All kinetic runs were made with 1.0×10^{-3} M ROTs (RONs) and 1.2×10^{-3} M potassium acetate. Infinity ($10t_{1/2}$) titers of these solutions gave the following percent reaction: **1**-OTs (100°), 94.2%; **1**-ONs (80°), 97.3%; **1**-ONs (100°), 97.8%.

All preparative scale buffered acetolyses were determined using 0.010 M ROTs and 0.012 M potassium acetate. The solutions were sealed in flasks and placed in the constant-temperature bath for the allotted time. After removal from the bath and quenching in ice–water, the contents were poured from the flasks into water and extracted with methylene chloride which was washed with water, 5% aqueous $NaHCO_3$, and water and dried (Na_2SO_4). Evaporation of the solvent and chromatography of the residue then gave the products.

Acknowledgments. The authors thank the National Science Foundation (GP-10691) for support of this research and for matching funds to purchase the NMR and mass spectrometers.

Registry No.—**1**-OH, 54798-03-7; **1**-OTs, 54798-04-8; **1**-ONs, 54798-05-9; **1**-OAc, 54798-06-0; **1**-OAc 1,3,5-trinitrobenzene complex, 54798-07-1; **2**, 3806-02-8; **3**, 36044-40-3; **4**, 54832-62-1; **5**, 54798-08-2; **6**, 54522-71-3; **6** 1,3,5-trinitrobenzene complex, 54798-09-3; **7**, 54798-10-6; **8**, 54798-11-7; **10**, 54798-12-8; **11**, 54798-13-9; **12**, 53477-10-4; **12** 1,3,5-trinitrobenzene complex, 54798-14-0; ethyl cyanoacetate, 105-56-6; 2-chlorotropone, 3839-48-3; 2-chloroazulene, 36044-31-2; 2-chloro-1-trifluoroacetylazulene, 54798-15-1; methyl 2-chloro-1-azulenecarboxylate, 54798-16-2; 2-chloro-1-azuloic acid, 54798-17-3; *p*-nitrobenzenesulfonyl chloride, 98-74-8; tosyl chloride, 98-59-9.

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(7) (a) K. Conrow, *Org. Synth.*, **43**, 101 (1963); (b) H. E. Petty, Ph.D. Thesis, Kansas State University, Manhattan, Kans., 1971; (c) A. P. Ter Borg, R. Van Helden, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **81**, 177 (1962).
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(10) P. D. G. Dean, *J. Chem. Soc.*, 6655 (1965).
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(12) A. G. Anderson and R. G. Anderson, *J. Org. Chem.*, **27**, 3578 (1962).
(13) J. R. Curtis, Ph.D. Thesis, Kansas State University, Manhattan, Kans., 1971.
(14) R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **38**, 138 (1972).
(15) Available from R-M Research Products, Inc., Manhattan, Kans. 66502. The small (3 ml) working volume of this conductance cell and the ability to work at elevated temperatures with this cell [4,14] made these studies possible.
(16) E. Heilbronner in "Non-Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, p 200.
(17) S. Winstein, P. E. Klinedinst, and G. C. Robinson. *J. Am. Chem. Soc.*, **83**, 885 (1961); E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).
(18) Footnote 21 in ref 2.
(19) Melting points were determined on a Kofler hot stage and are uncorrected. Spectra were determined with commercial instruments (ir, Perkin-Elmer 137; NMR, Varian A-60 and T-60; uv–visible, Cary 11; mass, AEI-MS9). NMR spectral data are listed as centers except for multiplets, where the range of the signals is given.

Molecular Rearrangements. XII.[1a] Reactions of 2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide and 2-Chlorobicyclo[2.2.2]oct-2-ene Oxide with Lithium Diethylamide

