alkyl and aryl substituents can be ignored, as a first approximation, although, in those cases where there is a selectivity among reactions predicted by the proposed method, that selectivity may arise in part from a combination of the effects of substituents on polarity, polarizability, and steric bulk. The effect of heteroatomic substituents (other than carbonyl) is not easily rationalized in the framework of the present scheme.[22]

Two problems remain; the first has to do with valence tautomerism in the starting materials. For instance, no way has been found within the present scheme to aid in explaining the difference between cyclooctatetraene reacting with itself ($_\pi 8 + {}_\pi 2$) in monocyclic form,[5] and reacting with most dienophiles ($_\pi 4 + {}_\pi 2$) as the bicyclic valence tautomer.[23]
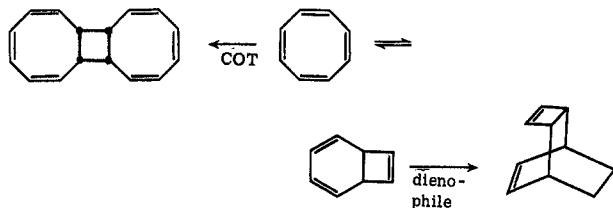
The second problem is concerned with stereochemistry. Particularly in borderline cases, it is difficult to assess how much effect the spatial arrangements of the atoms will have on the course of a cycloaddition reaction. The reactants in Table I are for the most part geometrically constrained in such a way that the distinctions between stereochemically plausible and im-

(22) Note, for instance, the differences between tropone and 2-chlorotropone on reaction with cyclopentadiene [S. Itô, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, 775 (1969)].

(23) G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim, 1965, pp 48–50.

plausible reactions are relatively clear-cut; for instance, anti cycloadditions are unlikely in all these cases. Exceptions to this situation are likely to occur.

Applications of the proposed method to predict the products from several simplified model systems are shown in Table II. Neither the steric likelihood of each

TABLE II

PREDICTIONS FOR MODEL COMPOUNDS[a]

[a] Only all-syn additions of open-chain valence tautomers are considered. No stereochemistry about double bonds is intended by the structural formulas.

reaction nor the possibility of valence tautomerism has been considered in making the predictions in this table.

Carbenoids with Neighboring Heteroatoms. III. Electrophilic Reactions of Two α-Halocyclopropyllithium Compounds[1a,b]

K. GRANT TAYLOR,* W. EDWARD HOBBS,[1c] MELVIN S. CLARK, AND JAMES CHANEY

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208

Solutions of carbenoids 4a and 11a were prepared by the reaction of alkyllithiums with dihalocyclopropanes 1. Carbenoid 4a had limited stability at −80° but could be trapped by carbonation which gave 2 in low yield and by protonation which gave 4b in high yield. Bicyclobutane 5 was the major product of thermal decomposition of 4a. Carbenoid 11a was more stable at −80° as evidenced by reactions with H₂O, D₂O, and benzophenone. Thermal decomposition of 11a at −20° gave diene 14, presumably via dimerization of 1-methoxycyclohepta-1,2-diene (16).

We recently reported on the stereoselective preparation and nucleophilic reactivity of intramolecularly stabilized α-halocyclopropyllithium reagents.[1b] With the aim of preparing stereochemically known α-halolithium reagents which display the entire range of carbenoid reactivity, we have been investigating the structural requirements for the preparation of stabilized carbenoids. In this paper we wish to report on some nucleophilic and two electrophilic reactions (C–H

insertion, allene formation) of the carbenoids derived from 1-methoxy-7,7-dihalobicyclo[4.1.0]heptane (1).

The Carbenoid from 1-Methoxy-7,7-dichlorobicyclo[4.1.0]heptane.—Treatment of the known[2] dichloronorcarane derivative 1a with 1 equiv of ethereal butyllithium for 10 min at −80° followed by carbonation of the reaction mixture afforded a 7% yield of a neutral, crystalline product formulated as 2. The structure of 2 rests on the following data and reasoning. We had previously encountered an α-chloro-γ-lactone, 3, from the carbonation of 7-*exo*-chloro-2-oxabicyclo-

(2) D. G. Lindsay and C. B. Reese, *Tetrahedron*, **21**, 1673 (1965).

1a, X = Cl
b, X = Br

2

3
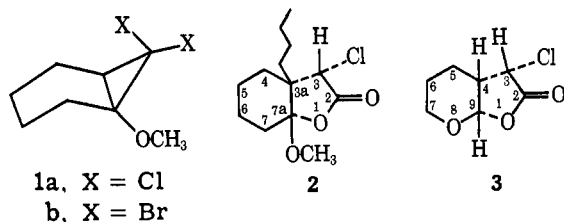
[4.1.0]heptyllithium,[1b] and the 1780-cm⁻¹ C=O band of **2** indicated that it, likewise, was an α-chloro-γ-lactone. The nmr spectrum of **2** showed a singlet (1 H) at δ 4.82 assigned as the C-3 H by analogy with the C-3 H signal of **3**, δ 4.78 (1 H, d, J = 6.5 Hz). Elemental analysis (and nmr) indicated the presence of a butyl group in **2**, and its location was tentatively assigned as C-3a on the basis of the singlet nature of the C-3 H nmr signal, and was confirmed on the basis of subsequent work. A cis ring juncture would be expected for **2**, and the C-3 H was assigned an exo stereochemistry because of the similarity of its chemical shift with the C-3 H of **3**.

The 10-min carbonation reaction described above, which had yielded **2**, also yielded starting **1a**. This, together with the isolation of a butyl-containing product from the foregoing reaction, indicated that simple halogen–metal interchange might not be taking place between **1a** and butyllithium. In fact, when **1a** was treated with 1 equiv of butyllithium (−80°, 30 min) and then quenched with methanol, the nmr of the crude reaction mixture showed methoxyl signals attributable to unreacted **1a** (δ 3.42) and a monochloro derivative, **4b** (δ 3.28), in about a 1:1 ratio. Also,
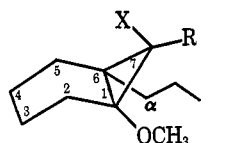
4a, X = Cl; R = Li
b, X = Cl; R = H
c, X = Cl; R = D
d, X = R = H

5

6
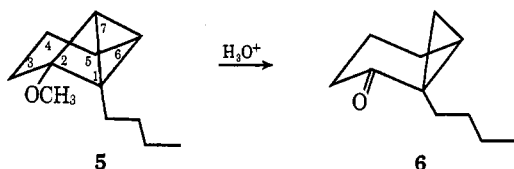
treatment of **1a** with at least 2 equiv of butyllithium was necessary for complete reaction of the starting material. Nmr analysis indicated that **4b** was the major product of the quenched reactions, and analytical vpc also indicated a heat-sensitive, major product (70–90%) plus minor products, usually of shorter retention time. The thermal sensitivity of **4b** prevented its purification by distillation and preparative vpc. However, its structure was firmly established and rests on the following data. A rapid, positive chloride test confirmed the presence of chlorine. In the nmr spectrum, upfield from the δ 3.28 methoxyl signal, was a singlet (1 H relative to the methoxy) at δ 2.93. This was assigned as the C-7 proton, an assignment which finds a chemical shift analogy in the C-7 proton (δ 3.13) of 1-ethoxy-7-*endo*-chlorobicyclo[4.1.0]hep-

tane.[3] By way of confirming this assignment, the δ 2.93 signal of **4b** was absent in the spectrum of **4c**, which was prepared by methanol-*O-d* quench of carbenoid **4a**. Reduction of a crude preparation of **4b** with sodium in liquid ammonia afforded the stable cyclopropane **4d** in over 50% yield. Compound **4d** gave a satisfactory elemental analysis and was distinguished by a high-field AB quartet at δ 0.24 and 0.40 (2 H, J_{gem} = 5.5 Hz, C-7 endo and exo, respectively) in its nmr spectrum.

