

trans-piperylene along with cyclopentene as an internal standard were carried out in much the same manner described here except that a closed system arrangement was used in order to avoid any changes in diene concentration due to evaporation caused by the bubbling of gas through the system. The oxygen pressure was maintained by repressuring a reservoir whenever it became necessary. Samples were withdrawn periodically diluted with an excess of a 5% NaOH solution to

remove methanol and thiol. The oil which came to the top was subjected to a bulb-to-bulb vacuum distillation to isolate the mixtures of piperylene and cyclopentene which were then analyzed by v.p.c.

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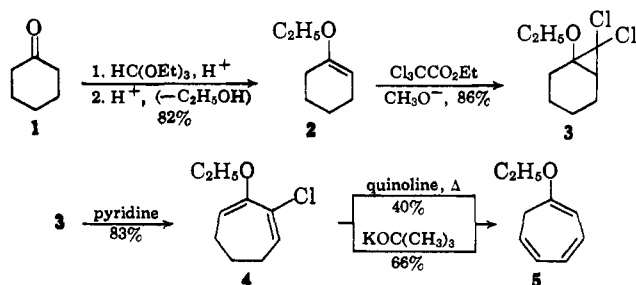
Reactions of Enol Ethers with Carbenes. V. Rearrangements of Dihalocyclopropanes Derived from Six-, Seven-, and Eight-Membered Cyclic Enol Ethers¹

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1,1-Dihalocyclopropanes have been prepared from enol ethers derived from cyclohexanone, cycloheptanone, and cyclooctanone. The product derived from cyclohexanone affords 1-ethoxy-1,3,5-cycloheptatriene (5) in 55% over-all yield by a two-step process involving pyridine with subsequent reaction of the intermediate chlorodiene 4 with potassium *t*-butoxide, or in 37% yield by a one-step process involving quinoline. Cyclopropanes derived from the larger ring enol ethers do not react with hot pyridine, but give products with hot quinoline formed by transannular reactions. Other reactions of products and intermediates are discussed.

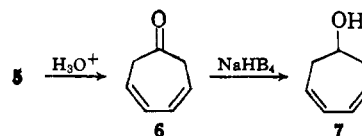
The conversion of cyclohexanone to 1-ethoxycycloheptatriene (5), by a process involving reaction of the intermediate 3 with hot quinoline, was described in a preliminary communication.³ This reaction scheme



was subsequently extended,⁴ as we had suggested, to the synthesis of tropone and β -tropone by employing cyclic enol ethers containing an additional double bond. In this paper we wish to present details of these and

related reactions, and describe certain transformations of the reaction products and intermediates.

The reaction of 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (3) with hot quinoline produced 1-ethoxycycloheptatriene (5) in 38% yield. The triene 5 was characterized by its conversion in low yield to a solid adduct with *N*-phenylmaleimide, by oxidation with selenious acid to a mixture containing tropone (~38% yield),

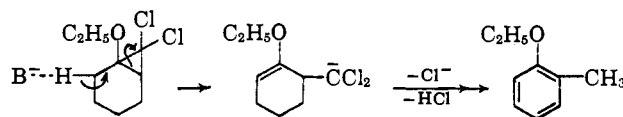


and by hydrolysis to 3,5-cycloheptadienone (6, 91% yield). The 3,5-cycloheptadienone was, in turn, identified by its conversion to the known adduct with *N*-phenylmaleimide, and by its reduction to 3,5-cycloheptadien-1-ol (7) and to cycloheptanone. The positions of the double bonds in 1-ethoxy-1,3,5-cycloheptatriene⁵ (5) were evident from the n.m.r. spectrum; of the four possible position isomers, only 5 would show the observed doublet for the ring methylene protons.

The cyclopropane 3 did not react with alcoholic silver nitrate at room temperature or with hot methanolic sodium methoxide, but gave a complex mixture containing 1-ethoxy-1,3,5-cycloheptatriene (5, 3.3% yield) and *o*-methylphenetole (24% yield) upon reaction with potassium *t*-butoxide in dimethyl sulfoxide.⁶ When 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (3) was treated with boiling pyridine the intermediate 2-

(5) E. Weth and A. S. Dreiding [*ibid.*, 59 (1964)] have shown that thermal equilibration of the methoxycycloheptatrienes leads predominantly to the formation of 1-methoxy-1,3,5-cycloheptatriene.

(6) Formation of *o*-methylphenetole may be rationalized as shown



(1) This work was supported by Grants NSF-G14458 and GP-159 from the National Science Foundation.

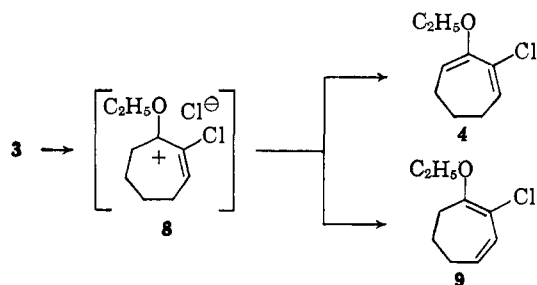
(2) In part from the Ph.D. Thesis of James R. Throckmorton, The University of Minnesota, 1964.

(3) W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Am. Chem. Soc.*, **84**, 1755 (1962).