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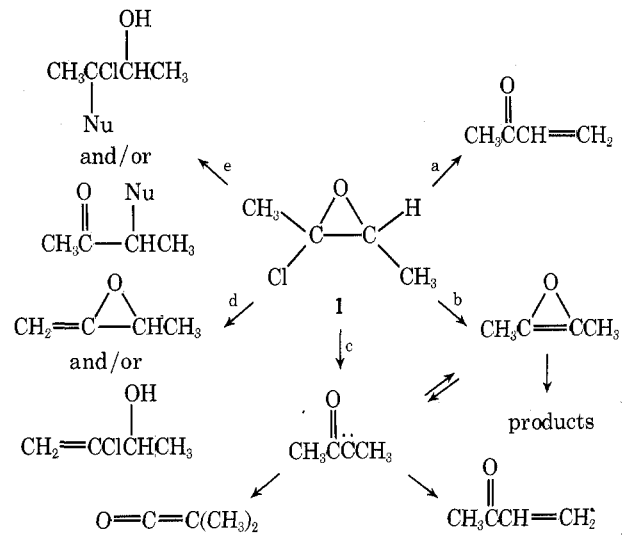
The reactions of two bicyclic α-chloro epoxides, 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide (**2**) and 2-chlorobicyclo[2.2.2]oct-2-ene oxide (**3**), with lithium diethylamide have been investigated. With **2**, refluxing benzene–ether and ether (0 to −15°) were examined as solvents while, with **3**, only refluxing benzene–ether was studied. From **2** the major product was tricyclo[2.2.1.$0^{2,6}$]heptan-3-one (**4**). The amount of the minor product, tricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**5**), was solvent and base concentration dependent. Using **2**-*3-d* in ether, no deuterium was found in **4** and none at C_3 of **5**. While the formation of **4** can be readily rationalized as involving transannular insertion by the α-keto carbene formed by α elimination at C_3 of **2**, the pathway **2** → **5** is unclear. From **3**, two major products, tricyclo[3.2.1.$0^{2,7}$]octan-6-one (**15**) and *N,N*-diethylbicyclo[2.2.1.]heptane-7-carboxamide (**16**), and two minor products, 3-chlorobicyclo[2.2.2]octan-2-one (**13**) and bicyclo[2.2.2]octanone (**14**), were isolated. Ketone **15** and amide **16** are believed derived from the α-keto carbene, **15** by transannular insertion and **16** by Wolff ring contraction, while ketones **13** and **14** probably arise via thermal rearrangement of **3**. These results are compared with those from other methods of generating the respective bicyclic α-keto carbenes or carbenoids. The site specificity in these conversions of bicyclic α-chloro epoxides **2** and **3** to tricyclic ketones **4** and **15**, respectively, may prove synthetically useful.

The reactions of strong bases with acyclic, cyclic, and bicyclic epoxides have been studied by a number of researchers,[2] notably Cope, Crandall, and Rickborn. The major types of processes observed were α elimination (yielding insertion and ketone products), β elimination, and nucleophilic epoxide ring opening. The extent of involvement of these processes was dependent on structural effects in both the epoxide and the base.

Our interests in the chemistry of α-chloro epoxides[1,3] led us to consider how the α-chloro substituent might effect the outcome of such strong base reactions. Using (*Z*)-2-chlorobutene oxide (**1**) as an example, the conceivable pathways are listed in Scheme I. Nouri-Bimorghi[4] reported that varying amounts of β elimination (pathway a) and nucleophilic epoxide ring opening (pathway e) were observed when three acyclic α-chloro epoxides were allowed to react

Scheme I

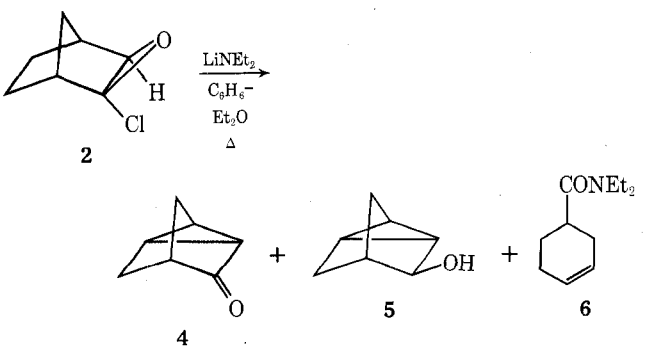


with phenyllithium. As expected, the extent of involvement of these pathways was dependent on the substrate structure.

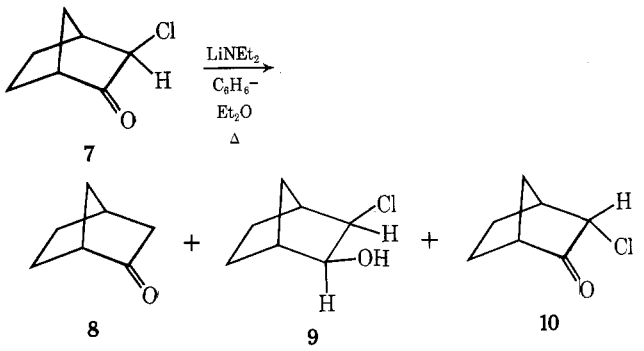
For the present study, we wished to limit the probable reaction pathways given in Scheme I to c, which would enable us to evaluate it as a method of accomplishing Wolff-type rearrangements via α-keto carbenes (or carbenoids). Such should be possible using certain bicyclic α-chloro epoxides where pathways a, b, d, and e should be disfavored, as should the eqilibrium shown between α-keto carbene and oxirene structures.[5] The α-chloro bicyclic epoxides chosen were 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide[1,6] (**2**) and 2-chlorobicyclo[2.2.2]oct-2-ene oxide[7] (**3**), since we had previously studied their neat, thermal, and certain catalyzed rearrangements, and Crandall[2f,j] had reported on lithium diethylamide reactions of the parent bicyclic epoxides.

