# Bridged Polycyclic Compounds. LIV. Rearrangements Attending the Radical-Anion Reduction of Dehydronorbornyl and Nortricyclyl Chlorides[1]

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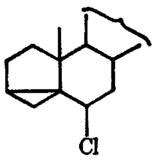
*exo*-Dehydronorbornyl chloride (**7** Cl), its *endo* epimer (**9** Cl) and nortricyclyl chloride (**8** Cl) were reduced by sodium biphenyl radical anion to mixtures of norbornene (**7**, Y = H) and nortricyclene (**8**, Y = H). At room temperature, all three chlorides gave identical mixtures containing about two-thirds nortricyclene. However, at −58° the unsaturated chlorides gave mixtures substantially richer in norbornene (*ca.* one-third nortricyclene), and the tricyclic chloride gave mixtures richer in nortricyclene (*ca.* 87% **8**, Y = H). Rapid carbonation of the reaction mixture from the *exo* chloride resulted in the formation of 3-nortricyclenecarboxylic acid (**12**) in very low yield. The results are rationalized in terms of an initial reduction to classical radicals and competition between rearrangement of these radicals to each other and capture by reduction to carbanions.

For some time we have been interested in homoallylic free-radical systems and in their interconversions with the corresponding cyclopropylcarbinyl systems. All of the work which we and others have done indicates that cyclopropylcarbinyl and homoallyl free radicals are not significantly stabilized by electron delocalization; that is, they have the properties of classical free radicals.[2]

The reduction of 3,5-cyclocholestan-6-yl chloride (**1**) and of cholesteryl chloride (**2**) with sodium biphenyl radical anion in glyme (1,2-dimethoxyethane) has recently been described.[2] In that work, it was shown that each of these chlorides reacts by electron transfer and loss of halide ion to give the related classical radical (**1** → **3** and **2** → **4**), and that, given sufficient lifetime, the cyclopropylcarbinyl radical **3** rearranges to the homoallyl radical **4**. Capture of the radical **3** by another biphenyl radical anion with electron transfer to give the carbanion related to **3** competes effectively with rearrangement. That carbanion is neutralized by proton transfer from glyme faster than rearrangement. The net result was that the ratio of the hydrocarbons **5** to **6** from **1** was related to the concentration of radical anion. Put another way, larger concentrations of radical anion led to an increasing amount of capture of **3** rather than rearrangement to **4**, and thus led to larger amounts of **5** compared with **6**. Radical **4** appeared to be thermodynamically more stable than **3**, so that **2** gave only **6** as product.



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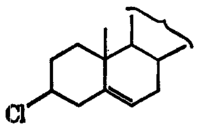

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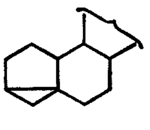

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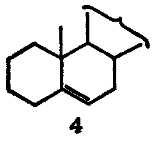

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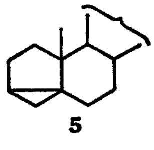

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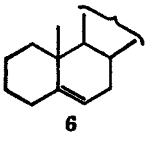
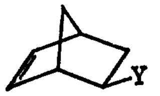


**6**

It seemed worthwhile to extend these experiments to the dehydronorbornyl–nortricyclyl system, a system in which extensive studies of homoallyl–cyclopropylcarbinyl rearrangements have been carried out.[2,3] In the first reported study of the relationship of dehydronorbornyl and 3-nortricyclyl free radicals in which the free radicals were generated from both dehydronorbornyl and 3-nortricyclyl derivatives, Warner, Strunk, and Kuivila[4] investigated the tri-*n*-butyltin hydride and the triphenyltin hydride reductions of dehydronorbornyl (**7** and **9**) and 3-nortricyclyl (**8**) chlorides and bromides. With tri-*n*-butyltin hydride, dehydronorbornyl and nortricyclyl halides were reduced to the same mixture of norbornene (**7**, Y = H) and nortricyclene (**8**, Y = H). However, the reductions of **8** Br with triphenyltin hydride produced product mixtures the compositions of which were dependent upon the concentration of the reducing agent, with more nortricyclene (**8**, Y = H) produced at higher hydride concentration. These data are consistent with a pair of classical radicals, rather than with a nonclassical intermediate.



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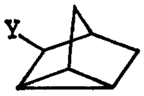

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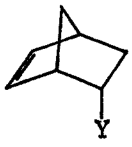

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## Procedure and Results

The three isomeric chlorides, *exo*-dehydronorbornyl (**7**), *endo*-dehydronorbornyl (**9**), and nortricyclyl (**8**), were reduced with sodium biphenyl radical anion using two different experimental procedures and two different temperatures. In the first procedure, a solution of the chloride in pentane or 1,2-dimethoxyethane (glyme) was added under nitrogen to an excess of a stirred solution of sodium biphenyl in glyme. In Table I, this mode of addition is designated "normal." The second procedure involved the addition, under nitrogen, of an excess of sodium biphenyl in glyme to a stirred solution of the chloride in pentane or glyme. In Table I, this mode of addition is designed "inverse."