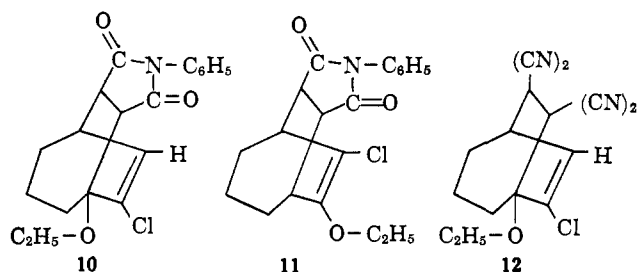
(4) A. J. Birch and J. M. H. Graves, *Proc. Chem. Soc.*, 282 (1962).

ethoxy-3-chloro-1,3-cycloheptadiene (**4**) was formed and was isolated in 83% yield. The chlorodiene **4** did not react with alcoholic silver nitrate or with sodium methoxide in hot methanol; however, with hot quinoline it gave the triene **5** in 40% yield. Reaction of **4** with potassium *t*-butoxide in dimethyl sulfoxide gave the triene **5** in 66% yield. This two-step conversion of **3** to **5** (55% yield) represents a distinct improvement over the one-step process involving quinoline (38% yield).

The ring expansion of **3** to the chlorodiene **4** was expected by analogy⁷ with ring expansions of related systems; however, one might expect that loss of a proton from the proposed intermediate **8** would give



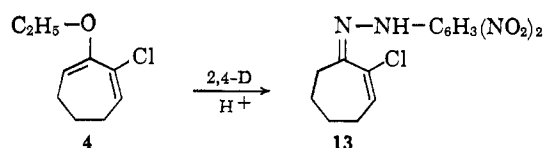
either of two chlorodienes (**4** and/or **9**). Furthermore, it would not be unexpected for either **4** or **9** to be isomerized by hot pyridine hydrochloride which is produced during the reaction. The n.m.r. spectrum of the chlorodiene showed, in addition to ethoxy and ring methylene, only two sharp triplets for the two olefinic hydrogens, an observation consistent for the isomer **4** but not for **9**. In spite of the apparent homogeneity of **4**, the diene gave adducts with *N*-phenylmaleimide (31% yield, pure) and tetracyanoethylene (57% yield, crude) which appear to be **10** and **12**, products logically derived from **9**. The adduct with *N*-phenylmaleimide was recovered unchanged (93% recovery) from a boiling ethanol-water-hydrochloric acid mixture, which would



preclude the enol ether structure **11**. The n.m.r. spectrum of this adduct showed olefinic hydrogen as a clean doublet (τ 3.79 and 3.93). Similarly, the adduct with tetracyanoethylene showed n.m.r. absorption for olefinic hydrogen as a doublet (τ 3.69 and 3.55) which is consistent for **12** but not for other isomers considered including derivatives of cyclobutane.

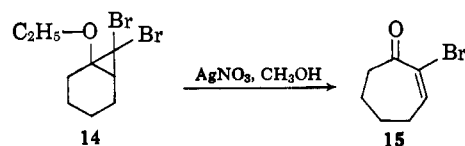
Reaction of the chlorodiene **4** with 2,4-dinitrophenylhydrazine reagent gave an 82% yield of crude product composed primarily of an orange 2,4-dinitrophenylhydrazone. The composition, as well as infrared and n.m.r. spectra, of this hydrazone are consistent (see Experimental) for those of the expected 2,4-dinitrophenylhydrazone of 2-chloro-2-cycloheptenone (**13**); however, the ultraviolet spectrum of the hydrazone

(7) W. E. Parham and E. Schweizer, *Org. Reactions*, **13**, 55 (1963).



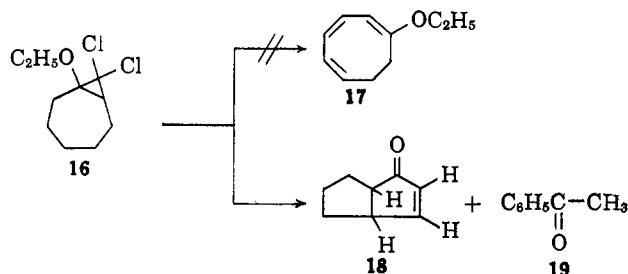
[λ_{\max} 365 μ (ϵ 26,000)] occurred at a lower frequency than expected.⁸

The reaction of 1-ethoxycyclohexene with dibromocarbene was investigated to determine whether the products formed would offer any advantages over those derived with dichlorocarbene for the synthesis of 1-ethoxy-1,3,5-cycloheptatriene (**5**); however, the derived products were found to be less stable and more difficult to process. 1-Ethoxy-7,7-dibromobicyclo[4.1.0]heptane (**14**) was obtained in 72% yield by reaction of the enol ether **2** with bromoform and potassium *t*-butoxide; however, this product could not be distilled without extensive decomposition. The cyclopropane **14** reacted with quinoline to give 1-ethoxy-1,3,5-cycloheptatriene (**5**) in 32% yield, and with alcoholic silver nitrate to give 2-bromo-2-cyclohepten-1-one (**15**, 87% yield) which was characterized by its conversion to the corresponding 2,4-dinitrophenylhydrazone (72% yield). The n.m.r., ultraviolet, and infrared spectra of the 2,4-dinitrophenylhydrazone of



15 were quite similar to those of the corresponding hydrazone **13** derived from **4**.

The facile conversion of cyclohexanone into 1-ethoxy-1,3,5-cycloheptatriene directed our attention to similar reactions involving enol ethers of larger ring size. 1-Ethoxycycloheptene was prepared in 48% yield by acid-catalyzed dealcoholation of the corresponding ketal (75% yield from cycloheptanone). Reaction of this enol ether with ethyl trichloroacetate and sodium methoxide gave the corresponding cyclopropane **16** in 94% yield. The cyclopropane **16**, unlike the analog **3**, did not react with boiling pyridine. Reaction of