Results and Discussion

When [2.2.1] α-chloro epoxide **2**[6] was heated under reflux in benzene–ether solution containing excess lithium diethylamide and diethylamine for 50 hr, the product (3.05 g from 4.35 g of **2**) was found to contain 84% tricyclo[2.2.1.$0^{2,6}$]heptan-3-one (**4**), 8% tricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**5**), 2% recovered **2**, and 2% of an amide tentatively identified as *N,N*-diethylcyclohex-3-enecarboxamide (**6**) along with four minor unidentified components (by GLC). Using cyclohexene–ether as solvent in this reaction gave essentially identical results.



To establish that **4** and **5** especially were primary products in the above reaction and not artifacts of thermal rearrangement of **2** → *exo*-chlorobicyclo[2.2.1]heptan-2-one[1,6] (**7**), **7** was treated under the reaction conditions. The product was shown to contain 63% bicyclo[2.2.1]heptan-2-one (**8**), 12% *exo*-3-chlorobicyclo[2.2.1]heptan-*exo*-2-ol (**9**), 11% **7**, and 14% *endo*-3-chlorobicyclo[2.2.1]heptan-2-one (**10**).



Since we had previously shown that **4** is reduced to a mixture of **4** and **5** under these reaction conditions (albeit under reflux for 4 days), the formation of **8** and **9** from **7** is rationalized by carbonyl reduction of **7** to **9** (or its C_2 epimer) followed by dehydrochlorination.

Formation of amide **6** from **2** and lithium diethylamide can be considered to arise by attack of the base on the carbonyl of *exo*-2-chlorobicyclo[2.2.1]heptan-7-one, a major product in the neat, thermal rearrangement of **2**.[1,6] Generation of the amide group carbonyl, C_1–C_7 bond cleavage, and loss of chloride ion from C_2 would yield **6**.

In an effort to shorten the reaction time of **2** with lithium diethylamide, to obtain complete reaction, and to study the effect of solvents on this process, we examined several benzene–ether mixtures as well as ether as solvents. In short, the benzene–ether mixtures gave nonreproducible results.

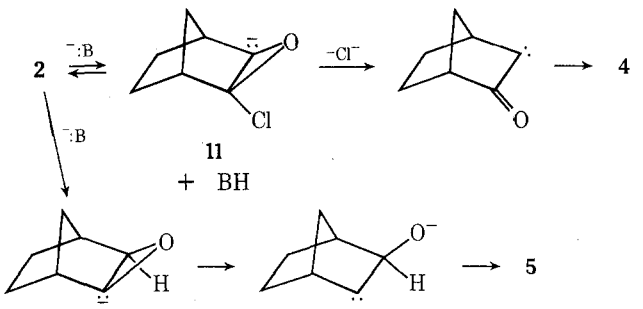
In refluxing either with 1.1 equiv of lithium diethylamide, the product derived from **2** was found to contain 10% **8**. Thus it appeared that thermal rearrangement of **2** → **7** followed by reduction was a competing process under these conditions. The amount of **8** could be lowered to <0.5% if 2 equiv of base was employed. Significantly, the **4**:**5** ratios from these two experiments were nearly the same, 2.85 and 3.00, respectiviely, suggesting that lithium diethylamide did not effect the **4** → **5** reduction in refluxing ether as had been observed in refluxing benzene–ether.

It was then found that reproducible yields, **4**:**5** product ratios, and complete conversion of **2** could be obtained in ether at reduced temperatures. The **4**:**5** product ratio was found to be 2.06 ± 0.05 with conditions ranging from 50% excess lithium diethylamide at −15° with a 30-min reaction time to that involving 300% excess base at 0° with 4.5-hr reaction time. Neither **8** nor **6** were observed in the product. It was inferred from the constant product ratio with large variations in base concentration and reaction time that **4** → **5** reduction by lithium diethylamide was unimportant under these reaction conditions.