Carbenoid **4a** was less thermally stable than anticipated.[1b] After the mixture was stirred at −78° for 48 min and carefully quenched, the nmr spectrum indicated that bicyclobutane **5** (methoxyl at δ 3.49, see Table I) comprised about 6% of the mixture, the

TABLE I
CHEMICAL SHIFTS (δ) OF KEY PROTONS
IN SELECTED COMPOUNDS[a]

| Compd	OCH₃	C-7
1a	3.42	
1b	3.43	
4b	3.28	2.93
4c	3.28	
4d[b]	3.31	0.24, 0.40
5	3.49	0.69
11b	3.22	3.3
12a	3.25	0.23 (endo)

[a] In CDCl₃. [b] In CCl₄.

major component of which was still **4b**. After 3.5 hr at −78° and careful quenching, bicyclobutane **5** was seen to comprise 35%, and **4b** 52%, of the reaction mixture as evidenced by integration of the methoxyl region of the nmr spectrum of the mixture. Slight warming brought about rapid α elimination, and, if patience was not exercised in the addition of butyllithium solution (at room temperature) to ethereal **1a** (at −78°), crude reaction mixtures containing about equal amounts of **5** and **4b** (plus other products) resulted after stirring in a Dry Ice–acetone bath for 50 min. Either warming a solution of **4a** to room temperature or stirring at −35° for 65 min yielded the bicyclobutane **5** as the major component (>60% by vpc) of a chlorine-free, multicomponent mixture. An nmr spectrum of a crude preparation of **5** typically showed a dominant methoxyl singlet at δ 3.49 (see Table I) and smaller singlets in the δ 3.18–3.12 region. Also in the spectra of these mixtures was a narrow doublet (J = 1 Hz) at δ 0.69 which, relative to the methoxyl signal at δ 3.49, integrated for 1 H. Further, this doublet was reduced in intensity by 55–60% (relative to the δ 3.49 methoxyl) when **5** was stirred with excess butyllithium for 4 hr at room temperature and then quenched with D₂O.[4] Since the methoxyl signal at δ 3.49 was clearly associated with the major reaction product, it was assigned as the methoxyl signal of **5**, and the doublet at δ 0.69 as (tentatively) the C-7 bridgehead proton of **5**. Distillation and preparative vpc attempts resulted in the partial alteration of **5** with a concomitant increase in the complexity of the reac-

(3) W. E. Parham, F. M. Parham, J. F. Dooley, and M. K. Meilahn, *J. Org. Chem.*, **33**, 3651 (1968).
(4) The $t^{1/2}$ for exchange of the bridgehead proton of tricyclo[4.1.0.0²·⁷]-heptane is 3 hr. See L. E. Closs and G. L. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963).
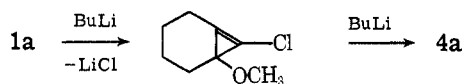
tion mixture. The structure of **5** was proven by mild acid hydrolysis to the ketone **6**, which could be isolated in 46% yield (>90% pure) by distillation from the reaction mixture (yielded 50.4% by vpc determination). Actually, the possible structures **6**, **7**, and **8** all were consistent with the ir spectrum of **6**: 3070 (cyclopropyl CH) and 1695 cm^{-1} (cyclohexanone conjugated with a cyclopropane). Structure **6**, however, was chosen for synthesis first and its preparation is outlined in Scheme I and elaborated in the Experimental

Scheme I
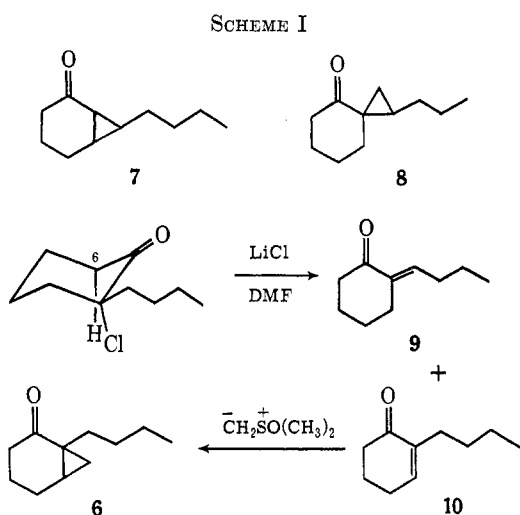
Section. The nmr spectrum of 2-butyl-2-chlorocyclohexanone was interesting in that a triplet of doublets, 1 H, appeared at δ 3.12, somewhat downfield from the main broad multiplet. First-order analysis indicated splittings of $(-)$ 14, 14.5, and 5.5 Hz, consistent with J_{gem}, $J_{\text{ax-ax}}$, and $J_{\text{ax-eq}}$ for an axial proton, most likely the one on C-6. The observed chemical shift for this proton can be explained if the conformation of 2-butyl-2-chlorocyclohexanone is as shown in Scheme I. Calculations by the method of Zurcher[5] predict that this proton should be deshielded by 0.5 ppm relative to the observed δ 2.3 chemical shift of the α protons of 2-butylcyclohexanone.[6] If a van der Waals interaction is included in the above calculation[5,7] ($r_{\text{Cl-H}} = 2.8$ Å) the predicted deshielding is 0.74 ppm (0.50 + 0.24). Since the observed deshielding is about δ 0.8, the above assignment of the δ 3.12 signal as that of the axial H-6 seems reasonable.

Thus, by the proof of structure **6**, the structure of the major reaction product of carbenoid **4a** was firmly established as the C–H insertion product, bicyclobutane **5**.

The formation of carbenoid **4a** from **1a** can be envisioned as occurring by way of the following reaction sequence.


Supporting this proposition are the following facts and analogies. (1) Two equivalents of butyllithium

was required for complete disappearance of **1a**. (2) Methoxyl groups are known to facilitate the abstraction of cis β protons by alkyllithium reagents[8] and this structural feature of **1a** could enable the β-elimination reaction to compete favorably with chlorine–metal interchange. (3) Base-catalyzed dehydrochlorination of 7,7-dichloronorcarane proceeds as shown.[9a] (4) Magid has demonstrated that phenyllithium undergoes cis addition to cyclopropene.[9b]
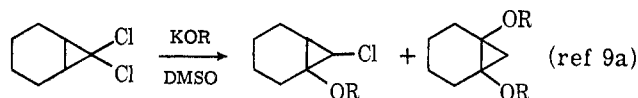
The preceding results provided reasonable evidence that the carbenoid **4a** was present in the reaction mixture. While **4a** was less stable than anticipated, it still appeared to be more stable than 7-*endo*-chlorobicyclo[4.1.0]hept-7-yllithium,[10] and provided us with our first example of an electrophilic reaction which had proceeded *via* an intramolecularly stabilized carbenoid. However, the rather circuitous route of formation of **4a** and the somewhat complex and unstable nature of its thermolysis products discouraged us from examining the chemistry of **4a** further at this time. Finally, there was evidence that insertion into other C–H bonds had occurred[11] and the following only provides a partial explanation for the rather high specificity of insertion demonstrated by the formation of **5**. Moore and coworkers[12] have established a selectivity sequence of tertiary > secondary > primary C–H for the C–H insertion reaction of "cyclopropylidines." In the absence of conformational effects, insertion into a C–H bond adjacent to a cyclopropane ring would permit stabilization of the transition state by the electron-donating cyclopropane ring. This should be a favorable process and probably accounts for the high yields of bicyclobutanes from these reactions.[12] Regarding carbenoid (or "cyclopropylidine") **4a**, the C–H bond on C-5 will be more reactive than the C–H on C-2 because of the electron-withdrawing effect, on the latter hydrogen, by the C-1 methoxyl group. If insertion does indeed take place on the α CH$_2$ of the butyl side chain,[11] no ready explanation for the preference of insertion at C-5 relative to the side chain can be given at this time.