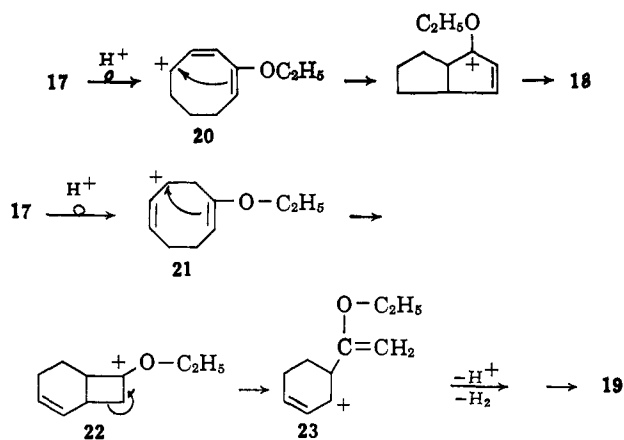


16 with hot quinoline resulted in considerable tar formation; however, a low yield (2.8 g. of product from 20 g. of **16**) of distilled product was obtained which was shown to contain *cis*-bicyclo[3.3.0]oct-3-en-2-one (**18**, 87%) and acetophenone (**19**, 10%). There was no evidence for the presence of the triene **17**. The two products were resolved by gas chromatography. The structure of the unknown ketone **18** was established

(8) The corresponding hydrazone of 2-cyclohepten-1-one shows λ_{\max} 377 μ (ϵ 21,000): E. D. Bergmann and S. Yaroslavsky, *J. Am. Chem. Soc.*, **81**, 2772 (1959).

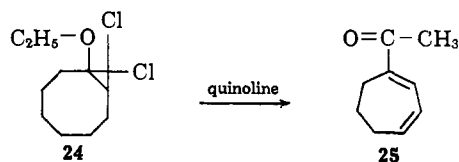
by (1) the n.m.r. spectrum,⁹ (2) the infrared spectrum, which showed carbonyl at 1704 cm.⁻¹ characteristic of an α,β -unsaturated ketone in five-membered rings,¹⁰ (3) the ultraviolet spectrum¹¹ [λ_{\max} 220–221 m μ (ϵ 9800)], (4) conversion to the 2,4-dinitrophenylhydrazone [$\lambda_{\max}^{\text{HCCl}_3}$ 381 m μ (ϵ 25,700)],¹² and (5) by reduction to *cis*-bicyclo[3.3.0]octan-2-one (m.p. of the semicarbazone 177.5–179°, lit. 178.8–180.2°,^{13a} 180°,^{13b} 181°,^{13c} and 197–198°.^{13d})

Transannular reactions in intermediate-sized ring systems are well known and formation of products **18** and **19** is not unique.¹⁴ One possible scheme for the formation of these products is shown briefly in the accompanying equations. Other transannular reactions



can be formulated to account for these products. Meinwald and Emerman¹⁴ have isolated acetophenone and 1-cyclohexenyl methyl ketone from the base degradation of pseudopelletierine methiodide for which they postulate the intermediate formation of 2,7-cyclooctadienone. Similar unsaturated ketones and related reaction paths could account for the formation of **18** and **19** since hot quinoline hydrochloride, a reaction product, is an efficient reagent for the cleavage of ethers or enol ethers.

1-Ethoxycyclooctene (95% pure by v.p.c.) was prepared in 77% yield from the diethyl ketal of cyclooctanone. Reaction of this enol ether with dichlorocarbene under usual conditions gave a very poor yield (10.9%) of the cyclopropane **24**. The yield of **24** was raised to 28% by using a larger excess of the dichlorocarbene precursors. The cyclopropane **24** did not react with hot pyridine, but gave a mixture containing 32.7%



(9) Compare (see Experimental) with photo- γ -tropone methyl ether: O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **82**, 3642 (1960).

(10) W. G. Dauben, G. A. Boswell, and W. H. Templeton, *ibid.*, **83**, 5006 (1961).

(11) 2-Cyclopentenone has λ_{\max} 218 m μ (ϵ 9500): W. M. Shubert and W. A. Sweeney, *ibid.*, **77**, 2297 (1955).

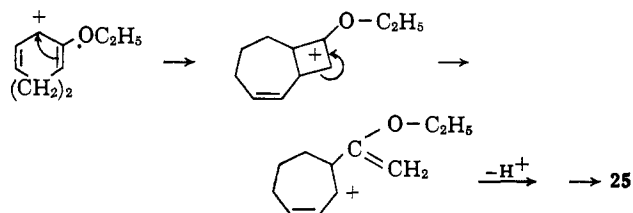
(12) The 2,4-dinitrophenylhydrazone of 5-methoxy[3.2.0]-3-hepten-2-one, 2,4-dinitrophenylhydrazone shows $\lambda_{\max}^{\text{HCCl}_3}$ 377 m μ (ϵ 29,800).⁹

(13) (a) A. Cope and W. Schmitz, *J. Am. Chem. Soc.*, **72**, 3056 (1950); (b) A. Cope and R. Linstead, *ibid.*, **56**, 946 (1934); (c) N. Jones and H. Taylor, *J. Chem. Soc.*, 4017 (1959); (d) R. Granger, P. Naw, and J. Naw, *Trav. Soc. Pharm. Montpellier*, **18**, 142 (1958); *Chem. Abstr.*, **53**, 1699g (1959).

(14) J. Meinwald and S. L. Emerman, *J. Am. Chem. Soc.*, **78**, 5087 (1956).

yield (by v.p.c.) of a ketone believed to be **25**. The ketone was separated from minor products by preparative gas chromatography; however, the purest sample [λ_{\max} 287 m μ (ϵ 12,070)] showed a shoulder in the v.p.c. which was not resolved. The 2,4-dinitrophenylhydrazone of the ketone was readily prepared and showed λ_{\max} 391.5 m μ (ϵ 29,200). Comparison of the spectral data obtained from the ketone and the 2,4-dinitrophenylhydrazone with those of related compounds^{14–16} supports the assigned positions of the double bonds in **25**. Conclusive proof for the carbon structure was obtained by reduction of **25** to 1-acetylcycloheptane. Comparison (melting point and mixture melting point) of the semicarbazone of 1-acetylcycloheptane from **25** with authentic¹⁷ 1-acetylcycloheptane semicarbazone established the structure of **25**.