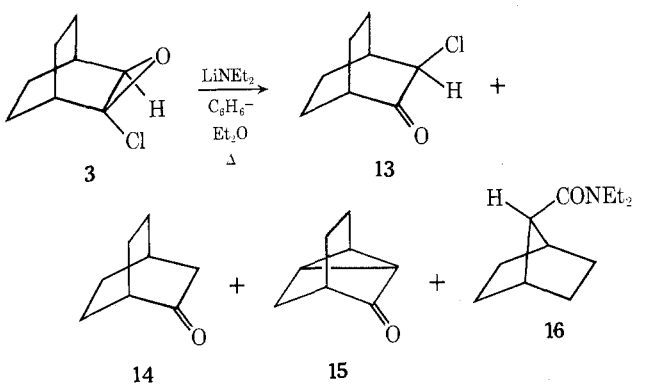
To decide how the products **4** and **5** were formed in this reaction, we prepared **2**-*3-d* containing 77% deuterium at C_3 (based on NMR spectral analysis). Reaction of **2**-*3-d* with 2.5 equiv of lithium diethylamide at −10 to 0° for 15 min as above gave after work-up and short-path distillation (analyses cited above carried out this way) the **4**:**5** ratio of 2.20. More careful solvent removal and redistillation gave the **4**:**5** ratio as 2.40 and a total yield, **4** + **5**, of 85%; a duplicate run gave the **4**:**5** ratio of 2.44 and a yield of 92%. Low-voltage (15 eV) mass spectral analysis showed 0 ± 2% excess deuterium in **4** from both experiments, while in **5** 2 ± 2% and **6** ± 2% excess deuterium was found. Multiple integrations of the NMR spectrum of **5** indicated no excess deuterium at C_3.

These results are in keeping with a mechanism of formation of **4** involving α elimination from C_3 and chloride ion

loss from C_2 of **2** followed by transannular insertion of the α-keto carbene at C_5. However, since simple reduction of **4** → **5** does *not* appear to occur under these conditions, the nature of the processes by which **5** is produced containing no deuterium at C_3 starting from **2-3-*d*** is not at all clear. One possibility is that the amine, ether solvent, or "some other species"[8] may be serving as a proton source in the equilibrium formation of anion **11**.[9] If reduction of the C_2–Cl bond in **2** by lithium diethylamide competes with carbene formation, anion **12** would be formed which could proceed to **5** by the mechanism shown by Crandall.[2f] Bicyclo[2.2.1]hept-2-ene *exo*-oxide might then be produced as an intermediate by protonation of **12**. Equilibrium between this epoxide and **12** would also account for further losses of deuterium at C_3 in **5**.

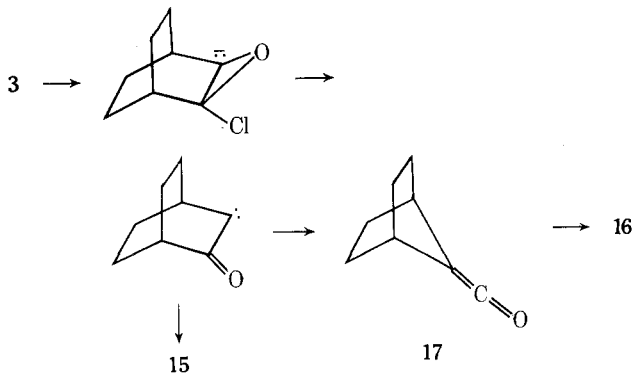


Turning our attention now to the reaction of lithium diethylamide and the [2.2.2] α-chloro epoxide **3** in benzene–ether, we find a somewhat different result. The product was shown to contain 8% unreacted **3**, 8% 3-chlorobicyclo[2.2.2]octan-2-one (**13**), 1% bicyclo[2.2.2]octanone (**14**), 52% tricyclo[3.2.1.$0^{2,7}$]octan-6-one (**15**), and 23% *N,N*-diethylbicyclo[2.2.1]heptane-7-carboxamide (**16**) along with five unidentified minor components.



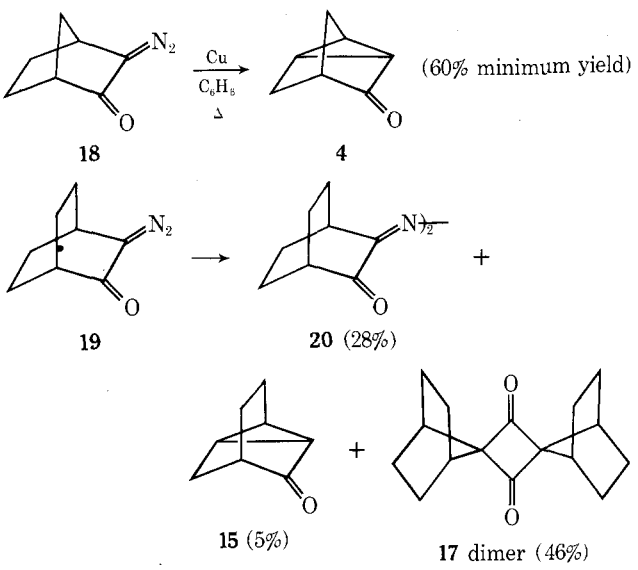
It appears that **13** and **14** are formed via thermal rearrangement of **3** leading to **13** as the primary product. Ketone **14** was shown to be the only product, although in low yield, when **13** was treated under the reaction conditions. The reaction of **3** with lithium diethylamide was not studied in ether, but from our experiences with **2** we suspect that formation of **13** and **14** can be greatly reduced, if not eliminated completely, by carrying out the reaction in ether at reduced temperatures.

