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Photochemical Transformations. XII. Photochemical Reduction of Some Dehydronorbornyl Derivatives[1]

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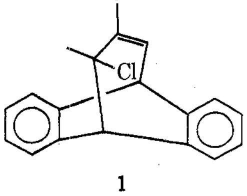
Received January 6, 1975

The photosensitized irradiation of exo and endo isomers of 5-chloronorbornene, 5-hydroxynorbornene, and 5-acetoxynorbornene, as well as of 5,5-dichloronorbornene, with a variety of sensitizers and solvents led to saturation of the double bond to give the corresponding norbornanes. No rearrangements, epimerizations, or solvolyses were observed.

Some years ago, it was discovered[3] that sensitized irradiation of **1** led to **2**, which is the photochemical equivalent of a Wagner–Meerwein rearrangement. That this is a true photochemical process, rather than a chain process, was clear from the fact that **1** is thermally stable with respect to **2**. The possibility that the photorearrangement involved carbenium ion–chloride ion pairs was suggested at that time and led to the idea that other systems which could accept triplet energy from photosensitizers and could undergo carbenium-ion formation readily might show similar interesting chemistry. Although the idea of carbenium-ion intervention remains to be proven or disproven,[4] it led to the discovery[5] that photosensitization of allylic chlorides and bromides results in the formation not only of products of 1,3-sigmatropic (allylic) rearrangement, but also of 1,2-rearrangement–cyclizations (allyl to cyclopropyl rearrangements). These reactions have been shown to be quite general.[1,4,6]



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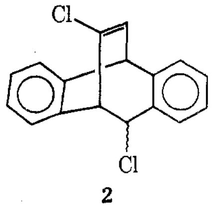

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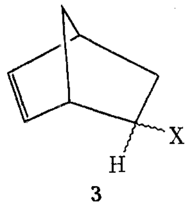

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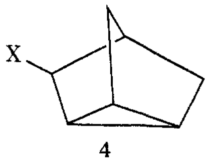

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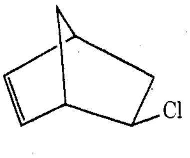
As the dehydronorbornyl (**3**)–nortricyclyl (**4**) system represents one in which reversible rearrangements attend carbenium ion processes,[7] we thought that photosensitized rearrangement of **3** to **4** might occur and that one might also possibly see some interesting stereochemical consequences of exo (**5**) and endo (**6**) isomerism in the halides. Accordingly, we subjected **5** and **6** to irradiation in acetone using thin-walled Pyrex filters ($\lambda > 280$ nm, $T\% > 10\%$). Both compounds were reactive under these conditions, but no trace of the isomeric nortricyclyl chloride (**4**-Cl) could be found. Instead, photoreduction occurred to give norbornyl chloride of retained stereochemistry (i.e., **5** → **7** and **6** → **8**) in yields of 10–20% as the only products of this volatility. Nortricyclyl chloride (**4**-Cl) was not reactive under similar conditions.



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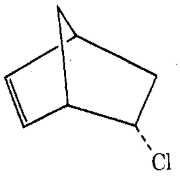

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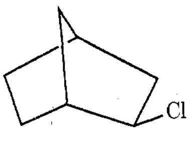

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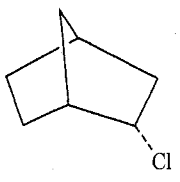

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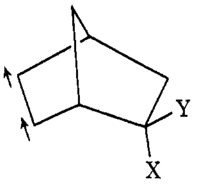
Sensitization of **6** with *m*-xylene (λ 254 nm) or with *p*-methoxyacetophenone ($\lambda > 280$ nm)[8] in pentane also gave only **8** (no **4-Cl**, **5**, or **7** was noted) in the appropriate volatility range.