1-Methoxy-7-*endo*-bromobicyclo[4.1.0]hept-7-yllithium (11a).—Dibromocyclopropane **1b**, reported as being thermally unstable above 50°,[2] could be obtained satisfactorily pure by chromatography followed by low-temperature recrystallization. Reaction of **1b** with ethereal methyllithium–lithium bromide at −80°

(5) R. F. Zurcher in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 2, J. W. Emsley, J. Feeny, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N. Y., 1967, Chapter 5.

(6) B. B. Elsner and H. E. Strauss, *J. Chem. Soc.*, 588 (1957).

(7) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, Chapter 8.

(8) R. G. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951).
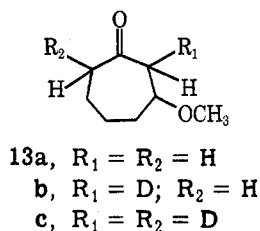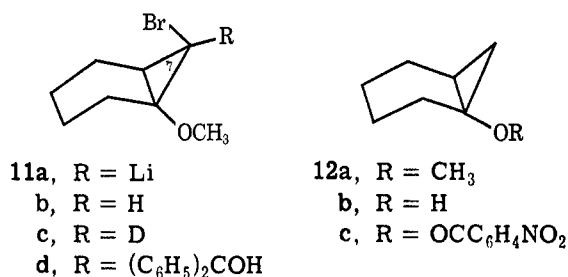
(9) (a) T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *J. Amer. Chem. Soc.*, **87**, 3026 (1965); (b) J. G. Welch and R. M. Magid, *ibid.*, **89**, 5300 (1967).

(10) G. Kobrich and W. Goyert, *Tetrahedron*, **24**, 4327 (1968).

(11) A red (conjugated) DNP, isomeric with that from ketone **6**, was isolated from hydrolysis of reaction mixtures containing bicyclobutane **5**. Also, when **6** was prepared from samples of cyclohexenone **10** which contained some isomer **9**, a minor ketone product was formed which had a vpc retention time identical with that of a minor product obtained by hydrolysis of crude bicyclobutane **5**. The above data points to structure **8** as that of one of the minor products isolated when crude **5** was hydrolyzed and indicates that **4a** also yielded insertion into the α-CH$_2$ of the butyl side chain. One of the methoxyl signals near δ 3.12 in crude **5** may be due to the methoxyl group of this bicyclobutane.

(12) (a) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1877 (1971); (b) W. R. Moore and J. B. Hill, *Tetrahedron Lett.*, 4343 (1970).

afforded carbenoid **11a** which, in contrast to **4a**, gave no evidence of decomposition at that temperature. Water or methanol quenching of **11a** gave **11b** in 70–90% yields. The monobromocyclopropane **11b** was less thermally stable than **1b** and was readily disposed toward solvolysis. As a consequence an analytical sample could not be prepared, but the weight of evidence in the chemistry cited below firmly characterized **11b**, and hence **11a**. The nmr spectrum of **11b** showed the C-7 H doublet ($J = 7$–8 Hz) at δ 3.22, partially obscured by the methoxyl signal. In **11c**, prepared by D_2O quenching of **11a**, the signal attributed to the C-7 H was absent and the base of the methoxyl signal was narrowed. The mass spectrum of crude **11b** gave weak molecular ions at m/e 204 and 206 in the correct intensity ratio for bromine-containing molecules and an intense base peak at m/e 125 due to $M \cdot {}^+$–Br. In **11c**, this base peak was moved to m/e 126.

11a, R = Li
b, R = H
c, R = D
d, R = $(C_6H_5)_2COH$

12a, R = CH_3
b, R = H
c, R = $OCC_6H_4NO_2$

13a, $R_1 = R_2 = H$
**b**, $R_1 = D$; $R_2 = H$
c, $R_1 = R_2 = D$

Reduction of **11b** with lithium in ethylamine gave **12a** as a minor product (11%), which was also prepared in good yield by sodium–liquid ammonia reduction of **1a** and **1b**. The major product (71%) of the Li–ethylamine reduction was, interestingly, cyclopropanol **12b**, characterized by its close nmr similarity to **12a** and by elemental analysis on it and a crystalline *p*-nitrobenzoate derivative **12c**.

Solvolysis of **11b** in acidic methanol–water was facile ($t_{1/2} \cong$ 3–4 hr) at room temperature, yielding 3-methoxycycloheptanone (**13a**).[3] Nmr spectra of the reaction mixture at intermediate times showed a pattern of olefinic protons which indicated the presence of 2-cycloheptenone,[3] and vpc analysis corroborated the ketone's presence. After long reaction times the unsaturated ketone had disappeared and the major product was **13a**, formed in part, presumably, by conjugated addition of methanol to 2-cycloheptenone. In ethanol–water, the 3-ethoxy derivative was formed. The solvolysis of **11b** and **11c** showed some promise as a method for the synthesis of certain deuterium analogs of **13a**. Thus, solvolysis of **11c** under mild conditions yielded **13b**. With **11b** in CH_3OD–D_2O–D^+, mild conditions gave **13c**,[13] while more vigorous acid conditions yielded 2,2,7,7-tetradeuterio-**13a**.

Carbenoid **11a** was further characterized by reaction with benzophenone, which afforded the crystalline, relatively stable carbinol **11d** in moderate yield.

Thermolysis of 11a.—When ether solutions of **11a** were warmed from −80°, precipitation of a white solid (LiBr?) began at about −20°. Subsequent work-up yielded an oil, of which the major component (60–85%) was **14** (vpc). Diene **14** was thermally

14

15a, X = O
b, X = H, H

16
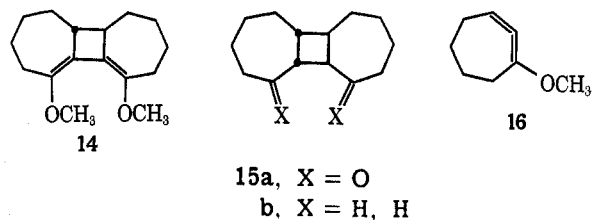
unstable, slowly dimerizing or polymerizing when kept neat at room temperature. Analytical vpc of **14** was possible and a small sample collected at low exit port temperatures showed a $M \cdot {}^+$ at m/e 248 in a mass spectrum recorded soon after collection. The nmr spectrum of crude **14** showed a single methoxyl peak at δ 3.60 (vinyl methoxyl) and a uv spectrum showed λ_{max} 264. Crude **14** reacted with maleic anhydride and *N*-phenylmaleimide with loss of its methoxyl groups, as evidenced by the nmr spectrum of the crude product. The preceding results are consistent with the (*S*)-*cis*-1,3-diene formulation of **14**. Mild acid hydrolysis rapidly converted diene **14** to the crystalline diketone **15a**, mp 78–79°, in about 50% yield. The structure and stereochemistry of **15a**, and hence **14**, rest on the following data. In addition to satisfactory elemental analysis and molecular weight determination, **15a** had a uv spectrum with λ_{max} 285 nm (ϵ 110) consistent with a diketone having isolated chromophores. The nmr spectrum of **15a** showed a two-proton doublet ($J = 9$ Hz) at δ 3.78 assigned as the two tertiary protons adjacent to the C=O groups. A four-proton, broadened triplet was centered at δ 2.4 and assigned as the four other α hydrogens. The chemical shift of the two remaining cyclobutane protons was determined as δ 2.2, because irradiation of the sample at that region caused the collapse of the δ 3.78 doublet to a sharp singlet. Further, diketone **15a** was configurationally stable to basic conditions which were capable of exchanging all six α hydrogens, thereby indicating cis fusion for the ring junctures. The unusually low field location of the nmr signal of the tertiary α hydrogens was more consistent with a cis–anti–cis ring system than with a cis–syn–cis ring system. Drieding models indicated that with cis–anti–cis geometry both tertiary α hydrogens lie in the plane of, and hence should be deshielded by, the nonadjacent carbonyl groups.[14] Finally, Wolff–Kishner reduction of **15a** gave hydrocarbon **15b** as a crystalline solid, mp 63–64°, different from the cis–syn–cis isomer, mp 53°, firmly characterized by Criegee and Reinhardt.[15]

The most logical precursor of diene **14** is 1-methoxy-cyclohepta-1,2-diene (**16**). If this is the case, then the methoxyl group of **16** causes little or no perturbation

---

(13) D content was measured by nmr integration only. Since the C-7 protons of **13a** were not magnetically distinguishable, **13c** probably contained 7,7-dideuterio and 7,7-dihydro species as well.