Formation of ketone **15** and amide **16** indicates that in this system the α-keto carbene has two competitive reaction channels, one involving transannular C–H insertion (→ **15**) and the other Wolff ring contraction (→ **16**) via ketene **17**. From **3** we were not able to detect the presence of the tricyclic alcohol corresponding to the reduction of **15**, as had been observed from **2**; however, this alcohol may be one of the five minor unidentified components.



It is interesting to compare the above results with those reported by Yates and Crawford[10] for the copper-catalyzed reactions of 3-diazobicyclo[2.2.1]heptan-2-one (**18**) and 3-diazobicyclo[2.2.2]octanone (**19**). Their results carried out in refluxing benzene are given in Scheme II.

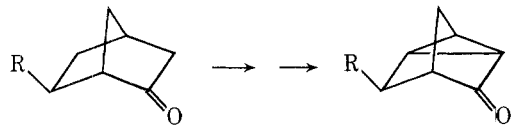
Scheme II



In the [2.2.1] series, the products from both **2** and **18** are quite similar considering that the reaction of lithium diethylamide and **2** appears to have an additional reaction channel leading to alcohol **5**. The predominate or exclusive product is ketone **4**, apparently arising by transannular C–H insertion by the carbene or carbenoid. Wolff ring contraction,[5] which is the major pathway in the photochemical decomposition of **18** in methanol,[11] is not observed in the strong base reaction of **2** or the copper-catalyzed decomposition of **18**.

Before comparing the results from **3** and **19** we must delete those products from processes unique to that particular substrate and reaction type. This then removes the production of **13** and **14** from **2** and azine **20** from **19**. Comparing the insertion:Wolff rearrangement ratios we have 0.11 (**15**:**17** dimer) from **19** and 2.26 (**15**:**16**) from **3**. These ratios show that there is a major difference in the nature of the product forming intermediates and/or the pathways by which the products are produced in these two reactions.

The sequence of reactions involved in the synthesis of α-chloro epoxides from the corresponding ketones combined with pathway c in Scheme I for the strong base reaction promises site specificity for generation of the α-keto carbene and its subsequent reactions, e.g., **21** → **22** conversion. This coupled with large insertion:Wolff rearrangement should make this sequence synthetically useful in certain circumstances. Such site specificity is not possible with



21 22

certain syntheses of α-diazo ketones using monoderivatization of α-diketones.[11]

Experimental Section[12]

Reaction of 2-Chlorobicyclo[2.2.1]heptene *exo*-Oxide (2)[6] with Lithium Diethylamide in Benzene–Ether. A solution of lithium diethylamide was prepared by treating a cold solution (ice bath) of 6.4 g (88 mmol, 9.0 ml) of diethylamine (distilled from barium oxide) in 25 ml of benzene (distilled from sodium) with 31.8 ml of 1.6 *M* (51 mmol) methyllithium in ether. After approximately 20 min, 4.35 g (30 mmol) of **2**[6] in 5 ml of benzene was added. The reaction mixture was heated under reflux for 50 hr, during which time a white precipitate formed and the color changed from colorless to light yellow. After cooling, the reaction mixture was decanted onto ice and extracted with chloroform, and the combined extracts were washed with saturated ammonium chloride and water. After drying ($MgSO_4$) the chloroform was removed by distillation and the residue was distilled through a short-path column (bath temperatures 60°, 0.2 mm), which gave 3.05 g of product. Analysis by GLC (12 ft × 0.25 in. 10% Carbowax 20M column) indicated the presence of seven components (integrated percent): 2% unreacted **2**, 84% **4**, 8% **5**, 2% of an amide tentatively identified as **6**, with the unknown components having integrals of 3, 1, <1, and <1%, respectively. Ketone **4** and alcohol **5**, mp 108–109.5° after sublimation (lit.[13] mp 108–109°), were identified by comparison of their NMR and ir spectra with those in the literature.[13,14]

The amide was GLC collected as a liquid and on the basis of the following spectral data was structurally assigned as *N,N*-diethylcyclohex-3-enecarboxamide (**6**): ir (neat) 6.09 μ (C=O, amide); NMR ($CDCl_3$, internal TMS) τ 4.33 (slightly broadened singlet, 2), 6.64 (q, *J* = 7 Hz, 4), 7.0–7.45 and 7.45–8.5 (m's, total ca. 7), and 8.9 (two overlapping t's, 6). The NMR chemical shifts at τ 4.33 (assigned as vinyl H's), 7.0–7.45 (assigned as C_1H), and 7.45–8.5 (assigned as C_2, C_5, and C_6 H's) are almost exactly those reported for cyclohex-3-enecarbonitrile;[15a] such are similarly reported for cyclohex-3-enecarboxaldehyde,[15b] cyclohex-3-enecarbonyl chloride,[15c] and methyl cyclohex-3-enecarboxylate.[15d] Likewise the coupling patterns observed in the multiplets at τ 7.0–7.45 and 7.45–8.5 are similar to those reported in the nitrile[15a] and acid chloride.[15c] The overlapping CH_3 triplets centered at τ 8.9 indicate that the NC_2H_5 groups are nonequivalent with one CH_3 group being shielded by the ring C=C.