Transannular reactions analogous to those described for the formation of acetophenone from **16** can be formulated to account for the formation of **25**.



Experimental

Cyclohexanone diethyl ketal (b.p. 65–66° at 7–8 mm., n_D^{25} 1.4330, 453 g., 88% yield; lit.¹⁸ b.p. 75–76° at 13 mm.) was prepared by a procedure essentially identical with that described.¹⁸

1-Ethoxycyclohexene (**2**) was prepared in 93% yield as previously described¹⁹ from cyclohexanone diethyl ketal. The enol ether (325 g., b.p. 59° at 18 mm., n_D^{25} 1.4525; lit.¹⁹ b.p. 47–48° at 10 mm.) showed: infrared spectrum (neat, in cm.⁻¹) =CH (3040), =COC (1212–1180 and 1055), and trisubstituted olefin (785); n.m.r. (10% in CCl₄, τ -units) CH₃ (triplet, 8.90, 8.76, and 8.64), OCH₂ (quartet, 6.61, 6.49, 6.37, and 6.25), —C(OC₂H₅)=CH (triplet, 5.63, 5.57, and 5.51), CH₂ (complex, 8.56–8.28), and CH₂ (complex, near 8.04).

1-Ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (**3**). To a 1-l., three-necked flask, fitted with a dropping funnel (fitted with a gas-inlet tube), a mechanical stirrer, and a calcium chloride drying tube, under 1 atm. of nitrogen, were added commercial sodium methoxide from a previously unopened bottle (13.8 g., 0.26 mole), olefin-free petroleum ether (b.p. 39–45°, 150 ml.), and freshly distilled 1-ethoxycyclohexene (23.65 g., 0.18 mole). To this cold (0–5°), stirred mixture was added ethyl trichloroacetate (46.0 g., 0.24 mole) in one portion.²⁰ The mixture was stirred and maintained at 0–5° for 7 hr., and was then allowed to warm to room temperature overnight. The solid was removed by filtration and washed with petroleum ether (b.p. 30–60°).

(15) E. Pesch and S. L. Friess, *ibid.*, **72**, 5756 (1950).

(16) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

(17) S. Freiss and R. Pinson, Jr., *J. Am. Chem. Soc.*, **73**, 3512 (1951).

(18) A. Johannissian and E. Akunian, *Bull. univ. etat. R.S.S. Armenia*, No. 5, 245 (1931); *Chem. Abstr.*, **25**, 921 (1931).

(19) A. Johannissian and E. Akunian, *Bull. univ. etat. R.S.S. Armenia*, No. 5, 235 (1931); *Chem. Abstr.*, **25**, 992 (1931).

(20) W. E. Parham and E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

The combined organic layers were concentrated on a rotary evaporator and distilled. After a small forerun (3.17 g., b.p. 62–65° at 0.8 mm., $n^{24.5D}$ 1.4798) pure 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (23.0 g., 86%, n^{25D} 1.4885) was collected at 63–65° (0.6–0.8 mm.).

Anal. Calcd. for $C_9H_{14}Cl_2O$: C, 51.69; H, 6.75. Found: C, 51.86; H, 6.99.

The infrared spectrum of **3** showed the absence of olefin absorption, and characteristic bands (in cm^{-1}): 2980, 2880, and 1375 (CH_3), 2942, 2860, and 1475 (CH_2), 1010 (cyclopropane), and 805 (C–Cl). The n.m.r. spectrum (neat) showed (in τ -units): $-OCH_2CH_3$ (triplet, 8.94, 8.82, 8.69), $-OCH_2CH_3$ (quartet, 6.54, 6.42, 6.30, 6.17), CH_2 (complex, 8.57–7.88).

1-Ethoxy-7,7-dibromobicyclo[4.1.0]heptane (14). To a 1-l., three-necked flask, fitted with a dropping funnel with an attached gas-inlet tube, a mechanical stirrer, and a calcium chloride drying tube, under 1 atm. of nitrogen, were added commercial potassium *t*-butoxide (37.0 g., 0.33 mole), olefin-free petroleum ether (b.p. 39–45°, 300 ml.), and freshly distilled 1-ethoxycyclohexene (22.65 g., 0.179 mole). To this cold (0–5°), stirred mixture was added bromoform (68.25 g., 0.27 mole) dropwise over a period of 45 min. The cold (0–5°) mixture was stirred for 8 hr. and then allowed to come to room temperature overnight. The solid was removed from the mixture by filtration, and the solvent was removed on a rotary evaporator. The remaining liquid was concentrated under vacuum at room temperature. This left 48.9 g. (91% yield) of crude 1-ethoxy-7,7-dibromobicyclo[4.1.0]heptane (n^{25D} 1.5275) which was unstable to distillation. The product was chromatographed on alumina (300 g.) and the cyclopropane **14** (38.2 g., 72.2% yield) was eluted with petroleum ether (b.p. 30–60°). A small amount (2.33 g.) of additional material which contained cyclohexanone and vinyl ether(s) was eluted with chloroform; a small amount (1.12 g.) of potassium bromide was eluted with methanol.

A sample of chromatographed cyclopropane (n^{25D} 1.5210) was rechromatographed over alumina, with high recovery, to give fractions with n^{25D} 1.5265–1.5303. Material with n^{25D} 1.5303 was analyzed. The material was unstable to heat.

Anal. Calcd. for $C_9H_{14}Br_2O$: C, 36.27; H, 4.73. Found: C, 37.03; H, 4.94.

