dimethyloctane with over-all retention of configuration and an optical purity of at least 20%. They have interpreted their results as favoring eq 1 as the mechanism for such reductions. The low optical purity of the product presumably reflects the fact that carbanions derived from tetrahedrally substituted halides are not very optically stable. Hoff, Greenlee, and Boord[4] have carried out the reduction of 3-chloro-*cis*-3-hexene and 3-chloro-*trans*-3-hexene and obtained *cis*-3-hexene and *trans*-3-hexene, respectively. Again these results have been interpreted to favor a carbanionic mechanism rather than one of radical nature and support the existing acceptance of configurational stability of trigonally hybridized carbanions.

It has been well established that the cyclopropyl carbanion derived from optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**) is capable of retaining its optical activity and configuration.[5] It has also been demonstrated that when the corresponding radical is generated, the bulk of the products isolated are racemic.[6] For these reasons it was believed that one could use the reduction of this optically active halide with sodium in liquid ammonia as a tool to shed further light on the mechanism of such reductions.

The chemical composition and physical properties of solutions of sodium in liquid ammonia have been known for some time to depend upon the concentration of these solutions. In particular, physical measurements have generally shown that such solutions pass from conditions where they contain essentially free solvated electrons at very high dilution (0.003 *M*), through solutions having saltlike characteristics

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(1) The support of this work by grants from the National Science Foundation and the Petroleum Research Fund is gratefully acknowledged.

(2) "Chemistry in Nonaqueous Ionizing Solvents," Part 2: H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, New York, N. Y., 1963, p 206.

(3) P. E. Verkade, K. S. DeVries, and B. M. Wepster, *Rec. Trav. Chim.*, 83, 367 (1964).

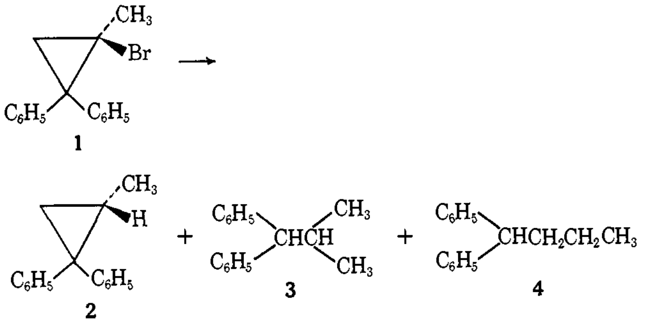
(4) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Am. Chem. Soc.*, 73, 3329 (1951).

(5) (a) H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, 86, 3283 (1964); (b) H. M. Walborsky and A. E. Young, *ibid.*, 86, 3288 (1964); (c) J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, 33, 1962 (1968).

(6) (a) H. M. Walborsky, C.-J. Chen, and J. L. Webb, *Tetrahedron Letters*, 3551 (1964); (b) H. M. Walborsky, *Record Chem. Progr.*, 23, 75 (1962).

(0.003 to 1.0 *M*), to solutions that behave as metals at very high concentrations.[7] In view of these changes it was thought that one might be able to influence the chemistry of processes occurring in these solutions by changing their concentrations. Of the two possible mechanisms of the reduction of organic halides by solutions of sodium in liquid ammonia as shown in eq 1 and 2 one might expect that, if both mechanisms were possible, the latter would be more probable in the highly paramagnetic dilute solutions and the former more probable in the diamagnetic concentrated solutions. Using the tool provided by the reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane, we hoped not only to attempt to decide between the two possible mechanisms of reduction but also to determine if such reductions were affected by changing the concentration of the reducing solutions.

The reduction of 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**) with sodium in liquid ammonia gives three products as shown below. These products were identified by their gas chromatographic retention times and by their nmr and infrared spectra. The products could not be separated by distillation or by thin layer chromatography. Product **3** was easily separated from **2** and **4** by gas chromatography and thus could be identified by comparison of its infrared and nmr spectra with those of authentic material. However, separation of **2** and **4**, although adequate to determine the relative amounts of each, was not sufficient to allow a pure sample of each to be obtained. However, both the infrared and nmr spectra of the mixture were identical with those of a mixture of authentic **2** and **4** in the proportion indicated by the gas chromatographic analysis.