Bicyclo[2.2.1]heptan-2-one-*3,3-d*$_2$. Using the method of Schaefer, Dagani, and Weinberg,[16] 15.4 g of bicyclo[2.2.1]heptan-2-one was deuterated with CF_3CO_2D to give 13.6 g (87%) of the product.

Anal. Calcd for $C_7H_8D_2O$: 20.00 atom % excess deuterium. Found: 19.6 atom % excess of deuterium by mass spectral analysis (17 eV).

2,2-Dichlorobicyclo[2.2.1]heptane-*3,3-d*$_2$. A solution of 19.0 g (170 mmol) of bicyclo[2.2.1]heptane-2-one-*3,3-d*$_2$ in 35 ml of dry methylene chloride was added dropwise over a period of 12 min to a stirred, cooled mixture of 52.0 g (250 mmol) of PCl_5 and 35 ml of PCl_3. The internal temperature was held at 10–12° during the addition. The mixture was stirred while being allowed to warm to 28° over a period of 1 hr. After stirring for an additional 5.5 hr at 28–29°, the mixture was cooled to 10°, poured onto 350 g of ice, and shaken continuously for 18 min. The layers were allowed to separate and the aqueous layer was extracted with three 15-ml portions of methylene chloride. The combined organic layers were washed with 50 ml of 5% sodium bicarbonate solution, dried (Na_2CO_3), redried ($MgSO_4$), and filtered. Most of the solvent was removed by distillation using a 13 mm × 30 cm Vigreux column. The product was distilled on a semimicro platinum spinning band column to give 24.2 g (85%) of the deuterated dichloride, bp 67–86° (17 mm). A forerun of 1.32 g (6%) of 2-chlorobicyclo[2.2.1]heptene-*3,d*, bp 53–59° (32 mm), was also obtained. NMR analysis indicated that it was pure chloroolefin with less than 2% H at C_3.

2-Chlorobicyclo[2.2.1]heptene-*3-d*. In a dry nitrogen atmosphere, a mixture of 23.3 g (139 mmol) of 2,2-dichlorobicyclo[2.2.1]heptane-*3,3-d*$_2$ dissolved in 45 ml of dry THF (distilled from $LiAlH_4$) was added to a solution of 31.0 g (276 mmol) of resublimed potassium *tert*-butoxide in 215 ml of dry THF. The mixture was heated under gentle reflux in a nitrogen atmosphere for 23.75 hr, poured into 250 ml of ice water, and extracted with five 100-ml portions of purified pentane. The combined organic layers were washed with three 100-ml portions of dilute brine, dried ($MgSO_4$), and filtered. The pentane was removed by distillation on a Vigreux column. The crude chloroolefin was distilled on a semimicro platinum spinning band column to yield 13.65 g (76%) of the product.[6] The integrated NMR spectrum showed that the deuterium content at C_3 was 77%.

Attempts to carry out this dehydrochlorination in *tert*-butyl alcohol[6] gave yields up to 84% but with deuterium contents of <50%.

2-Chlorobicyclo[2.2.1]heptene-*3-d exo*-Oxide(2-*3-d*). The published procedure was followed.[6] From 9.05 g of 2-chlorobicyclo[2.2.1]heptene-*3-d* (77% deuterium) and 16.8 g of *m*-chloroperbenzoic acid we obtained 7.69 g (76%) of **2-*3-d***. NMR spectral analysis indicated 77% excess deuterium at C_3.