The infrared spectrum of **14** (neat) showed (in cm^{-1}): 2940–2860 (CH_3 and CH_2), 1485 (CH_2), 1387 (CH_3), absence of C=C stretch, 1020 (cyclopropane), and 767 (C–Br). The n.m.r. spectrum (neat) showed (in τ -units): $-OCH_2CH_3$ (triplet, 8.93, 8.82, and 8.70), $-OCH_2CH_3$ (quartet, 6.50, 6.39, 6.26, and 6.13), CH_2 and CH (complex, 8.58–7.91), and absence of olefinic hydrogen.

Reaction of 1-Ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (3). *A. With Pyridine.* A mixture of **3** (35.77 g., 0.17 mole) and pyridine (70 ml., 68.74 g., 0.87 mole) was heated at the reflux temperature for 75 min. The solid pyridine hydrochloride was removed from the cooled reaction mixture by filtration and was washed with dry ether. The ether was removed from the combined organic product on a rotary evaporator, and the excess pyridine was removed by vacuum distillation at room temperature. Distillation of the residue gave 24.75 g. (83.3% yield) of 2-ethoxy-3-chloro-1,3-cyclo-

heptadiene (**4**) as a colorless liquid (b.p. 30–63°, at 0.85–1.2 mm. n^{25D} 1.5045–1.5050). Redistillation of this product (under nitrogen) gave 20.5 g. (70.5% yield) of pure product (b.p. 49° at 0.4 mm., n^{25D} 1.5052).

Anal. Calcd. for $C_9H_{13}ClO$: C, 62.61; H, 7.59. Found: C, 62.39; H, 7.87.

The ultraviolet spectrum of 2-ethoxy-3-chloro-1,3-cycloheptadiene (**4**) showed: $\lambda_{max}^{95\% EtOH}$ 243 $m\mu$ (ϵ 3966) and λ_{max} 203 $m\mu$ (ϵ 11,600). The infrared spectrum (neat) showed (in cm^{-1}): =CH (3060, shoulder at 3050), CH_3 (2980, 2880, and 1370), CH_2 (2935, 2860, and 1475), C=C (1615), =C–O–C (1220 and 1050), and trisubstituted olefin (790 and 820). The n.m.r. spectrum showed (in τ -units): $-OCH_2CH_3$ (triplet, 8.82, 8.70, and 8.58), $-OCH_2CH_3$ (quartet, 6.45, 6.32, 6.20, and 6.08), CH_2 (complex, near 8.03), $-CH=C(OC_2H_5)$ (triplet, 4.94, 4.82, and 4.70; $J = 6.7$ c.p.s.), and C(Cl)=CH– (triplet, 3.82, 3.76, and 3.64; $J = 6.7$ c.p.s.).

B. With Quinoline. To a 100-ml., three-necked flask, fitted with a gas-inlet tube, a water condenser, and a glass stopper were added freshly distilled 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (17.85 g., 0.085 mole) and redistilled quinoline (36 ml.). This mixture was heated under nitrogen to 160° (oil bath temperature) at which time the now black mixture underwent a mild, easily controlled, exothermic reaction lasting from 3 to 5 min. Heating was continued at 160–180° for an additional 5 to 10 min. The cooled reaction mixture was filtered, the solid was washed with ether, and the combined organic product was concentrated on a rotary evaporator. Distillation of the residual black oil, under nitrogen, gave 4.37 g. (37.7%, b.p. 50–60° at 5.8 mm., n^{25D} 1.5230) of 1-ethoxy-1,3,5-cycloheptatriene (**5**). Vapor phase chromatography (silicone oil and fluorinated silicone oil columns at 148 and 174°) showed it to be 99% pure. This sample was rechromatographed (preparative v.p.c.) and the product was distilled through a semimicro spiral wire column. Pure 1-ethoxy-1,3,5-cycloheptatriene (n^{25D} 1.5210) was collected at 60° (5.0 mm.).

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.31; H, 9.10.

The ultraviolet spectrum of **5** showed: $\lambda_{max}^{95\% EtOH}$ 290 $m\mu$ (ϵ 3840) and λ_{max} 207 $m\mu$ (ϵ 17,050). The infrared spectrum (neat) showed (in cm^{-1}): =CH (3050 and 3015), CH_3 (2957, 2880, and 1370), CH_2 (2930, 2830, and 1470), C=C (1610 and 1525), =C–O–C (1250 and 1030), trisubstituted olefin (795), and disubstituted olefin (700). The n.m.r. spectrum (10% in CCl_4) showed (in τ -units): $-OC_2CH_3$ (triplet, 8.84, 8.70, and 8.58, $J = 6.7$ c.p.s.), $-OCH_2CH_3$ (quartet, 6.45, 6.34, 6.20, and 6.08; $J = 6.7$ c.p.s.), ring CH_2 (doublet, 7.64 and 7.52; $J = 6.7$ c.p.s.), $-C(OC_2H_5)=CH-$ (doublet, 4.85 and 4.76; $J = 4.5$ c.p.s.), and remaining olefinic hydrogens (complex, 3.68–3.98).

In an additional experiment the reaction mixture was heated for 45 min. at 160° after the exothermic reaction had subsided. The yield of 1-ethoxy-1,3,5-cycloheptatriene was 5%.

C. Attempted Reaction with Silver Nitrate. A saturated solution of 90% ethyl alcohol containing 8.0 g. (0.047 mole) of silver nitrate and 7.8 g. (0.037 mole) of **3** rapidly deposited a trace amount of silver

chloride at room temperature. The mixture was allowed to stand at room temperature and then overnight in the refrigerator, but no more silver chloride precipitated. The mixture was processed and only recovered **3** (6.0 g., b.p. 61–65° at 1.0 mm., 77%) was detected.