The photoreduction of norbornene and of its derivatives, as an accompaniment to dimeric, hydrodimeric, and radical solvent incorporation products both with sensitization and upon direct irradiation, has been known for some time,[9] and the yields which have been reported are consistent with those we have noted. In addition, we note that *exo*- and *endo*-dehydronorborneols and dehydronorbornyl acetates also give saturated products in similar yields. The mechanism of such reductions has not been clarified. Although cationic intermediates have been suggested, no evidence for their intervention seems at hand. Rather, as Scharf has suggested,[9] radicals seem to be involved. The fact that triplet sensitizers may be used suggests that the triplet biradical of the olefin (**9**) is an intermediate. This triplet might rearrange to **10** by a 1,3 shift of the endo substituent, assuming that it is long lived. Such a rearrangement would not be observable with **6** (X = Cl; Y = H), as hydrogen transfer from solvent to the 1,3-biradical still would give **8**, but **5** (X = H; Y = Cl) would be expected to give appreciable amounts of **8**, rather than **7**, from preponderant hydrogen transfer from the exo side.[10] Failure to see exo–endo isomerism (or the reverse) speaks against such a process. Similarly, the clean photoreduction of **11** to **12**, without the formation of **13** or **14** or of any of their epimers, is of interest. While free-radical rearrangements of saturated radicals are rare at low temperatures, even in norbornyl systems,[10] rearrangements of triplet biradicals are quite common, both by 1,2 and 1,3 shifts,[11] and migration of halogen atoms occurs even in monoradicals.[12]



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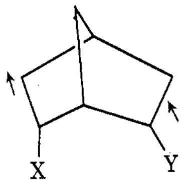

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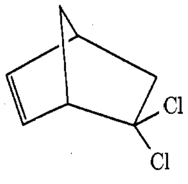

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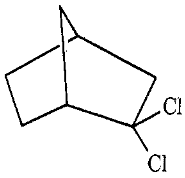

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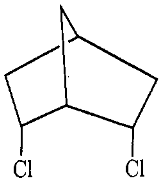

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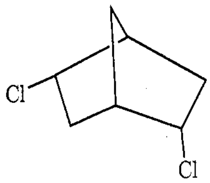

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We have recently noted that chlorobenzene (ϵ 14, 280 nm) in acetonitrile is an excellent sensitizer for photoallylic rearrangements and that photosolvolysis occurs readily for certain allylic systems with chlorobenzene and methanol. When a mixture of **5** and **4-Cl** was irradiated in the latter system, the **4-Cl** was inert and the **5** was converted to 20% of **7**. In chlorobenzene, irradiation of a mixture of **5** and **4-Cl** again found **4-Cl** inert; **5** was converted to higher molecular weight materials, and neither **6** nor **7** was produced.

In no case, then, have we observed either homolytic or heterolytic cleavage of the carbon–chlorine bond in these sensitized reactions. One rationalization might be that the reduction reactions are so fast as to overwhelm competing reactions. A preliminary quantum yield measurement for the $5 \rightarrow 7$ reaction in acetone was 0.007, and that for $6 \rightarrow 8$ was 0.002, so that the quantum yields for disappearance of these halides are in the order of 0.01–0.05, somewhat lower than those we have generally observed for the allylic and allyl to cyclopropyl chloride rearrangements. The results with the dehydronorbornyl chlorides thus offer no insight into the nature of the other rearrangements we have reported earlier.

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A or A-60 spectrometer. Infrared spectra were run in carbon tetrachloride, using either Perkin-Elmer Model 337 or Model 137 spectrophotometers. Mass spectra were obtained on a Varian MAT Model CH-7 mass spectrometer. Analyses of some experiments were carried out on a Varian Aerograph Model A-90P-3 instrument, while preparative separations were carried out on an Aerograph Autoprep Model A-700 gas chromatograph. Irradiations were performed with a Hanovia 450-W mercury arc lamp (Engelhardt-Hanovia, Inc., Newark, N.J., Model L-639A-36) inserted into a water-cooled quartz immersion probe. In quantitative experiments, samples were placed into preconstricted 13 × 100 mm Pyrex test tubes, degassed on a vacuum line with five freeze–pump–thaw cycles and sealed at pressures less than 10^{-5} Torr. Sealed tubes were then irradiated in parallel with *cis*-2-pentene actinometer solutions[13] in a merry-go-round photolysis apparatus.

Materials. All solvents and sensitizers were spectroquality grade, except for chlorobenzene, which was twice distilled reagent-grade material. Nortricyclyl and *exo*- and *endo*-dehydronorbornyl chlorides[14] and acetates[15] were prepared as previously described, as was 5,5-dichloro-2-norbornene.[16] Norbornene, *exo*- and *endo*-norborneol, and *exo*- and *endo*-dehydronorbornyl alcohol were commercially available samples.