(14) Eaton and Lin isolated **15a** [mp 79–81°, nmr δ 3.7 (2 H, d, $J = 9$ Hz)] as a secondary product of the thermal dimerization of *trans*-2-cycloheptenone. We thank Professor Eaton for this information. See also P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **87**, 2052 (1965).

(15) R. Criegee and H. G. Reinhardt, *Chem. Ber.*, **101**, 102 (1968).

of the normal stereochemistry of dimerization of cyclic, strained allenes.[16] However, the methoxyl did dramatically alter the reactivity of the carbenoid, since previously investigated "cyclopropylidines" in the bicyclo[4.1.0]heptyl series did not display any evidence of allene formation.[12a,16b]

Experimental Section

General.—All melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Vapor phase chromatography (vpc) analyses were performed on an F & M Scientific Corp. instrument Model 5750 fitted with a flame ionization detector or Model 700 fitted with a thermal conductivity detector. The following columns were used: (A) 15% polytetramethylene ether glycol 3000 on Chromosorb G-NAW; (B) 10% Carbowax 20M on Chromosorb G-NAW; (C) 2% polytetramethylene ether glycol on Chromosorb G-NAW; (D) 10% silicone rubber UCW 98 on Chromosorb G-NAW; (E) 2% silicone rubber UCW 98 on Chromosorb G-NAW; (F) 2% silicone rubber UCW 98 on Diatoport S; (G) 5% UCW 98 on Chromosorb W; (H) 20% SE-52 silicone on Chromosorb G-NAW; (I) 10% Carbowax 20M on Chromosorb W 80–100; (J) 10% UCW 98 on Diatoport S; (K) Carbowax 20M on Chromosorb W-AW + DMCS, 60/80. Nmr spectra were obtained with a Varian Associates A-60A spectrometer with tetramethylsilane as an internal standard and, unless otherwise specified, deuteriochloroform was the solvent. Infrared spectra were determined on a Perkin-Elmer Model 337 grating spectrophotometer, ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer, and mass spectra were obtained with an Hitachi RMU-6. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

All the reactions which involved the use of potassium metal, carbene addition, or the use of alkyllithium reagents were conducted in an atmosphere of dry nitrogen. The methyllithium and butyllithium reagents were titrated when required by the method of Gilman and Haubein, substituting ethylene dibromide for benzyl chloride.[17]

2-Oxo-3-chloro-3a-butyl-7a-methoxyoctahydrobenzofuran (2). —To a cooled ($-80°$) solution of 2.0 g (10.88 mmol) of $1a^2$ in 30 ml of ether was added butyllithium (10.88 mmol) during a period of 10 min. The solution was stirred for an additional 10 min and dry CO_2 was passed into the stirred solution for a period of 1 hr. The reaction was quenched with water, and the basic water layer was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was dried (MgSO$_4$) and concentrated *in vacuo* to yield 0.19 g (6.7%) of an oil which solidified on standing. Recrystallization from ether-petroleum ether (bp 30–60°) yielded a white, crystalline compound: mp 76–77°; ir 1780 (C=O), 1158 (m), and 1130 cm^{-1} (w, -CO); nmr δ 4.82 (s, 1 H), 3.34 (s, 3 H), 1.6 (m, 17 H).

Anal. Calcd for $C_{13}H_{21}ClO_3$: C, 59.88; H, 8.12; O, 18.41. Found: C, 59.70; H, 7.98; O, 18.45.

6-Butyl-*endo*-7-chloro-1-methoxybicyclo[4.1.0]heptane (4b).— To a cooled ($-78°$), stirred solution of 0.735 g (3.80 mmol) of 1a in 12 ml of ether was added 10 ml (10.8 mmol) of a pentane solution of butyllithium during a period of 12 min. The mixture was stirred at $-78°$ for 45 min and quenched by the slow addition of methanol. The solution was washed with water, dried (K$_2$CO$_3$), and concentrated *in vacuo* to 1.10 g of light yellow oil. Vpc (column F) showed one major component, 4b (74%), and two minor components of lower retention time, one of which was demonstrated to be 5 by vpc analysis (column J, 6 ft × 0.125 in., and column I, 3 ft × 0.125 in.). Analysis of the crude mixture showed the following absorptions: nmr δ 3.28 (s, 3 H, -OCH$_3$ of 4b), 2.93 (s, 1 H, C-7 of 4b), and 2.2–0.8 (multiplets, 4b), plus a minor singlet at 3.49 (OCH$_3$ of 5) having 6% of the intensity of the singlet at 3.28; ir 3045 cm^{-1} (C–H stretch, cyclopropane). Attempts at purifying 4b by preparative vpc resulted in the collection of decomposition products.

6-Butyl-*endo*-7-chloro-*exo*-7-deuterio-1-methoxybicyclo[4.1.0]- heptane (4c).—To a cooled ($-78°$), stirred solution of 0.785 g (4.03 mmol) of 1a in 10 ml of ether was added 10 ml (10.8 mmol)

of a pentane solution of butyllithium over a period of 13 min. After an additional 15 min of stirring at this temperature the mixture was quenched by the slow addition of 1 ml of methanol-*O-d*. After working up as for 4b there was obtained 0.925 g of light yellow oil. Vpc using columns F, J (6 ft × 0.125 in.) and I showed one major component comprising 76, 80, and 91% of the total peak area, respectively: nmr δ 3.28 (s, 3 H, OCH$_3$ of 4c) and 2.2–0.8 (m, 17 H).

6-Butyl-1-methoxybicyclo[4.1.0]heptane (4d).—To a cooled ($-78°$), blue solution of 0.20 g (8.7 g-atoms) of sodium in 15 ml of liquid ammonia was added, over 10 min, 0.40 g of crude 4b (from above) in a few milliliters of pentane. After five additional minutes of stirring the cooling bath was removed and the solution was allowed to reflux for 40 min using a Dry Ice–acetone condenser. The blue color was discharged by the slow addition of ammonium chloride. There was then added 0.5 ml of methanol, the ammonia was evaporated, and 10 ml each of ether and water was added. After washing, drying (K$_2$CO$_3$), and concentrating *in vacuo* there was obtained 0.275 g of light yellow oil. Vpc (column K) showed that the major product (4d) comprised 61% of all the components and the estimated yield by vpc was greater than 50%. The major component was collected from column K and recollected from column J for spectra and elemental analysis: nmr (CCl$_4$) δ 3.31 (s, 3 H, OCH$_3$), 2.2–0.8 (multiplets, 17 H), 0.40 (d, 1 H, $J_{gem} = -5.5$ Hz), and 0.24 (d, 1 H, $J_{gem} = -5.5$ Hz); ir (CCl$_4$) 3065 cm^{-1} (C–H stretch, cyclopropane).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.84; H, 12.00.