The reaction of the chlorides with sodium biphenyl was very rapid at room temperature and complete in a few minutes even at the lower temperature. After completion of the reaction, excess sodium biphenyl was

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[1] Previous paper in series: S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7133 (1968).

[2] For leading references, see S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968).

[3] A review of such rearrangements may be found in an article by D. I. Davies and S. J. Cristol, *Advan. Free-Radical Chem.*, **I**, 155 (1966).

[4] C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

TABLE I

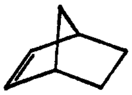
REDUCTION OF *exo*-DEHYDRONORBORNYL (**7**), *endo*-DEHYDRONORBORNYL (**9**), AND 3-NORTRICYCLYL (**8**) CHLORIDES WITH SODIUM BIPHENYL RADICAL ANION

| Chloride | Addition mode | Temp, °C | Mixture composition | |
|---|---|---|---|---|
| | | | % **7** (Y = H)[a] | % **8** (Y = H)[a] |
| 7 | Normal | 25 | 38 | 62 |
| 7 | Inverse | 25 | 33 | 67 |
| 7 | Inverse | −58 | 64 | 36 |
| 9 | Normal | 25 | 35[b] | 65[b] |
| 9 | Inverse | 25 | 37[b] | 63[b] |
| 9 | Inverse | −58 | 73[b] | 27[b] |
| 8 | Normal | 25 | 35 | 65 |
| 8 | Inverse | 25 | 32 | 68 |
| 8 | Inverse | −58 | 13 | 87 |

[a] Average of from two to five runs. The extreme values deviated from the average no more than 5% and were usually within 3%. [b] One run only.

destroyed with water, and the mixture was extracted with pentane. After gross distillation, the product mixture was analyzed for norbornene (**7**, Y = H) and nortricyclene (**8**, Y = H) using vapor phase chromatography (vpc). The results are tabulated in Table I.

The data in Table I show that, at room temperature, essentially the same mixture of norbornene and nortricyclene is formed regardless of the chloride used as a reactant, and that, at room temperature, the product distribution is insensitive to the concentration of radical anion in the reaction mixture. These results could be accommodated by postulating a single nonclassical radical as an intermediate common to all three reaction systems or by proposing that, under the conditions of the experiments, rearrangement between the classical radicals **10** and **11** occurs more rapidly than capture of either by electron transfer from biphenyl radical anion. That the second alternative is the correct one seems inescapable considering the low temperature reduction and results listed in Table I. Reductions at −58° (the freezing point of glyme) clearly result in different product mixtures depending upon the reactant chloride, even though the reactions were run under "inverse" conditions. Thus the reduction of nortricyclyl chloride at −58° yields mostly nortricyclene, and the reduction of either *exo*- or *endo*-dehydronorbornyl chloride yields mostly norbornene. It is apparent that with **8** Cl the initially formed nortricyclyl radical (**11**) is reduced to the nortricyclyl anion[2] before it can rearrange completely to its equilibrium mixture with the dehydronorbornyl free radical **10**. At −58°, a similar situation obtains with *exo*- and *endo*-dehydronorbornyl chlorides. (The slight difference in composition with **7** Cl and **9** Cl listed in Table I is probably within the limits of experimental uncertainties.) The data then leave little doubt that classical radicals intervene in these reactions.[2,3,4]



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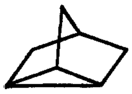

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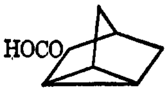

**12**

Just as in the rearrangement of cyclocholestanyl radical **3** to cholesteryl radical **4** and the competitive electron transfers, rearrangement is favored by higher temperatures. Put another way, the Arrhenius activation energy is greater for the rearrangement of **10** to **11** or *vice versa* than for the electron-transfer reduction of these radicals to carbanions by biphenyl radical anion.

To demonstrate the intermediacy of carbanions in the sodium biphenyl reduction of alkyl halides, *exo*-dehydronorbornyl chloride (**7** Cl) was treated with an excess of sodium biphenyl radical anion in glyme and immediately quenched with solid carbon dioxide. After a series of extraction procedures, a mixture of acidic materials was obtained from the reaction mixture. From this mixture, 3-nortricyclenecarboxylic acid (**12**) was isolated in low yield. The structure of this material was confirmed by its melting point and a mixture melting point with an authentic sample. In addition, its infrared (ir) spectrum and that of an authentic sample were identical. Since we know of no case in which a free radical has been carbonated, this substantiates the postulate[2,5,6] that in radical-anion reductions of alkyl halides, the free radical is converted (at least in part) into a carbanion by a second mole of radical anion and the carbanion then forms products by abstracting a proton from solvent.