Reaction of 2-Chlorobicyclo[2.2.1]heptene *exo*-Oxide (2) with Lithium Diethylamide in Ether. A 50-ml two-necked flask equipped with a magnetic stir bar, nitrogen inlet, and outlet was flamed out under a dry nitrogen sweep for 15 min. The outlet was closed with a rubber septum and the flask was cooled to −15°. Ether (freshly distilled from $LiAlH_4$) (10 ml) was injected by dry syringe, followed by 2.30 g (31.5 mmol) of diethylamine (distilled from barium oxide). A 1.57 *N* solution (18.8 ml, 29.5 mmol) of freshly prepared methyllithium in ether was injected by syringe over a period of 10 min with vigorous stirring at a bath temperature of −15 to −5°. The bath was cooled to −15°, and after 5 min a solution of 2.00 g (13.8 mmol) of **2** in 8 ml of dry ether was injected with stirring and cooling over a period of 8 min at a bath temperature of −15 to −10°. The flask was placed in an ice bath and the contents were stirred for 60 min. The mixture was poured onto 25 g of ice water and shaken, and the layers were allowed to separate. The aqueous layer was extracted with two 15-ml portions of ether. The combined ether extracts were washed with two 10-ml portions of water, dried (Na_2SO_4), redried ($MgSO_4$), and filtered. The entire solution was short-path distilled [25–95° (0.1 mm)]. GLC analysis of the distillate on a 6 ft × 0.25 in. 5% FFAP column showed only solvent, diethylamine, **4**, and **5** under conditions where unreacted **2**, **7**, or **8** would have been detected if present in amounts of 1% or greater. The solvent was removed by distillation on a 13 mm × 30 cm Vigreux column, yielding 1.920 g of light brown oil which was analyzed under the same GLC conditions. The mixture contained 69.7% of the bicyclic compounds in a **4:5** ratio of 2.13, corresponding to 0.911 g (63.3%) of **4** and 0.427 g (29.2%) of **5**. The identity of the bicyclic compounds was confirmed by chromatographic separation with methylene chloride on a basic, activity II alumina column, evaporation of the solvent, and comparison of the ir and NMR spectra with those in the literature.[13,14]

Similar treatments of **2** with 300% excess lithium diethylamide at 0° for 4.5 hr, 100% excess lithium diethylamide at 0° for 95 min, and 50% excess lithium diethylamide at −15° for 30 min gave **4:5** ratios of 2.09, 2.01, and 2.11, respectively, in the short-path distillates.

Several treatments of the α-chloro epoxide with less lithium diethylamide gave erratic results with varying amounts of unreacted starting material. Reaction at higher temperatures, especially in mixed benzene–ether solvent, gave up to 8% bicyclo[2.2.1]heptan-2-one (**8**) (identified spectrally and by GLC on a FFAP column) presumably arising by reduction of *exo*-3-chlorobicyclo[2.2.1]heptan-2-one (**10**), which is the major product of thermal rearrangement of **2**.[1,6]

Reaction of 2-Chlorobicyclo[2.2.1]heptene-*3-d exo*-Oxide (2-*3-d*) with Lithium Diethylamide in Ether. In the same manner as described above, a solution of 1.99 g (13.7 mmol) of **2-*3-d*** (76.7% excess deuterium at C_3) in 8 ml of dry ether was injected with stirring and cooling over a period of 10 min at a bath temperature of −15 to −10° into a solution prepared from 10 ml of ether, 2.27 g (31.0 mmol) of diethylamine, and 18.8 ml (29.5 mmol) of a 1.57 *N* solution of methyllithium in ether. The flask was placed in an ice bath and the contents were stirred for 60 min and worked up as described previously. GLC analysis of the short-path distillate under the previously described conditions showed, in addition to solvent and diethylamine, **4** and **5** with a **4:5** ratio of 2.2. Concentration on a Vigreux column and redistillation gave 1.350 g of colorless oil which contained, in addition to 6.6% solvent and diethylamine, **4** and **5** in a ratio of 2.40, corresponding to 0.890 g (60.1% based on C_7H_8O) of **4** and 0.371 g (24.6% based on $C_7H_{10}O$) of **5**. Low-voltage mass spectral analysis of portions of the products pu-

rified by GLC on a 6 ft × 0.25 in. FFAP column indicated 0 ± 2% C_7H_7DO in **4** and 2 ± 2% C_7H_9DO in **5**. The integrated NMR spectrum indicated no excess deuterium at C_3 of **5** within the detection limits of the Varian T-60 NMR spectrometer.

A duplicate experiment using 2.28 g (31.2 mmol) of diethylamine, 18.8 ml (29.5 mmol) of methyllithium solution, and 2.02 g (13.90 mmol) of **2-3-d** gave 0.982 g (65.3%) of **4** and 0.401 g (26.2%) of **5** based on GLC analysis as above. Mass spectral analysis indicated 0 ± 2% C_7H_7DO and 6 ± 2% C_7H_9DO in **4** and **5**, respectively. The integrated NMR spectrum of **5** again showed no excess deuterium at C_3.

Reaction of Ketone 4 with Lithium Diethylamide. This reaction involved 108 mg (1.0 mmol) of **4**, 2.1 g (2.9 mmol) of diethylamine, 1.4 ml of 1.6 *M* (2.24 mmol) methyllithium in ether, and 10 ml of benzene in a dry, nitrogen atmosphere. The reaction mixture was heated under reflux for 4 days, poured into ice–water, extracted with ether, and dried ($MgSO_4$). The ether and benzene were removed in a short-path distillation, leaving 100 mg of product. GLC analysis on a 6 ft × 0.25 in. QF-1 column showed the presence of two components, **4** and **5**, in equal amounts.