In reactions carried out for similar lengths of time the yields of **2**, **3**, and **4** were found to vary with the concentration of the sodium–liquid ammonia solution used in the reduction. In particular, with excess sodium and at very high concentration (>8%) the only product is 1-methyl-2,2-diphenylcyclopropane, at intermediate concentrations (between 1 and 8%) a mixture of all three products is obtained, and at low concentrations (<1%) only the ring-opened products are produced. We have also found that the ring in 1-methyl-2,2-diphenylcyclopropane (**2**) is opened to give 1,1-diphenyl-2-methylpropane (**3**) and 1,1-diphenylbutane (**4**) under these conditions and that the ratio of these products to recovered starting material also varies with the concentration of the sodium in liquid ammonia solution. Furthermore, the ratio of these products to recovered starting material is the same as obtained when the corresponding bromide is reduced by a solution of sodium in liquid ammonia of the same concentration. Hence, it is believed that 1-methyl-2,2-diphenylcyclopropane is likely the primary product resulting from reduction of the corresponding bromide and that the ring-opened products **3** and **4** probably result from further reduction of this product. One can also produce mixtures of **2**, **3**, and **4** by carrying the reductions out in dilute solutions but using less than an equivalent amount of sodium metal. It appears that reduction of the bromide to give **2** and reduction of **2** to give **3** and **4** have similar rates under these conditions for, even though just enough sodium is used to reduce the bromide to **2**, a mixture of all three products and recovered bromide is obtained. The subject of the opening of the cyclopropyl ring in 1-methyl-2,2-diphenylcyclopropane and other cyclopropane derivatives will be discussed in greater detail in a later paper.[8]

The three products of the reduction (when all three were produced) were separated well enough by gas chromatography to allow the relative yields of each to be determined. The optical activity of the mixture was then determined, and it was subsequently corrected to take into account the amounts of inactive ring-opened products (**2** and **3**) present. Reductions carried out in solutions of 0.5% sodium in liquid ammonia or greater were performed with excess sodium in 50 ml of ammonia, and the sodium content was varied to change the concentration (method a). In order to produce some 1-methyl-2,2-diphenylcyclopropane in solutions below 0.5% sodium in liquid ammonia such reductions were carried out using only enough sodium to theoretically reduce the bromide to the cyclopropane hydrocarbon and varying the volume of ammonia to give the desired concentration (method b). In these cases the recovered bromide was separated from the hydrocarbon fraction by preparative tlc, and the hydrocarbon fraction was then analyzed as above.

It was found that (−)-(*R*)-1-bromo-1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{30}{}_{\mathrm{Hg}}$ −128.5°, gave (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane with an optical purity which depended upon the concentration of the sodium in liquid ammonia solution used in the reduction. The relative and absolute configurations of these products have been previously established[9] so it is known that the reduction occurs with retention of configuration. The variation of optical purity of the resulting cyclopropane hydrocarbon as a function of the concentration of sodium in liquid ammonia is given in Table I. It is seen from these results that one can indeed influence the optical purity of the resulting hydrocarbon by changing the concentration of the sodium in liquid ammonia solution. In very dilute solutions the product is racemic or essentially so and there is a gradual increase in optical purity as more and more concentrated solutions are used. The optical purity appears to level out at about 45%, and this presumably represents the maximum optical stability of the 1-methyl-2,2-diphenylcyclopropyl carbanion as derived from the bromide, stabilized by the sodium gegenion, and solvated by liquid ammonia.

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(7) M. C. Symons, *Quart. Rev.* (London), **13**, 99 (1959), and references cited therein.

(8) H. M. Walborsky and J. B. Pierce, *J. Org. Chem.*, in press.

(9) H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Am. Chem. Soc.*, 83, 2517 (1961); H. M. Walborsky and C. G. Pitt, *ibid.*, 84, 4831 (1962).

Table I. Sodium–Liquid Ammonia Reduction of (−)-(*R*)-1-Bromo-1-methyl-2,2-diphenylcyclopropane

Concn of Na in NH_3, %	% optical purity of I	Method used
0.06	0.5	b
0.12	11.1	b
0.23	13.4	b
0.45	17.8	b
0.51	23.8	b
0.72	*a*	a
1.08	35.2	b
1.64	40.4	a
5.38	43.0	a
7.33	49.0	a
7.61	43.0	a
11.1	43.0	a
15.0	46.4	a

[a] Ring-opened products only.