## Experimental Section

**Materials.**—Sodium biphenyl (1 *M*) in glyme was prepared according to the method of Liggett,[7] and a mixture (75:25) of nortricyclyl chloride (**8** Cl) and *exo*-dehydronorbornyl chloride, (**7** Cl) was prepared according to the procedure of Schmerling.[8] The isomers were separated using preparative vpc on a 20 ft × ⅜ in. column packed with 30% QF-1-0065 on 70–80 mesh Anakrom SD. The nortricyclyl and dehydronorbornyl chlorides separated in this fashion were determined to be 98.5 and 98% pure, respectively. The data in Table I have not been corrected to account for these small deviations from 100% purity. *endo*-Dehydronorbornyl chloride (**9** Cl) was prepared according to the procedure of Roberts[9] and purified by a combination of chromatography on a 4.3 × 95 cm alumina column and fractional distillation. The material used was determined by analytical vpc on a 20 ft × 0.25 in. stainless steel column packed with 20% QF-1-0065 on 70–80 mesh Anakrom ABS to contain 80% *endo*-dehydronorbornyl chloride (**9** Cl), 9% *exo*-dehydronorbornyl chloride (**7** Cl), and 11% nortricyclyl chloride (**8** Cl). The data in Table I have been corrected to account for this composition.

**Procedure.**—In a typical procedure, a 100-ml three-necked flask was fitted with a pressure-equalizing dropping funnel, the top of which was fitted with a Claisen adapter. One arm of the adapter served as a nitrogen inlet and the other was sealed with a rubber serum cap. The second neck of the flask was sealed with a serum cap and the system was exhausted through the third neck which was connected to a mercury trap. After the system had been swept with nitrogen for 1 hr, 20 ml of a 1 *M* solution of sodium biphenyl in glyme was injected into the reaction flask using a hypodermic syringe. The dropping funnel was then charged using a syringe with a solution of 1.0 g of the chloride in 5 ml of glyme, and the reaction flask was immersed in a bath at the appropriate temperature. The chloride solution was added dropwise over a period of 0.6 hr to the rapidly stirred solution of sodium biphenyl. After the addition was complete, the reaction mixture was poured into 100 ml of cold water. The resulting mixture was extracted with four 50-ml portions of pentane. The pentane extracts were combined and extracted with five 10-ml portions of water to remove most of the glyme.

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(5) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966).

(6) S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966).

(7) L. M. Liggett, *Anal. Chem.*, **26**, 748 (1954).

(8) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Amer. Chem. Soc.*, **78**, 2821 (1956).

(9) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

After the pentane solution had been dried over magnesium sulfate it was concentrated by distilling the pentane through a semimicro column (30 × 1 cm) packed with glass helices. After most of the pentane had been distilled, 2 ml of chlorobenzene was added to the distillation flask. The distillation was continued and the portion boiling from 70 to 120° was collected. This material was analyzed by vpc at 98° on a 20 ft × ⅜ in. column packed with 30% SE-30 on Chromosorb 60–80 mesh.