Reaction of *exo*-3-Chlorobicyclo[2.2.1]heptan-2-one (7) with Lithium Diethylamide. A solution of 0.66 g (9.0 mmol) diethylamine in 10 ml of benzene (distilled from sodium) was cooled in an ice bath and treated with 3.13 ml of 1.6 *M* (5.0 mmol) methyllithium in ether under a nitrogen atmosphere. The reaction vessel had been previously flamed out under a nitrogen atmosphere. After 10 min, 434 mg (3 mmol) of **7** was injected with the immediate appearance of a blood-red color which turned brown after refluxing a few minutes. After heating under reflux for 24 hr, then cooling to room temperature, saturated, aqueous ammonium chloride was added to the reaction mixture and the organic layer separated. The aqueous phase was extracted with ether. The combined extracts were dried and the ether and benzene were removed for the most part by distillation (semimicro platinum spinning band column). GLC analysis on a 12 ft × 0.25 in. Carbowax 20M column showed this mixture to be composed of 63% **8**, 12% **9**, 11% **7**, and 14% **10**. GLC collection gave 170 mg of **8**, 15 mg of **9**, 11 mg of **7**, and 14 mg of **10**. Each component was identified by comparison of their GLC retention times and NMR spectra with those of known samples.

Reaction of 2-Chlorobicyclo[2.2.2]octene Oxide (3) with Lithium Diethylamide. An ice-cold solution of 3.5 g (48 mmol, 5 ml) of diethylamine in 25 ml of benzene was treated with 15 ml of 1.6 *M* (24 mmol) methyllithium in ether under a nitrogen atmosphere. After 20 min, 2.5 g (15.8 mmol) of **3** dissolved in 20 ml of benzene was added. After heating under reflux for 4 days the reaction mixture was worked up in the usual manner. The ether and benzene were removed in a short-path distillation, leaving 1.86 g of reaction product. GLC analysis on a 6 ft × 0.25 in. QF-1 column showed the presence of ten components. Those components identified by comparison of their GLC retention times and/or spectra with those of authentic samples were unreacted **3** (8%), **13** (8%), **14** (1%), and **15**[14a,17] (52%).

A fifth component isolated as a liquid by GLC collection was identified as the ring contraction product, *N,N*-diethylbicyclo[2.2.1]heptane-7-carboxamide (**16**): ir (neat) 6.1 μ (s, amide C=O); NMR (CCl_4, internal TMS) τ 6.63 (quartet, broadened, NCH_2–, 4) and 7.5–9.2 (m, peaks at τ 7.65, 8.07, 8.45, 8.55, 8.70, 8.81, and 8.9, 17 H); mass spectrum (70 eV) *m/e* (rel intensity) 195 (M^+·, 40), 141 (100), 100 (27), 95 (80), and 58 (36).

Anal. Calcd for $C_{12}H_{21}NO$: mol wt, 195.1623. Found: mol wt, 195.1626 (mass spectrally with a resolution of ca. 30,000).

Reaction of 3-Chlorobicyclo[2.2.2]octan-2-one (13) with Lithium Diethylamide. A cold solution (ice bath) of 0.66 g (9.0 mmol) of diethylamine in 10 ml of benzene was treated with 3.13 ml of 1.6 *M* (5.0 mmol) methyllithium in ether. After a few minutes 474 mg (3.0 mmol) of **13** was added and the mixture was heated to reflux. After 47 hr, GLC analysis indicated the presence of two components in the ratio of 52:48. Retention time comparisons with authentic samples showed that the first eluted component was **14** and the second component was **13**. The reaction was continued for a total of 108 hr. Saturated ammonium chloride was added to the reaction mixture extracted with ether. After drying the ether was distilled. A short-path distillation of the residue gave 187 mg of reaction product as a white solid and left a polymeric residue. Analysis by GLC on a 6 ft × 0.25 in. QF-1 column again showed only the presence of the same two components **13** and **14** but the **13**:**14** ratio had changed to 3. It thus appears that while **13** is converted to **14**, **14** is being destroyed in the reaction. Samples of **13** and **14** were GLC collected and their ir and NMR spectra were found to be identical with those of authentic samples.

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Registry No.—**2**, 16709-75-4; **2-3-d**, 54831-45-7; **3**, 23804-45-7; **4**, 695-05-6; **6**, 3811-07-8; **7**, 10464-71-8; **13**, 23804-48-0; **16**, 54798-00-4; lithium diethylamide, 816-43-3; bicyclo[2.2.1]heptan-2-one-*3,3-d*$_2$, 18153-61-2; 2,2-dichlorobicyclo[2.2.1]heptane-*3,3-d*$_2$, 54798-01-5; 2-chlorobicyclo[2.2.1]heptene-*3-d*, 54798-02-6.

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