Irradiation of *exo*- (5) and *endo*- (6) Dehydronorbornyl Chloride in Acetone. *exo*-Dehydronorbornyl chloride (15 mg, 0.12 mmol) was dissolved in 0.6 ml of acetone in a Pyrex NMR tube, and 60 μl of *n*-heptane was added as internal standard. The tube was capped with a serum stopper and deaereated with nitrogen. After irradiation for 1.5 hr, analysis by gas chromatography (30% SE-30 on Chromosorb W 60/80 mesh, 20 ft × 0.375 in. Al column) indicated that total loss of starting material had occurred, and that the product mixture consisted of 15% of *exo*-norbornyl chloride (**7**) and 85% of unidentified higher molecular weight material. No nortricyclyl chloride (**4-Cl**), *endo*-dehydronorbornyl chloride (**6**), or *endo*-norbornyl chloride (**8**) were detected.

Similar treatment of *endo*-dehydronorbornyl chloride led to 10% formation of *endo*-norbornyl chloride (**8**) after 1.5 hr of irradiation. No other products of similar volatility were noted.

Irradiation of *endo*-Dehydronorbornyl Chloride (6) in *m*-Xylene and in *p*-Methoxyacetophenone–Pentane. *endo*-Dehydronorbornyl chloride (44 mg, 0.35 mmol) and 15.0 μl of *n*-heptane were dissolved in 0.6 ml of *m*-xylene in a quartz tube. The sample was treated as outlined above, and after 96 hr of irradiation, the product mixture contained 32% of **6**, 13% of **8**, and 54% of unidentified higher molecular weight material. No isomerization could be detected.

endo-Dehydronorbornyl chloride (21 mg, 0.16 mmol), 15 μl of *n*-heptane, and 60 μl of *p*-methoxyacetophenone in 0.6 ml of pentane was treated similarly and placed in a Pyrex NMR tube. After 1.5 hr the product mixture consisted of 95% of **6** and 4% of **8**.

Irradiation of *exo*- and *endo*-Dehydronorborneols in Acetone. *endo*-Dehydronorborneol (15 mg, 0.14 mmol) and 15.0 μl of *n*-heptane was dissolved in 1.0 ml of acetone in a Pyrex NMR tube, and the sample was treated as described above. After 18 hr of irradiation 10% of *endo*-norborneol was obtained, but no isomerization was noted.

Similar treatment of *exo*-dehydronorborneol gave 15% of *exo*-norborneol after 18 hr. Again no isomerization was detected.

Irradiation of *exo*- and *endo*-Dehydronorbornyl Acetate in Acetone. *exo*-Dehydronorbornyl acetate (31 mg, 0.20 mmol) and 15.0 μl of *n*-heptane were dissolved in 1.0 ml of acetone in a Pyrex NMR tube, and the sample was treated as described above. After 6 hr of irradiation, the product mixture consisted of 15% of *exo*-norbornyl acetate, 0% of *exo*-dehydronorbornyl acetate, and 85% of higher molecular weight material. No isomerization was detected.

Similar treatment of the endo acetate gave 12% of *endo*-norbornyl acetate after 6 hr. Again, no isomerization was detected.

Irradiation of 5,5-Dichloro-2-norbornene (11) in Acetone. 5,5-Dichloro-2-norbornene (57 mg, 0.35 mmol) was dissolved in 0.5 ml of acetone and placed in a Pyrex NMR tube. The sample was handled as outlined above; after 4 hr of irradiation, total loss of starting material was noted. The product was analyzed by GC (3% SE-52 on Aeropak 30 100/120, 5 ft × 0.25 in. stainless steel), and it was found to consist of 20% of the saturated dichloride **12** and 80% of higher molecular weight material. No rearranged products could be detected.

Irradiation of Nortricyclyl Chloride (4-Cl) in Chlorobenzene and in Chlorobenzene–Methanol. Nortricyclyl chloride (200 mg, 1.6 mmol) was dissolved in 5.0 ml of chlorobenzene–

methanol (1:4) and placed in an 8 × 0.375 in. Pyrex tube. The sample was handled as outlined above; after 100 hr of irradiation, the ^{1}H NMR spectrum showed no change.

Nortricyclyl chloride (200 mg, 1.6 mmol) in 5.0 ml of chlorobenzene treated similarly showed no change in the ^{1}H NMR spectrum, even after 75 hr of irradiation.

Irradiation of *exo*-Dehydronorbornyl Chloride (5) in Chlorobenzene–Methanol. *exo*-Dehydronorbornyl chloride (250 mg, 1.94 mmol) was dissolved in 5.0 ml of chlorobenzene–methanol (1:4) solution and the sample was treated as outlined for nortricyclyl chloride. After 75 hr of irradiation, ^{1}H NMR analysis indicated that the product was composed of 20% of **5** and 80% of saturated compounds, of which at least 80% was dimeric or polymeric material. No absorption corresponding to –OMe could be detected.