6-Butyl-*endo*-7-chloro-1-methoxybicyclo[4.1.0]hept-7-yllithium (4a) at $-78°$ for 3.5 Hr.—To a stirred, cooled ($-78°$) solution of 0.173 g (0.89 mmol) of 1a in 5 ml of ether was added 1.75 ml (1.89 mmol) of a pentane solution of butyllithium. The solution was stirred at $-78°$ for 3.5 hr and remained clear. The mixture was quenched by the slow addition of an equimolar mixture of methanol and methanol-*O-d*. After washing, drying (K$_2$CO$_3$), and evaporating solvent *in vacuo* there was obtained 0.176 g of nearly colorless oil. The vpc traces (columns I and J) showed the two major components to be 4b(c) and 5 in amounts of 45 and 22%, respectively.

Nmr analysis showed singlets at δ 3.57–3.15 and multiplets at δ 2.2–0.8 in a ratio of 1:6. The major singlets were at δ 3.49 (OCH$_3$ of 5) and 3.28 (OCH$_3$ of 4b) and they constituted 35 and 52%, respectively, of the total peak area in the methoxyl region. Also there was a singlet at δ 2.93 (C-7 of 4b) integrating for $^1/_6$th of the singlet at δ 3.49. (This fact indicated that carbenoid 4a had not abstracted H from the reaction medium during the reaction time.) Also, there was a doublet at δ 0.69 ($J = 1$ Hz, C-7 of 5) with an intensity equal to $^1/_3$rd of the δ 3.49 singlet.

Stability of 4a at $-35°$.—To a cooled ($-78°$) stirred solution of 0.20 g (1.03 mmol) of 1a in 4 ml of ether was added, over 12 min, 2.1 ml (2.27 mmol) of a pentane solution of butyllithium. The mixture was stirred at $-78°$ for an additional 5 min, warmed over a 20-min period to $-35°$, and maintained at this temperature ($\pm 3°$) for 65 min, by which time a heavy, white precipitate was noted. The reaction mixture was quenched by the addition of methanol. After washing, drying (K$_2$CO$_3$), and evaporating solvent *in vacuo* there was obtained 0.196 g of light yellow oil. Vpc by two columns (I and J, 6 ft × 0.125 in.) showed one major component accounting for 70% of the total peak area, two minor peaks of higher retention time, and no 4b.

Nmr showed absorptions at δ 3.49–3.13 (singlets) and 2.5–0.6 (multiplets) in a ratio of 1:5.6. The singlet at δ 3.49 accounted for greater than 60% of all the singlet integration. There was a doublet at δ 0.69 (C-7 of 5) which integration showed was $^1/_3$rd of the area of the singlet at δ 3.49.

Formation of 4a and 5 by Rapid Addition of Butyllithium to a $-78°$ Solution of 1a.—To a stirred, cooled solution of 0.42 g (2.15 mmol) of 2a in 6 ml of ether was added, over 3 min, 4.5 ml (4.82 mmol) of a pentane solution of butyllithium. Stirring was continued at $-78°$ for 47 min. The reaction mixture was quenched with methanol, washed with water, dried (K$_2$CO$_3$), and evaporated to 0.399 g of light yellow oil. Vpc (columns I and J, 6 ft × 0.125 in.) showed the major component, 4b, to account for 62 and 65%, respectively, of all the peak areas. Also, vpc using these columns indicated that one of the minor components in significant proportion was 5. In the nmr, the major low field singlets were at δ 3.49 (OCH$_3$ of 5), 3.28 (OCH$_3$ of 4b), and 2.93 (C-7 of 4a), in a ratio of 1.8:3:1. The ratio of high-field multiplets to the singlets at low field, exclusive of the C-7 H of 5 (δ 0.69, d) was 6.7:1. The reason for this ratio being slightly

(16) (a) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969); (b) W. R. Moore, and W. R. Moser, *ibid.*, **92**, 5469 (1970).

(17) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

greater than the expected 17:3 value might be explained by the fact that a blank experiment, using only butyllithium and ether, showed absorptions in the high-field region and none in the methoxyl region of the nmr spectrum.

1-Butyl-2-methoxytricyclo[4.1.0.0²,⁷]heptane (5).—To a cooled (−80°) solution of 9.0 g (49.1 mmol) of **1a** in 150 ml of ether was added butyllithium (122.0 mmol) during a period of 5 min. The mixture was stirred at −80° for 1 hr, allowed to warm to room temperature over 25 min, and quenched by the addition of water. The ether layer was washed with two portions of water, dried (MgSO₄), and concentrated *in vacuo*. This yielded 10.22 g of an amber oil. Vpc (column F, 6 ft × 0.125 in.) showed one major component and three minor components with higher retention times. Attempts to purify the major component by distillation and preparative vpc (columns A, B, D, F, H, 6 ft × 0.25 in.) were unsuccessful.

Deuterium Exchange at C-7 of 1-Butyl-2-methoxytricyclo[4.1.0.0²,⁷]heptane (5).—To a cooled (−78°), stirred solution of 0.30 g (1.55 mmol) of **1a** in 8 ml of ether was added, over 12 min, 3.8 ml (4.10 mmol) of a pentane solution of butyllithium. The solution was warmed to 25° over a 1-hr period, by which time a heavy precipitate had formed. To this mixture was added an additional 4.32 mmol of butyllithium, after which the mixture was stirred for 4 hr at room temperature (some darkening) and quenched with deuterium oxide. The usual work-up yielded 0.459 g of yellow oil. An nmr spectrum on this crude mixture clearly showed, in addition to increased absorption in the δ 2.5–0.8 region, an intensity reduction of 57 (±3)% for the doublet at δ 0.69 (C-7 of 5) relative to the singlet at δ 3.49 (OCH₃ of 5).

1-Butylbicyclo[4.1.0]heptan-2-one (6) from 5.—To a stirred ether solution of 10.22 g of the crude product containing **5** was added 4 drops of 4 *N* sulfuric acid. The reaction was followed by vpc (column F, 6 ft × 0.125 in.) by observing the disappearance of one major peak and the appearance of another at a higher retention time. The reaction was essentially complete after 18 hr. The ether solution was washed with sodium bicarbonate solution and water, dried (MgSO₄), and concentrated *in vacuo*. The remaining yellow oil was distilled and the fraction boiling at 80–83° (0.3 mm) was collected. This yielded 3.77 g of **6** (>90% purity) as a yellow oil or 46.5% based on starting compound **1a**. The vpc (column C, 6 ft × 0.125 in.) yield was found, using an internal standard (acetophenone), to be 50.4%: ir 3070 (CH cyclopropane), 1695 cm⁻¹ (C=O).

The red dinitrophenylhydrazone was prepared and recrystallized from ethanol (95%), mp 120–123°.

Anal. Calcd for C₁₇H₂₂N₄O₄: C, 58.94; H, 6.40; N, 16.17. Found: C, 58.85; H, 6.53; N, 16.28.

An isomeric DNP was also obtained as a minor product, mp 187–187.5°, red crystals from 95% ethanol.

Anal. Found: C, 58.95; H, 6.51; N, 16.30.

The semicarbazone was prepared with heating and recrystallized from ethanol–water, mp 189–190.5°.

Anal. Calcd for C₁₂H₂₁N₃O: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.40; H, 9.43; N, 18.76.

2-Chloro-2-butylcyclohexanone.—To a stirred solution of 35.22 g (0.23 mmol) of 2-butylcyclohexanone⁶ in 120 ml of dry carbon tetrachloride was added 33.8 g (0.25 mol) of sulfuryl chloride in 35 ml of carbon tetrachloride during a 1-hr period. The slightly exothermic reaction was moderated by cooling with a water bath at room temperature. After the addition was completed, stirring was continued for 2 hr. The clear, colorless solution was then washed successively with three portions of water, two portions of saturated sodium bicarbonate solution, and one portion of saturated salt solution, and dried (MgSO₄). The solvent was removed by distillation, first at atmospheric pressure and finally at reduced pressure (2.5 mm). The residue was distilled and yielded, after a small forerun, 36.6 g (85%) of a clear, colorless oil: bp 101–103° (2.5 mm); ir 1750 cm⁻¹ (C=O); nmr (CCl₄) δ 3.12 (triplet of doublets, J_{gem} = −14, J_{vic} − 14.5, 5.5 Hz, H-6 axial), 1.6 (m, 16 H).