D. Attempted Reaction with Sodium Methoxide in Methanol. A mixture containing **3** (5.0 g., 0.024 mole), sodium methoxide (1.5 g., 0.028 mole), and methanol (25 ml.) was heated at the reflux temperature for 24 hr., and was then filtered and distilled. There was obtained 3.7 g. (74%) of recovered 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (b.p. 62–66° at 1.0 mm.).

*E. Reaction with Potassium *t*-Butoxide in Dimethyl Sulfoxide.* To a stirred mixture of commercial potassium *t*-butoxide (24.69 g., 0.22 mole) in purified dimethyl sulfoxide (125 ml.), under nitrogen, was added 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (**3**, 20.9 g., 0.1 mole) at such a rate as to maintain the temperature at 55–70°. To the cool reaction mixture (ice bath) was added 125 ml. of water and 600 ml. of petroleum ether (b.p. 30–60°). The organic and aqueous layers were separated and the organic layer was washed with water. The combined aqueous layers were extracted with three 50-ml. portions of petroleum ether (b.p. 30–60°). The combined organic product and ether washings were dried (MgSO₄) and the solvents were removed on a rotary evaporator. The black liquid residue weighed 13.86 g.

The crude reaction product was chromatographed on alumina. The first fraction, consisting of 57% (6.09 g.) of the total product eluted from the column, was eluted with petroleum ether. Thin layer chromatography of this fraction showed: (1) the absence of starting material, (2) the absence of 2-ethoxy-3-chloro-1,3-cycloheptadiene (**4**, which would be in this fraction if it were present in the reaction mixture), (3) the presence of 1-ethoxy-1,3,5-cycloheptatriene, and (4) the presence of a component later identified as *o*-methylphenetole. Vapor phase chromatography of this material on a silicone grease column showed *o*-methylphenetole (54.5%), 1-ethoxy-1,3,5-cycloheptatriene (7%), and two unidentified components (2.4 and 36%, respectively).

Vacuum distillation of this sample gave fractions which, when treated with 2,4-dinitrophenylhydrazine reagent to remove enol ethers, gave 2.17 g. (16% yield) of pure *o*-methylphenetole (by infrared analysis, v.p.c., and thin layer chromatography).

The second fraction from the chromatogram (0.6 g.) was a mixture of *o*-methylphenetole (total yield 25%) and triene **5**. Other fractions from the chromatogram of the crude reaction mixture consisted of complex unstable mixtures which were not identified.

Reactions of 1-Ethoxy-7,7-dibromobicyclo[4.1.0]heptane (14). *A. With Quinoline.* A distilling flask containing a mixture of **14** (23.8 g., 0.08 mole) and redistilled quinoline (48.0 g., 0.37 mole) was attached to a semimicro, spiral-wire distilling column, and the pressure of the system was adjusted to 30 mm. The flask was immersed in an oil bath and was slowly heated. At 105–115° an exothermic reaction occurred. Distillation of product was begun 35 min. after heating was started and 5 min. after the exothermic reaction had occurred. One fraction (10.25 g., b.p. 33–105° at 19–13 mm., *n*²⁵_D 1.5365) was collected.

This product was fractionally distilled and the products were refractionated. The infrared spectrum of the product, 1-ethoxy-1,3,5-cycloheptatriene (b.p. 61–63° at 6.1 mm., *n*²⁵_D 1.5175, 32% yield) was identical with that obtained from **3**.

B. Reaction with Alcoholic Silver Nitrate. Formation of 2-Bromo-2-cyclohepten-1-one (15). A mixture of silver nitrate (16.98 g., 0.1 mole), 95% methyl alcohol (150 ml.), and 1-ethoxy-7,7-dibromobicyclo[4.1.0]heptane (23.21 g., 0.078 mole) was stirred at room temperature for 15 hr. The methyl alcohol was removed on a rotary evaporator and the residue was dissolved in chloroform, washed with water, and dried (MgSO₄). The residue was distilled to give 11.16 g. (87.3%) of crude 2-bromo-2-cyclohepten-1-one (b.p. 70–77° at 0.35 mm.).

The infrared spectrum of this product (neat) showed (in cm.⁻¹): =CH (3030), C=O (1675), C=C (1590), and trisubstituted olefin (750). The product appeared to be unstable. A sample was characterized by conversion to the 2,4-dinitrophenylhydrazone (72% yield, m.p. 131–133° from ethyl alcohol).

Anal. Calcd. for C₁₃H₁₃BrN₄O₄: C, 42.29; H, 3.55; N, 15.18. Found: C, 42.57; H, 3.70; N, 15.09.

The infrared spectrum of the 2,4-dinitrophenylhydrazone of 2-bromo-2-cyclohepten-1-one (7.5% in CHCl₃) showed (in cm.⁻¹): NH (3320), =CH (3105). The n.m.r. spectrum (8% in CDCl₃) showed (in τ -units): —N=C—CH₂ and =C—CH₂ (multiplet, 7.71–7.11), —N=C—CH₂CH₂CH₂ (complex, near 8.05), —N=C—C(Br)=CH (triplet, 3.30, 3.18, and 3.08; *J* = 5.7 c.p.s.), and aromatic protons (multiplet, 2.03–0.89).

Reaction of 2-Ethoxy-3-chloro-1,3-cycloheptadiene (4).