Irradiation of *exo*-Dehydronorbornyl Chloride (5) in Chlorobenzene. To two Pyrex tubes were added, respectively, 47 mg (0.37 mmol) and 85 mg (0.66 mmol) of **5** in 1.0 ml of chlorobenzene. The samples were then treated as outlined above. After 100 hr of irradiation, ^{1}H NMR analysis indicated that the first tube contained 56% of **5** and 44% of dimeric or polymeric material, while the second contained 43% of **5** and 57% of dimeric or polymeric material. No isomerization was detected.

Quantum Yield Determination for *exo*-Norbornyl Chloride (7) and *endo*-Norbornyl Chloride (8). *exo*-Dehydronorbornyl chloride (**5**, 29.5 mg, 0.230 mmol) was diluted to 3.0 ml with acetone and placed in a preconstricted Pyrex test tube. The sample was degassed on a vacuum line and sealed at pressures less than 10^{-5} Torr. After irradiation for 48 hr, analysis by gas chromatography (25% Carbowax 20M on Chromosorb P 60/80, 6 ft × 0.25 in. Al column) indicated that the tube contained 20% of **7** ($\phi = 0.007$).

endo-Dehydronorbornyl chloride (**6**) treated similarly gave 12% of **8** after 48 hr ($\phi = 0.002$).

Acknowledgments. G.A.L. was a NDEA Fellow during the course of this work. A portion of the work was supported by Public Health Service Grant CA-13199 from the National Cancer Institute.

Registry No.—4-Cl, 3509-46-4; **5,** 3721-19-5; **6,** 3721-18-4; **7,** 765-91-3; **8,** 2999-06-6; **11,** 4634-77-9; *endo*-dehydronorborneol, 694-97-3; *exo*-dehydronorborneol, 2890-98-4; *exo*-dehydronorbornyl acetate, 5257-37-4; *endo*-dehydronorbornyl acetate, 2890-95-1.

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Oxidations of Valencene

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Received February 21, 1975

Epoxidation of valencene (**1**) gives predominantly the β-epoxide **3**, and similarly, dihydrovalencene (**15**) gives predominantly **20**. Photosensitized oxidation of **1** gives 4α,10α-dimethyl-6β-isopropenyl-Δ^1-9β-octalol (**5**) and 4α,10α-dimethyl-6β-isopropenyl-Δ^8-1α-octalol (**6**). Epoxidation of nootkatone (**2**) gives β-epoxide **10**, which undergoes the Wharton–Bohlen rearrangement to β-octalol **5**. Hydroboration of dihydrovalencene (**15**) gives predominantly 4α,10α-dimethyl-6β-isopropyl-*trans*-1β-decalol (**16**). Stereochemical correlations are made and the results are discussed in reference to similar oxidations of other octalin derivatives.

The sesquiterpene valencene (**1**),[1] which is present in valencia orange oil, has been of considerable interest both for the synthesis of nootkatone (**2**) and for the synthetic challenge posed by the 4α,10α-dimethyl substituents. Because of the desirable fragrance–flavor properties of nootkatone (**2**), we embarked on a study of some of the other oxidative chemistry of the parent hydrocarbon, valencene (**1**).

Epoxidation of valencene (**1**) by means of 40% peracetic acid afforded a mixture of mono- and diepoxides in a ratio of 3.5:1. The stereochemistry of the monoepoxides, isolated by distillation, was initially assigned by inspection of the NMR spectra. The epoxy hydrogens of *trans*-5,6-epoxy steroids and *trans*-1,9-epoxy-2,2,5,5,10-pentamethyldecalin resonate at higher field than the corresponding hydrogens of the cis isomers.[2] Since the NMR spectrum of the major valencene epoxide (71%) showed the epoxy hydrogen as a triplet at δ 2.90, whereas the minor epoxide (29%) had this corresponding triplet at δ 3.00, the major and minor epoxides were assigned structures **3** and **4** (Scheme I), respectively. Preferential epoxidation of **1** trans to the C-10 axial methyl group is consistent with the observation[3] that epoxidation of 10-methyl-1(9)-octalin gives 60% trans epoxide.

Support for this stereochemical assignment was obtained by correlation of the major epoxide with the major product derived from photosensitized oxidation of **1**, which was first reported by Ohloff.[7]

Photosensitized oxygenation of **1** followed by reduction