**Isolation of 3-Nortricyclenecarboxylic Acid.**—A 60-ml separatory funnel was attached at its stem to a piece of glass capillary tubing (i.d. 1.0 mm). A second 60-ml separatory funnel was attached to a piece of capillary tubing (i.d. 1.7 mm). The smaller capillary tubing was joined to the larger one and the larger tubing was cut off 2 cm below the junction. By trial and error, conditions were found under which equivalent amounts of sodium biphenyl (1 *M*) in glyme and a mixture of dehydronorbornyl chloride and nortricyclyl chloride (*ca.* 80:20) would pass through the capillary tubes and meet at the junction. The funnel attached to the larger capillary was charged with 60 ml of 1 *M* sodium biphenyl in glyme and in the other funnel was placed 2.5 g of the chloride mixture. A slight pressure of nitrogen was applied to the funnel containing the chloride mixture and the stopcocks on the two funnels were opened simultaneously. As the reaction mixture issued from the capillary tubing, it dropped into an excess of vigorously stirred crushed Dry Ice. After the reaction was complete, the Dry Ice was allowed to sublime. The yellow liquid residue was treated with 50 ml of water and extracted with one 100-ml and two 50-ml portions of ether. The aqueous solution was acidified with concentrated hydrochloric acid and extracted with three 40-ml portions of ether. The combined ether extracts were washed with 10 ml of saturated sodium chloride solution and then dried over magnesium sulfate. After removal of the magnesium sulfate by filtration and concentration of the ether in a rotary evaporator, there remained approximately 1.5 g of a viscous yellow oil. Thin layer chromatography on silica gel indicated the presence of at least five components. Chromatography of 0.75 g of the oil on a 1 × 45 cm column and elution with 2% ether in Skelly-B resulted in the isolation of 237 mg of a foul-smelling amber oil. Thick layer chromatography of this material on silica gel and developing with 5% methyl alcohol in ether resulted in the isolation of 103 mg of a yellow-brown oil. Trituration of this oil with pentane followed by evaporation of the solvent left 80 mg of amber oil. Vapor phase chromatography of this oil (on a 7 m × 0.25 in. stainless steel column packed with 20% QF-1-0065 on 70–80 mesh Anakrom ABS) indicated the presence of three components. A minor component had the same retention time as biphenyl and the major component (probably 80% of the mixture assuming equal detector response) had the same retention time as authentic 3-nortricyclenecarboxylic acid. By collecting the major component of a portion of the mixture by gas chromatography on a 20 ft × ⅜ in. column packed with 30% QF-1-0065 on Anakrom SD 70–80 mesh, 14 mg of 3-nortricyclenecarboxylic acid was obtained. After one recrystallization from pentane, it had mp 49.5–51.6° (lit.[9] mp 49–50°) and a mixture melting point with an authentic sample was not depressed. The ir spectra of the major component of the oil and of authentic 3-nortricyclenecarboxylic acid were identical. Whether or not 5-norbornene-2-carboxylic acid was present was not determined.

**Registry No.**—**7** Cl (*exo*), 3721-19-5; **8** Cl, 3509-46-4; **9** Cl (*endo*), 3721-18-4.

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# The Addition of Trichloromethyl Radicals to Alkenylsilanes[1]

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Dibenzoyl peroxide catalyzed addition of bromotrichloromethane to various types of vinyl- and $\omega$-alkenylsilanes have been investigated. Six new addition compounds have been prepared and characterized. It has been found that the reactivity of the double bond in the series of $R(CH_3)_2SiCH{=}CH_2$, where R = Me, Et, *i*-Pr, and *t*-Bu, toward addition of the trichloromethyl radical is governed by the Taft steric factor, $E_s$, of R, while the reactivity in the series of $Cl_n(CH_3)_{3-n}SiCH{=}CH_2$ is approximately related to the inductive effect. In the series of $(CH_3)_3Si(CH_2)_nCH{=}CH_2$, where $n = 0$–4, the reactivity reaches a maximum when $n = 1$. Factors influencing the reactivity have been discussed.

The addition of reagents across the double bond of vinyl- and alkenylsilanes is one of the most useful reactions in preparing carbon-functional organosilicon compounds.[2] These reagents can involve electrophilic and nucleophilic ones, as well as free-radical, or carbene intermediates and the influence of the silicon atom upon the reactivities has been one of the fascinating problems in organosilicon chemistry.

Bromotrichloromethane has been known to undergo the reaction resulting in the formation of a carbon–carbon bond *via* the free-radical mechanism.[3a] A useful tabular survey[3b] has been compiled by Walling and Huyser.

For vinylsilanes, some examples of addition products with bromotrichloromethane by the free-radical mechanism have been reported; thus, dibenzoyl peroxide catalyzed[4] and light-induced[5] addition to (trichloro)-vinylsilane, light-induced addition to (methyldichloro)-vinylsilane,[4] and dibenzoyl peroxide catalyzed addition to (triphenyl)vinylsilane[6] are known. However, no systematic study on the reactivity of vinyl- and alkenyl-substituted silanes toward free radicals has been undertaken.

During the course of studies on the structure and reactivity in the homolytic process, we have been interested in the reactivities of these compounds toward the trichloromethyl radical and have found an interesting effect of rate enhancement of trimethylsilylmethyl group in the free-radical addition reaction of bromotrichloromethane to substituted ethylenes.

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(1) Presented in part at the 7th Symposium on Free-Radical Reactions, Osaka, Japan, Nov 30, 1966; Preprint, p 17.

(2) (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, Chapter 14; (b) V. Bažant, V. Chvalovský, and J. Rathousky, "Organosilicon Compounds," Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965, p 292.

(3) (a) M. S. Kharasch, W. Nudenberg, and E. Simon, *J. Org. Chem.*, **18**, 328 (1953); (b) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).

(4) Midland Silicones Ltd., British Patent 769,499 (1957); *Chem. Abstr.*, **51**, 13903 (1957).

(5) A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J. Chem. Soc.*, 4472 (1957).

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