*A. With Potassium *t*-Butoxide in Dimethyl Sulfoxide. Preparation of 1-Ethoxy-1,3,5-cycloheptatriene (5).* To a stirred mixture of commercial potassium *t*-butoxide (13.46 g., 0.12 mole) and purified dimethyl sulfoxide (75 ml.), under nitrogen, was added dropwise 2-ethoxy-3-chloro-1,3-cycloheptadiene (8.06 g., 0.047 mole). The reaction mixture was cooled during the addition so that the temperature did not rise above 50°. Water (100 ml.) and petroleum ether (b.p. 30–60°, 500 ml.) were then added to the cooled (ice bath) black reaction mixture, and the layers were separated. The organic layer was washed with four 100-ml. portions of water and was then dried (MgSO₄) and distilled. The yield of 1-ethoxy-1,3,5-cycloheptatriene (b.p. 60–62° at 5.5 mm., *n*²⁵_D 1.5210) was 4.2 g. (65.6% yield). The infrared spectrum of the product was identical with that prepared from **3** and **14**.

B. Reaction with Quinoline. A mixture of **4** (12.53 g., 0.73 mole) and redistilled quinoline (32.85 g., 0.25 mole) was heated slowly to 160° and held at 160–190° for 30 min. No exothermic reaction was apparent. The reaction product was processed as described earlier for the reaction of **3** with quinoline. The crude product was fractionated through a spiral-wire column to give 4.0 g. (40.2%) of 1-ethoxy-1,3,5-cycloheptatriene (b.p. 58–59° at 5.3 mm., *n*²⁵_D 1.5225). The material was characterized by its infrared and n.m.r. spectra.

*C. Reaction with *N*-Phenylmaleimide.* A solution of 2-ethoxy-3-chloro-1,3-cycloheptadiene (4.32 g., 0.05 mole) and *N*-phenylmaleimide (4.37 g., 0.025 mole) in benzene (25 ml.) was heated at the reflux temperature

under nitrogen for 10 days. Removal of the benzene followed by addition of ethyl alcohol to the residual oil gave 4.29 g. of a white solid, m.p. 150–185°. The product, after four recrystallizations from ethanol, weighed 2.64 g. (31% yield) and melted at 200–201°.

Anal. Calcd. for $C_{19}H_{20}ClNO_3$: C, 65.98; H, 5.83; N, 4.05. Found: C, 65.74; H, 5.95; N, 4.30.

Infrared spectrum (Nujol) of the Diels–Alder adduct showed (in cm^{-1}): C=O (1775 and 1715), C=C (1640), and trisubstituted olefin (838). The n.m.r. spectrum (10% in $CDCl_3$) showed (in τ -units): aromatic protons (complex, 2.61–2.73), C(Cl)=CH (doublet, 3.79 and 3.93; $J = 7$ c.p.s.), —CH— and —O—CH₂CH₃ (complex, 6.10–6.94), CH₂ (complex, 8.10–8.30), and O—CH₂CH₃ (triplet, 8.58, 8.70, and 8.82; $J = 7$ c.p.s.).

A solution of 70 mg. of adduct thought to be **11**, in 95% ethanol (10 ml.), containing 2 ml. of water and 2 drops of 12 *N* hydrochloric acid, was heated at the reflux temperature for 19 hr. The adduct (m.p. and m.m.p. 200–201°) was recovered in 93% yield.

D. Reaction with Tetracyanoethylene. To a solution of tetracyanoethylene (2.17 g., 0.017 mole) in tetrahydrofuran (20 ml.) was added redistilled 2-ethoxy-3-chloro-1,3-cycloheptadiene (3.45 g., 0.02 mole). The mixture was stirred under nitrogen at room temperature for 1 week. The tetrahydrofuran was removed on a steam bath, the residue was dissolved in chloroform, and petroleum ether (b.p. 30–60°) was added to effect crystallization. A total of 4.50 g. of crude, black solid was obtained. Several recrystallizations of this product from ether gave 2.91 g. (57% yield) of the crude adduct of tetracyanoethylene and 1-ethoxy-2-chloro-1,3-cycloheptadiene (m.p. 118–150°). The major product was isolated by repeated recrystallization of the crude material from ether. The white 1:1 adduct (~50% yield) melted at 151–152°.

Anal. Calcd. for $C_{15}H_{13}ClN_4O$: C, 59.90; H, 4.36; N, 18.65. Found: C, 59.97; H, 4.40; N, 18.39.

The infrared spectrum of the adduct (7.3% in $CDCl_3$) showed (in cm^{-1}): =CH (3075), CH₃ (2988, 2902, and 1350), CH₂ (2958, 2868, and 1470), CN (2255), C=C (1640), COC (1110), and trisubstituted olefin (820). The n.m.r. spectrum (7.3% in $CDCl_3$) showed (in τ -units): OCH₂CH₃ (triplet, 8.85, 8.70, and 8.55; $J = 6.7$ c.p.s.); OCH₂CH₃ (quartet, 6.26, 6.14, 6.02, and 5.90; $J = 6.7$ c.p.s.), CH₂ (complex, near 8.04), CH₂ (complex, near 7.79), *t*-CH (complex, 6.64–6.42), and C(Cl)=CH (doublet, 3.55 and 3.69; $J = 7.9$ c.p.s.).

E. Reaction with 2,4-Dinitrophenylhydrazine. The crude hydrazone (1.33 g., 82% yield, m.p. 126–155°) obtained from 2-ethoxy-3-chloro-1,3-cycloheptadiene (0.86 g., 0.005 mole), 95% alcohol (5 ml.), and acidic 2,4-dinitrophenylhydrazine reagent (0.99 g., 0.005 mole, of the hydrazine) was recrystallized from ethyl alcohol-ethyl acetate. The orange hydrazone (isolated >60% of crude product) melted at 160–164°.

Anal. Calcd. for $C_{13}H_{13}ClN_4O_4$: C, 48.09; H, 4.03; N, 17.26. Found: C, 47.97; H, 3.76; N, 16.94.