The direction of change in optical purity of the resulting hydrocarbon as a function of the concentration of sodium in liquid ammonia is as would be predicted for a change from a two-electron process (eq 1) at high concentrations to a one-electron process at low concentrations (eq 2). While we were originally led to investigate this system at various concentrations by thoughts along these lines we have now found that the interpretation of our results is by no means this simple and appears to also involve a heterogeneity factor. Like most organic halides 1-bromo-1-methyl-2,2-diphenylcyclopropane is only sparingly soluble in liquid ammonia. For this reason we desired to discover if the observed variation of the rotation of **2** with changes in the concentration of the reducing solution was in fact connected in any way to the fact that these reductions were carried out with an insoluble bromide. All results recorded in Table I were obtained by adding optically active crystalline 1-bromo-1-methyl-2,2-diphenylcyclopropane as a solid to the sodium in liquid ammonia solution. The apparatus was redesigned so that the bromide could be slowly extracted from a thimble contained in a modified Soxhlet extractor (see Experimental Section) by refluxing the liquid ammonia through it. Three separate experiments were then performed with this apparatus using concentrated sodium in liquid ammonia solutions (>8%) so as to avoid the formation of the ring-opened products, **3** and **4**, and so as to be working in the range of concentrations where 1-methyl-2,2-diphenylcyclopropane of highest optical purity had previously been obtained. In every case the product obtained was pure 1-methyl-2,2-diphenylcyclopropane but it was completely racemic. It was thought that this result might have been caused by racemization of the cyclopropane hydrocarbon during its relatively long time in contact with the sodium in liquid ammonia solution (5 hr *vs.* 1 hr for the reductions shown in Table I). However, it was shown in a separate experiment that optically active 1-methyl-2,2-diphenylcyclopropane did not racemize under the experimental conditions. It is thus evident that the variation of the optical purity of **2** as produced in the original reactions may be due to the fact that the corresponding bromide may be more soluble in the more dilute sodium in liquid ammonia solutions than in more concentrated ones. The observed optical activity for the cyclopropane hydrocarbon when solid bromide is added to the more concentrated sodium in liquid ammonia solutions would appear to be connected to some sort of surface effect. These results not only point out the danger of using experiments performed at one concentration of alkali metals in liquid ammonia to make mechanistic decisions but also show that heterogeneity can play a very important role in such reductions. Heterogeneity by itself, however, is not a sufficient factor to account for our results. If it was, then one would expect that the more insoluble halide would give the highest retention of optical activity. The relative solubilities of the halides were determined and shown to be 1:0.99:0.02 for the chloride, bromide, and iodide, respectively. Thus one would expect the largest retention of activity for the iodide. As we shall see, this is not the case (*vide infra*).

We have also studied the effect of the nature of the halogen in this reaction. Reduction of 1-chloro-1-methyl-2,2-diphenylcyclopropane[5b] gives results similar to those obtained for the corresponding bromide. In reductions carried out with excess sodium and in dilute solutions of sodium in liquid ammonia the only products are **2** and **3**. Reductions carried out in concentrated solutions give only 1-methyl-2,2-diphenylcyclopropane. When (−)-(*R*)-1-chloro-1-methyl-2,2-diphenylcyclopropane, $[\alpha]_{Hg}$ −76.0°, was reduced by adding it as a solid to a 9.2% solution of sodium in liquid ammonia containing a large excess of sodium the only product was (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{25}_{Hg}$ +86.5°. This corresponds to retention of configuration during the reduction and an optical purity of 58% for the cyclopropane hydrocarbon. This compares with 43% obtained for reduction of the corresponding bromide under similar conditions. Reduction of (−)-(*R*)-1-iodo-1-methyl-2,2-diphenylcyclopropane,[10] $[\alpha]_{Hg}$ 199°, by adding it as a solid to a 9.2% solution of sodium in liquid ammonia containing a large excess of sodium gave (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{25}_{Hg}$ +25.1°. Again this corresponds to retention of configuration, and the optical purity in this case is 17%. It seems significant that the optical purity of the resulting hydrocarbon as produced under similar conditions seems to parallel the strengths of the carbon–halogen bond in the halide being reduced. A similar effect has been observed in the reaction of these halides with magnesium and lithium metal to give the corresponding Grignard reagent[5b] and lithium[11] reagent, respectively, and in their reduction to 1-methyl-2,2-diphenylcyclopropane by controlled potential electrolysis.[12]

Neither the bond strength, heterogeneity, nor concentration of sodium in liquid ammonia is, by itself, a sufficient factor to account for our results. Indeed, all these factors are playing a significant role and must be taken into consideration.