Anal. Calcd for C₁₀H₁₇ClO: C, 63.64; H, 9.08; O, 8.48. Found: C, 63.86; H, 8.92; O, 8.71.

2-Butyl-2-cyclohexanone (10).[18]—To 60 ml of distilled dimethylformamide was added 36.6 g (0.19 mol) of 2-chloro-2-2-butylcyclohexanone and 6.0 g of anhydrous lithium chloride.

The stirred mixture was maintained, under a nitrogen atmosphere, at 100° (oil bath) for 45 min. The mixture was cooled, poured into 250 ml of ether and 250 ml of 2.5% sulfuric acid, and stirred at room temperature for 4 hr. The layers were separated and the water layer was saturated with sodium chloride, then extracted with two portions of ether. The organic layers were combined, washed with one portion of saturated sodium chloride solution and two portions of saturated sodium bicarbonate solution, dried (MgSO₄), and concentrated *in vacuo*. The residue was distilled through a heated column packed with glass helices and the fraction boiling at 81.5–92° (1.6 mm) was collected. Vpc (column F, 6 ft × 0.125 in.) showed two components in about a 4:1 ratio. This material was redistilled (6.8 mm) using spinning band apparatus. The major component was collected in an overall yield of 51% as estimated from vpc: uv λmax 237 nm (ε 8480), calcd λmax 237; ir 1675 (−C=O) and 1630 cm⁻¹ (C=C); nmr δ 6.67 (br t, *J* = 3–4 Hz, 1 H), 2.2 (m, 8 H), 1.4 (m, 4 H), 0.95 (∼t, *J* ≅ 6 Hz, 3 H).

Anal. Calcd for C₁₀H₁₆O: C, 78.89; H, 10.59; O, 10.51. Found: C, 78.64; H, 10.51; O, 10.24.

The dinitrophenylhydrazone was prepared and recrystallized from ethanol (95%) to yield red-orange crystals, mp 134–135°.

Anal. Calcd for C₁₆H₂₀N₄O₄: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.65; H, 6.27; N, 16.67.

2-Butylidenecyclohexanone (9).—The minor component from the above spinning band distillation was collected: uv λmax 244 nm (ε 8130), calcd λmax 242; ir 1695 (−C=O) and 1625 cm⁻¹ (C=C); nmr δ 6.61 (triplet of triplets, *J* = 7 and 2 Hz, 1 H), 2.6–1.2 (m, 12 H), 0.93 (t, *J* = 6 Hz, 3 H).

The dinitrophenylhydrazone was prepared and recrystallized from ethanol (95%) to yield deep red needles, mp 123.5–124.5°.

Anal. Calcd for C₁₆H₂₀N₄O₄: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.87; H, 6.26; N, 16.68.

1-Butylbicyclo[4.1.0]heptan-2-one (6) from the Reaction of 10.—Sodium hydride, 1.55 g (53.6% mineral oil dispersion), was washed three times with petroleum ether to remove the mineral oil. The remaining petroleum ether was removed under vacuum. The vacuum was released to a dry nitrogen source and 7.5 g (34.0 mmol) of dry powdered trimethylsulfoxonium iodide was added to the dry powdered sodium hydride. The mixture was stirred during the dropwise addition of 25 ml of dimethyl sulfoxide (distilled over calcium hydride). A vigorous evolution of hydrogen ensued, which ceased after 15–20 min to give a milky white reaction mixture. The reaction was submerged in a water bath and 4.7 g (31.0 mmol) of 10 in 5 ml of dimethyl sulfoxide was added. The reaction mixture was stirred at room temperature for 2 hr, then at 50° for 1 hr, poured into 80 ml of cold water, and extracted with ether. The ether extracts were washed with two portions of water, dried (MgSO₄), and concentrated *in vacuo* to leave a pale yellow oil. Distillation yielded 3.32 g (65.4%) of a colorless liquid, bp 97–99° (1.9 mm). The product was checked on three columns (C, E, and G, 6 ft × 0.125 in.) with the ketone **6** obtained from **5**. The retention times were identical in all three cases: ir 3070 (−CH cyclopropane) and 1695 cm⁻¹ (−C=O).

Anal. Calcd for C₁₁H₁₈O: C, 79.46; H, 10.90. Found: C, 79.71; H, 11.01.

The semicarbazone was prepared and recrystallized from ethanol–water, mp 189–190.5°. A mixture melting piont with the previously prepared semicarbazone of 6 was undepressed.

The dinitrophenylhydrazone was prepared and recrystallized from ethanol (95%), mp 121–125°. A mixture melting point with the previously prepared dinitrophenylhydrazone of 6 was undepressed.

Anal. Calcd for C₁₇H₂₂N₄O₄: C, 58.94; H, 6.40. Found: C, 59.23; H, 6.66.

1-Methoxy-7,7-dibromobicyclo[4.1.0]heptane (1b).—To 300 ml of *tert*-butyl alcohol (distilled over sodium) was added 9.8 g (0.25 mol) of potassium. The mixture was heated until dissolution occurred. The excess *tert*-butyl alcohol was removed *in vacuo* with mild heating. The remaining potassium *tert*-butoxide was broken up and 30.0 g (0.25 mol) of 1-methoxycyclohexene in 90 ml of pentane was added. The resulting slurry was cooled to −20° (ice–acetone) and 56.2 g (0.22 mol) of bromoform in 75 ml of pentane was added during a period of 1 hr. The mixture was stirred for an additional 1 hr at −20° and quenched with water. The organic layer was washed with two portions of water, dried (MgSO₄), and concentrated *in vacuo*. The residue was placed *in vacuo* at 0.5 mm for 15 min. The remaining red oil was dissolved in pentane and passed over a column (40.0 g)

---

(18) E. W. Warnhoff, D. G. Martin, and W. S. Johnson, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 162, report the synthesis of 2-methyl-2-cyclohexenone by this chlorination–dehydrochlorination sequence.

of neutral alumina. The first 150 ml of eluent was collected and concentrated *in vacuo* to yield 43.52 g (70.5%) of a yellow oil. This material could be further purified by low-temperature (−80°) crystallization. The yellow oil was dissolved in pentane and cooled to −80°. The supernate was decanted from the crystals. This was repeated twice to yield 23.3 g (33.2%) of a clear, colorless oil. This oil when stored at −20° gave a white, crystalline solid which appeared to be stable indefinitely at this temperature, nmr δ 3.43 (s, 3 H), 1.8 (m, 9 H).

1-Methoxybicyclo[4.1.0]heptane (12a) from 1b.—To a cooled (−80°) solution of 0.5 g (2.17 mmol) of sodium in 75 ml of ammonia was added 2.0 g (10.8 mmol) of 1b in 25 ml of ether during a period of 1 hr. The cooling bath was removed and the blue solution was refluxed, using a Dry Ice–acetone condenser, for 30 min. The blue color was discharged by the careful addition of ammonium chloride followed by the addition of 2 ml of methanol. The ammonia was allowed to evaporate, and an additional 30 ml of ether and 50 ml of water were added. The resulting ether layer was washed with two portions of water, dried (MgSO₄), and concentrated *in vacuo*. The major component was collected from preparative vpc (column D, 6 ft × 0.25 in.): ir 3070 (–CH cyclopropane) and 2825 cm⁻¹ (–OCH₃); nmr δ 3.25 (s, 3 H), 1.67 (m, 10 H), 0.23 (q, J_{gem} = −5.75 and J_{trans} = 4.5 Hz, 1 H).

Anal. Calcd for C₈H₁₄O: C, 76.14; H, 11.18. Found: C, 76.36; H, 11.19.

12a from 1a.—The above procedure was repeated using 1a. The major component was collected. The ir spectrum was identical with the one obtained from the reduction of 1b.

endo-7-Bromo-1-methoxybicyclo[4.1.0]heptane (11b).—To a stirred solution of 2.22 g (0.00783 mol) of 1b in 30 ml of anhydrous ethyl ether cooled to −80° was slowly added 1 equiv of methyllithium–lithium bromide in ether. The mixture was stirred for an additional 30 min at −80° before quenching with water. The solution was brought to room temperature and the organic layer was separated, washed with two portions of water, and dried (K₂CO₃). Concentration of the solution yielded 970 mg of a yellow oil: a test for bromide was positive and rapid; nmr δ 3.3 (d, 1 H at C-7), 3.22 (s, 3 H, –OCH₃), 2.2–1.0 (m, 9 H); mass spectrum *m/e* 204, 206 (M·⁺), 125 (base peak, M·⁺ − Br).

endo-7-Bromo-exo-7-deuterio-1-methoxybicyclo[4.1.0]heptane (11c).—To a stirred solution of 2.04 g (0.0072 mol) of 1b in 30 ml of anhydrous ethyl ether, cooled to −80°, was added 9 ml of CH₃Li–LiBr in ether. The solution was stirred for 15 min, quenched with deuterium oxide, and warmed to room temperature. The organic phase was washed twice with water and then dried (K₂CO₃). Concentration *in vacuo* yielded 1.10 g of yellow oil: a silver nitrate test for bromide was positive and rapid; nmr δ 3.25 (s, 3 H), 1.0–2.7 (m, 10 H); mass spectrum *m/e* 126 (base peak, M·⁺ − Br).

Bicyclo[4.1.0]heptan-1-ol (12b) from 11b.—Five grams (17.5 mmol) of 1b was treated with methyllithium and worked up as above.

To a blue solution of 250 ml of distilled ethylamine and 1.5 g of lithium metal (rinsed in pentane) was added the crude 11b from above in 50 ml of pentane at such a rate to maintain the blue color. The blue solution was refluxed, using a Dry Ice–acetone condenser, for 7 hr. The blue color was discharged with ammonium chloride and the excess lithium metal was removed with tweezers. The ethylamine was distilled and 100 ml of ether was added. The ether layer was washed with two portions of saturated sodium chloride solution, dried (MgSO₄), and concentrated *in vacuo*. Vpc (column C, 6 ft × 0.125 in.) showed one minor and one major component. The minor component was identified as 12a by comparing its retention time on three columns (C and F, 6 ft × 0.125 in., and G, 6 ft × 0.25 in.) with an authentic sample. The yield of 12a was 11.3% as estimated from vpc. Collection of the major component with preparative vpc (column G, 6 ft × 0.25 in.) yielded 1.4 g (71.2%, calculated from starting 1b) of 12b: ir 3300 (–OH) and 3075 cm⁻¹ (–CH cyclopropane); nmr δ 3.06 (s, 1 H), 1.76 (m, 10 H), 0.29 (q, J_{gem} = −5.5 and J_{trans} = 4.8 Hz, 1 H).

Anal. Calcd for C₇H₁₂O: C, 74.95; H, 10.78; O, 14.26. Found: C, 74.81; H, 10.68; O, 14.42.

The *p*-nitrobenzoate was prepared and recrystallized from ethanol (95%), mp 153–153.5°.

Anal. Calcd for C₁₄H₁₅NO₄: C, 64.35; H, 5.78; O, 24.49. Found: C, 64.60; H, 5.70; O, 24.26.

3-Methoxycycloheptanone (13a).—To a solution of 15 ml of methanol, 5 ml of water, and 1 drop of sulfuric acid was added

0.74 g of 11b. After stirring for 24 hr at room temperature, the organic phase was separated by addition of chloroform and washed three times with water. After drying (K₂CO₃), concentration *in vacuo* gave 460 mg of amber oil. Vpc (column F, 6 ft × 0.125 in.) showed only one component, 13a: nmr δ 3.4 (broad m, 1 H at C-3), 3.32 (s, 3 H, –OCH₃), 2.77 (m, 2 H at C-2), 2.65–2.27 (m, 2 H at C-7), 2.08–1.50 (m, 6 H); ir (neat) 1695 cm⁻¹. The nmr data were identical with those reported in the literature.³

3-Methoxy-2-deuteriocycloheptanone (13b).—To 0.103 g (0.000503 mol) of 11c was added 3 ml of 0.161 N standardized methanol–water (3:1)–sulfuric acid solution. After stirring for 29 hr at room temperature, the organic phase was separated by addition of chloroform, washed twice with water, dried (K₂CO₃), and concentrated *in vacuo* to give 60 mg of amber oil. Preparative vpc (column F, 6 ft × 0.25 in.) of the major component gave 13b: nmr δ 3.5 (m, 1 H at C-3), 3.35 (s, 3 H –OCH₃), 2.8 (m, 1 H at C-2), 2.65–2.30 (m, 2 H at C-7), 2.15–1.50 (m, 6 H).

3-Methoxy-2,7-dideuteriocycloheptanone (13c).—To 0.303 g (1.49 mmol) of 11b was added a 5-ml solution of methanol-*O*-*d₁*–deuterium oxide (3:1) sulfuric acid-*d₂* (taken from stock solution of 15 ml of methanol-*O*-*d₁*, 5 ml of deuterium oxide, and 1 drop of sulfuric acid-*d₂*). After stirring for 24 hr at room temperature the usual work-up gave 200 mg of amber oil. Vpc (column F, 6 ft × 0.25 in.) showed one major and one minor component. Preparative vpc of the major component gave 13c: nmr δ 3.5 (m, 1 H at C-3), 3.35 (s, 3 H, –OCH₃), 2.8 (m, 1 H at C-2), 2.65–2.30 (m, 1 H at C-7), 2.0–1.55 (m, 6 H).

Preparative vpc (column F, 6 ft × 0.25 in.) of the minor component gave 2-cycloheptenone.

3-Methoxy-2,2,7,7-tetradeuteriocycloheptanone.—To 0.144 g (0.7 mmol) of 11c was added a 3-ml solution of the methanol-*O*-*d₁*–deuterium oxide (3:1)–sulfuric acid-*d₂* (taken from the stock solution of 15 ml of methanol-*O*-*d₁*–5 ml of deuterium oxide, and 1 drop of sulfuric acid-*d₂*). After stirring for 29 hr the usual work-up gave 85 mg of amber oil. Preparative vpc (column F, 6 ft × 0.25 in.) of the major component gave the title compound: nmr δ 3.5 (m, 1 H at C-3), 3.34 (s, 3 H, –OCH₃), 2.8 (less than 0.1 H), 2.65–2.3 (m, 0.4–0.5 H at C-7), 2.1–1.5 (m, 6 H).

endo-7-Bromo-exo-7-(diphenylmethanol)-1-methoxybicyclo-[4.10]heptane (11d).—To 2.44 g (0.008 mol) of 1b in 25 ml of anhydrous ethyl ether at −80° was added 4.5 ml of methyllithium–lithium bromide. The solution was stirred at −80° for 30 min and then treated with 1.57 g of benzophenone in 5 ml of ether. The reaction mixture was stirred for an additional 15 min and then quenched with 5 ml of water and warmed to room temperature. The organic phase was washed thrice with water and then dried (K₂CO₃). Concentration *in vacuo* yielded, after triturating with pentane, 860 mg of crystals mp 91–96°. Recrystallizing from hexane gave 520 mg of 11d, mp 94–96°, ir (CCl₄) 3500 cm⁻¹.