Experimental Section[13]

Reductions of 1-bromo-1-methyl-2,2-diphenylcyclopropane which were carried out in sodium in liquid ammonia solutions above

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[10] F. J. Impastato and H. M. Walborsky, *J. Am. Chem. Soc.*, 84, 4838 (1962).

[11] H. M. Walborsky and M. Aronoff, *J. Organometal. Chem.* (Amsterdam), 4, 418 (1965).

[12] C. K. Mann, J. L. Webb, and H. M. Walborsky, *Tetrahedron Letters*, 2249 (1966).

[13] All rotations were taken on a Bendix-Ericcson automatic polarimeter at 5461 Å and 25°.

about 0.5% (method a) were performed at the boiling point of liquid ammonia at atmospheric pressure. The apparatus consisted of a reaction chamber which was an elongated, three-necked flask containing a magnetic stirring bar. In one neck an inlet tube, provided with a stopcock, led to a special mixing vessel. Another neck supported a Dry Ice condenser, and the third neck contained a curved addition tube in which the bromide was stored. The bromide was added as a solid to the sodium in liquid ammonia solution by simply turning this tube in the standard taper joint. The mixing chamber in which the sodium in liquid ammonia solutions were prepared consisted of a vacuum-jacketed, 100-ml graduated cylinder containing three standard taper joints on top and having an outlet tube fitted with a stopcock on the bottom. This tube was provided with a means of keeping a small filter pad of glass wool inside it and led into the reaction vessel. The three necks of the mixing vessel supported a mercury bubbler pressure release, a Dry Ice condenser connected to an ammonia tank, and a curved tube for adding sodium. The entire apparatus was also connected at various joints to a supply of dry argon so that the entire operation could be performed in an inert atmosphere.

A reaction was performed by weighing out the desired amount of bromide (usually 200 mg) and sodium and placing them in their respective curved tubes. The Dry Ice condenser on the mixing vessel was then charged with Dry Ice and acetone, and the required amount of ammonia (usually 50 ml) was condensed into the calibrated chamber. The sodium was added, and the solution was then stirred magnetically for about 10 min. Next, the bottom three-fourths of the reaction chamber was immersed in a Dry Ice–acetone bath, and the Dry Ice condenser on this chamber was also charged. The stopcock in the tube connecting the mixing chamber and reaction vessel was then opened to allow the sodium in liquid ammonia solution to flow through the glass wool plug and into the reaction chamber. This filtering action was particularly necessary when working with the more concentrated solutions, especially those near saturation (15%), where chunks of undissolved sodium were often left behind. The sides of the mixing chamber remained coated with a thin layer of sodium in liquid ammonia solution. Argon was passed through the mixing chamber and thence into the reaction vessel until it had carried all the ammonia as a vapor into the reaction vessel where it subsequently was recondensed. The sodium remaining in the mixing chamber was later titrated with standard HCl solution and hence the amount of metal in the reaction vessel could be determined. With a solution of sodium in liquid ammonia of known concentration in the reaction chamber, the Dry Ice bath was then removed to allow the solution to warm to the boiling point and then the bromide was added. The mixture was stirred for 0.5 hr and then dry hexane was added and the ammonia was allowed to slowly evaporate (about 1.5 hr). Finally, the excess sodium and sodium salts were filtered from the hexane solution, and the hexane-soluble residue was analyzed by gas chromatography at 200° on a 6-ft column of Carbowax on acid-washed Chromosorb P. Infrared and nmr spectra were also frequently taken to confirm the gas chromatographic analysis. Rotations were taken in chloroform solutions on a Bendix automatic polarimeter.