Anal. Calcd for C₂₁H₂₃BrO₂: C, 65.10; H, 5.95; Br, 20.67. Found: C, 64.91; H, 6.13; Br, 20.78.

From the mother liquors there was recovered 1.4 g of 11b.

3,14-Dimethoxytricyclo[7.5.0.0²,⁸]tetradeca-2,14-diene (14).—To a cooled (−80°) solution of 2.0 g of 1b in 25 ml of anhydrous ether was added 3.48 ml of methyllithium–lithium bromide (10% excess). The solution was stirred for an additional 15 min, and then warmed to room temperature and stirred for 30 min. After quenching with 5 ml of water, the organic layer was washed twice with 30 ml of water and dried (K₂CO₃). Concentration *in vacuo* yielded 0.570 g of amber oil. Vpc (column G) showed one major (85%) and at least one minor peak. A mass spectrum on a sample of the major peak collected from the vpc column gave *m/e* 248 (M·⁺): nmr δ 3.6 (s, 6 H, OCH₃), 2.8–1 (m, 18 H); uv λ_{max}^{EtOH} 264 nm.

Tricyclo[7.5.0.0²,⁸]tetradeca-3,14-dione (15a).—To a solution of 55 ml of methanol, 10 ml of water, and 5 drops of sulfuric acid was added 2.7 g of 14. After stirring for 24 hr at room temperature, the organic phase was separated by addition of chloroform, washed three times with water, dried (K₂CO₃), and concentrated *in vacuo* to give 2.2 g of amber oil. Column chromatography using acid-washed alumina and eluting with ether–pentane gave 1.16 g of crystals, mp 73–77°. Recrystallization from pentane gave white crystals: mp 78–79°; nmr δ 3.78 (d, 2 H, J = 9 Hz), 1.0–2.8 (m, 18 H); mol wt, 218 (Rast); 220 (mass spectrum); uv λ_{max}^{EtOH} 285 nm (ε 110).

Anal. Calcd for C₁₄H₂₀O₂: C, 76.33; H, 9.15. Found: C, 76.61; H, 8.88.

Base Stability of 15a.—A solution of 50 mg of **15a** and 1 equiv of sodium methoxide in 3 ml of anhydrous methanol was stirred at room temperature for 17 hr. The reaction solution was then poured into water, neutralized, and extracted three times with 10-ml portions of chloroform. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to yield a solid. The nmr of the solid was identical with that of **15a** before reaction.

Heating the same sample of **15a** under the above conditions at 55° for 20 hr showed no change in its nmr. Recrystallizing the resulting solid from pentane gave 15 mg, mp 74–76°. Vpc (column F) showed only **15a**.

At room temperature, treatment of **15a** with sodium methoxide in methanol-*O-d* resulted in the exchange of all six H's α to the carbonyl groups as determined by nmr.

Wolff–Kishner Reduction of 15a.—A solution of 103 mg (0.468 mmol) of dione **15a** and 4 ml of 99% hydrazine hydrate in 4 ml of diethylene glycol was refluxed for 2 hr. The excess hydrazine hydrate and water were distilled off and 0.4 g of sodium hydroxide was added. The temperature was then raised to 190° for 24 hr. The solution was cooled, poured into 100 ml of water, and extracted three times with 30-ml portions of pentane. After the organic phase was dried (Na₂SO₄), concentration *in vacuo* gave 80 mg of white, oily solid. Recrystallization from ethanol gave 40 mg of crystal, mp 64–65°, nmr δ 0.9–2.3. Preparative vpc gave an analytical sample, mp 64–65°.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. IV. The Exchange of Vinylic Chloride with Radioactive Lithium Chloride Catalyzed by Palladium(II) Chloride in Acetic Acid[1]
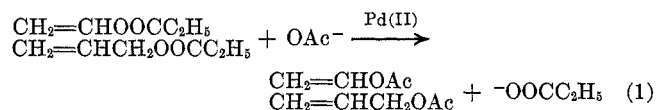
PATRICK M. HENRY[2]

Research Center, Hercules Incorporated, Wilmington, Delaware 19899

Received September 20, 1971

In its simplest form the rate expression for exchange is rate = $k[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ [vinyl chloride]. By analogy with the kinetics of other Pd(II)-catalyzed exchanges a more meaningful form of the rate expression is believed to be rate = k [Li₂Pd₂Cl₆] [vinyl chloride] [LiCl]/[LiCl]. This rate expression is consistent with a rapid pre-equilibrium to give a π complex followed by attack of chloride in the rate-determining step. Stereochemical results with *cis*- and *trans*-1-chloropropene were inconclusive because of a side reaction involving cis–trans isomerization without exchange. The mechanism most consistent with all the facts involves chloropalladation to give a σ-bonded Pd(II) intermediate. Dechloropalladation of this intermediate completes exchange. The fact that 1-chlorocyclopentene exchanges indicates that chloropalladation is not stereospecific. However, independent evidence suggests that cis chloropalladation using chloride from the coordination sphere of Pd(II) is more important than trans chloropalladation from outside the coordination sphere. Methyl substitution on the double bond retards chloride exchange but not as much as substitution retards acetate exchange of vinyl acetates. The difference is believed to be due to greater steric hindrance in trans acetoxypalladation than in cis chloropalladation.

The previous papers of this series have dealt with Pd(II)-catalyzed exchange and isomerization reactions of vinyl and allylic esters. The exchange reaction is shown in eq 1 using vinyl and allyl propionate as examples. This paper will be the first in the series to consider the reactions of another type of unsaturated substrate, namely vinylic chlorides. The reaction studied will be chloride exchange with radioactive chloride.

The previous studies showed that these Pd(II)-catalyzed vinylic[3] and allylic[4] ester exchanges with

$$\begin{array}{c}\text{CH}_2\!=\!\text{CHOOCC}_2\text{H}_5 \\ \text{CH}_2\!=\!\text{CHCH}_2\text{OOCC}_2\text{H}_5\end{array} + \text{OAc}^- \xrightarrow{\text{Pd(II)}}$$

$$\begin{array}{c}\text{CH}_2\!=\!\text{CHOAc} \\ \text{CH}_2\!=\!\text{CHCH}_2\text{OAc}\end{array} + {}^-\text{OOCC}_2\text{H}_5 \quad (1)$$

acetate have the rate expression shown in eq 2 where k' is the rate constant for an acetate independent reaction

$$\text{rate} = \frac{[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{olefin}]}{[\text{LiCl}]}(k' + k''[\text{LiOAc}]) \quad (2)$$

and k'' the rate constant for a reaction first order in acetate.

The first step in both reactions is apparently π-complex formation between the Pd(II) dimer and the olefin portion of the unsaturated ester. This π-complex

$$\text{Li}_2\text{Pd}_2\text{Cl}_6 + {>}\text{C}\!=\!\text{C}{<} \underset{\text{HOAc}}{\overset{}{\rightleftarrows}} \text{LiPd}_2\text{Cl}_5\,({>}\text{C}\!=\!\text{C}{<}) + \text{LiCl} \quad (3)$$

formation accounts for the first-order terms in [Li₂Pd₂Cl₆] and olefin, as well as the [LiCl] inhibition. The stereochemical evidence indicates that the next step in the exchange reactions almost certainly involves attack of solvent acetic acid or acetate ion to give an acetoxypalladation adduct which then undergoes deacyloxypalladation to give exchange. The allylic isomeriza-

(1) (a) Hercules Research Center Contribution No. 1563. (b) Paper III: P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 5200 (1972).

(2) Address correspondence to author at the Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

(3) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

(4) P. M. Henry, *ibid.*, **94**, 1527 (1972).