In a few reactions the bromide was not added as a solid but instead was gradually carried into the reaction vessel in solution in liquid ammonia. In these cases, a Soxhlet extractor was placed in the neck of the reaction vessel which usually held the Dry Ice condenser, and this condenser was then plugged into the top of the Soxhlet. The third neck of the reaction vessel was then stoppered. The Soxhlet extractor was modified so that surges of solvent (liquid ammonia) would not occur. That is, the side tube on the Soxhlet was lowered so that the liquid ammonia that was condensed by the Dry Ice condenser would drip through the solid bromide and hence directly back into the reaction flask without any large volume of it collecting in the Soxhlet chamber. The bromide was contained in a glass tube which was fitted on the bottom with a glass frit. Control experiments showed that it required about 5 hr to extract about 250 mg of bromide in this manner so that reactions carried out in this way took considerably longer (about 5 hr plus work-up) than did those above.

For reductions carried out in dilute solutions of sodium in liquid ammonia (<0.5%) there was no possibility of having undissolved sodium, and since the amounts of sodium used were very small (about 36 mg), it was more important to perform the reactions in the complete absence of water. It was found that the apparatus described above did not work well in these cases and another approach was made (method b). Reactions were performed in a conventional all-glass vacuum system containing a vessel for predrying the ammonia, a calibrated vessel for measuring the desired volume of ammonia, and a reaction vessel. The reaction vessel consisted of an elongated, two necked flask, one neck of which carried a curved tube containing the bromide and the other neck of which was plugged into the vacuum system. Reactions were carried out just below the boiling point of liquid ammonia at atmospheric pressure so that a mercury column connected to the vacuum system indicated a vapor pressure of ammonia of about 15 cm of mercury. Molten sodium was forced into capillary tubes, and a length of tubing was broken off to give the required amount of sodium. Titrations of various lengths of tubes containing sodium indicated that this method allowed one to measure out any desired amount of sodium very reliably. A reaction was performed by placing the desired amount of sodium (usually 36 mg = 0.00157 g-atom) in three or four 1-cm lengths of tubing into the reaction vessel. The bromide (usually 213 mg or 0.00743 mol) was then placed in the side arm tube, and the reaction vessel was connected to the vacuum system. The system was fully evacuated and then ammonia was condensed from a tank onto a large chunk of sodium in the drying vessel. After drying, the desired amount of ammonia was distilled from this chamber and condensed into the measuring tube. At this point, with the reaction chamber fully evacuated but the valve to the rest of the system closed, the bottom of the chamber was heated with a bunsen burner to distil the sodium metal out of the capillary tubes and onto the cooler sides of the reaction vessel. The ammonia in the measuring tube was then distilled into the reaction vessel, and after the vapor pressure in the system had reached the desired level, the bromide was added. Stirring was continued for 0.5 hr and then dry hexane was added, and the ammonia was allowed to evaporate through a bubbler that ensured that no water entered the system. Finally the hexane solution was filtered to remove the sodium bromide, and the filtrate was then analyzed as previously mentioned.

1,1-Diphenylbut-1-ene. To 143 g (0.786 mol) of benzophenone in 500 ml of dry ether was added 1.14 mol of *n*-propyl Grignard reagent in 600 ml of dry ether. After stirring for 3 hr the reaction mixture was worked up in the conventional manner. The residue crystallized from hexane to give 95 g or 66% of benzhydrol, mp 65–67°, mmp 65.5–68°. Infrared and nmr spectra were identical with those of authentic material. The residual benzhydrol was removed from the hexane-soluble residue by chromatography on alumina. The alkene fractions were combined and distilled to give 7.61 g or 4.7% of the desired alkene, bp 165–167° (18 mm) [lit.[14] bp 156° (12 mm)]. Infrared and nmr spectra were consistent with the proposed structure.

1,1-Diphenylbutane. A mixture of 1.50 g (0.00722 mol) of 1,1-diphenylbut-1-ene, 0.25 g of 5% palladium on charcoal, and 50 ml of absolute ethanol was shaken for 24 hr under 45 psi of hydrogen gas. The catalyst and solvent were removed and the residue distilled, bp 170–172° (18 mm) [lit.[14] 295° (760 mm)]. Gas chromatography of this material indicated that it was pure, and nmr and infrared spectra were consistent with the proposed structure. The nmr spectrum (δ, CCl_4) showed signals at 7.05 (10 H, singlet), 3.80 (0.97 H, triplet $J = 8$ cps), 1.70–2.18 (1.95 H, six peaks), and 0.67–1.55 ppm (5.2 H, complex).

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[14] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, 74, 365 (1952).