The infrared spectrum of **13** (7% in $HCCl_3$) showed (in cm^{-1}): nonbonded NH (3320) and =CH (3107 with shoulder at 3070). The n.m.r. spectrum (6.5% in $DCCl_3$) showed (in τ -units): N=C—CH₂CH₂CH₂ (complex, near 8.17), =CCH₂ and CH₂C=N (multiplet,

7.74–7.35), N=C—C(Cl)=CH (triplet, 3.61, 3.49, and 3.38; $J = 6.44$ c.p.s.), and aromatic protons (multiplet, 2.01–0.93). The ultraviolet spectrum showed: $\lambda_{max}^{95\% EtOH} 365 m\mu$ ($\epsilon 26,000$).

Reaction of 1-Ethoxy-1,3,5-cycloheptatriene (5) with N-Phenylmaleimide. A mixture of **5** (2.72 g., 0.02 mole) and N-phenylmaleimide (3.12 g., 0.018 mole) in benzene (20 ml.) was heated at the reflux temperature, under nitrogen, for 10 days. The benzene was removed and ether was added to the residue. The white solid (A, 0.33 g., m.p. 135–220°) was removed; concentration of the ether solution afforded an oil (B).

Recrystallization of the solid A from ethyl alcohol and ethyl acetate afforded 0.1 g. of tan crystals (m.p. 290–295° dec.) which were not identified.

Anal. Found: C, 70.30; H, 5.99; N, 3.36.

The oil B was chromatographed on alumina; however, no solid products resulted. The combined product was diluted with petroleum ether which precipitated some N-phenylmaleimide, and distilled carefully to remove unchanged **5**. The undistilled residue was sublimed under vacuum which removed additional N-phenylmaleimide (0.57 g., m.p. 85–89°). The residual oil solidified when its solution in alcohol was concentrated and allowed to stand under vacuum. The solid (0.25 g., 4% yield, m.p. 144–150°) was recrystallized from alcohol and melted at 150–152°.

Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.53; H, 6.14; N, 4.17.

3,5-Cycloheptadienone (6). A mixture containing 1-ethoxy-1,3,5-cycloheptatriene (3.87 g., 0.028 mole), water (2 ml.), 12 *N* hydrochloric acid (0.05 ml.), and methanol (7 ml.) was heated for 1 hr. and then poured into water (125 ml.). The water, containing a brown oil, was extracted with ether, and the ether was dried (Na_2SO_4) and distilled. 3,5-Cycloheptadienone (2.8 g., 91.5% yield) was collected at 43.5–45° (4.6 mm.). The ketone decomposed upon standing.

The infrared spectrum of the product was identical with that described for authentic²¹ 3,5-cycloheptadien-1-one. The ultraviolet spectrum showed: $\lambda_{max}^{95\% EtOH} 290 m\mu$ ($\epsilon 567$), a shoulder at 278 (602), and 204.5 (6820); lit.²¹ broad peak at λ 213–214 $m\mu$ ($\epsilon 5495$), with weak absorption at 290 $m\mu$ ($\epsilon 562$) due to an impurity of 2,4-cycloheptadien-1-one. The n.m.r. spectrum (10% in CCl_4) showed (in τ -units): CH₂ (doublet, 6.94 and 7.03, wt. 3.8), very weak absorption by an impurity (6.43, 7.50, and 7.64, wt. 0.6), and =CH (complex, 3.57–4.42, wt. 3.6).

The 2,4-dinitrophenylhydrazone of the ketone (m.p. 140–148°) decomposed²¹ during attempts to purify it by recrystallization from ethanol or by chromatography over alumina with benzene.

3,5-Cycloheptadienone was also characterized by conversion to its addition product with N-phenylmaleimide (m.p. 204–205°, lit.²¹ m.p. 200–206° and 199–202°).

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.87; H, 5.44; N, 4.92.

Conversion of 3,5-Cycloheptadien-1-one to Cycloheptanone Dinitrophenylhydrazone. 3,5-Cycloheptadien-1-one (0.235 g., 0.0021 mole) was reduced with hydrogen and platinum oxide (0.04 g.) in ethyl acetate (10 ml.). After 110 ml. of hydrogen was absorbed

(21) J. Meinwald, S. L. Emerman, N. C. Yong, and G. Buchi, *J. Am. Chem. Soc.*, 77, 4401 (1955).

(theory, 115 ml.), ethyl acetate was removed from the mixture and acidic 2,4-dinitrophenylhydrazine reagent was added. The product was chromatographed over alumina with benzene, and the solid was recrystallized from ethyl alcohol. The product (m.p. 143–144°) did not depress the melting point of authentic cycloheptanone dinitrophenylhydrazone (m.p. 143–145°).²² The infrared spectra of the two samples were identical.

Conversion of 3,5-Cycloheptadien-1-one to the p-Nitrobenzoate of 3,5-Cycloheptadien-1-ol. A sample of the ketone (0.7 g., 0.0062 mole) was reduced in methanol with sodium borohydride as previously described.²¹ The product [b.p. 45–52° at 6 mm., $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 244 m μ (ϵ 6770); lit.²¹ $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 242–245 m μ (ϵ 6918)] was converted to the *p*-nitrobenzoate, m.p. 81–82.5° (lit.²¹ m.p. 81.5–82.5°).

1,1-Diethoxycycloheptane. Cycloheptanone (185 g., 1.25 moles) was converted to 1,1-ethoxycycloheptane (140 g., 75% yield, n_{D}^{25} 1.4458, b.p. 71–74° at 4.3 mm.) by the procedure described for cyclohexanone. A 20-min. reaction time was employed.

Anal. Calcd. for C₁₁H₂₂O₂: C, 70.92; H, 11.90. Found: C, 70.84; H, 12.14.

1-Ethoxycycloheptene. The procedure described for the preparation of 1-ethoxycyclohexene was employed. The product obtained, b.p. 90–184°, was redistilled. From 70 g. (0.372 mole) of ketal there was obtained 25.0 g. (48% yield, n_{D}^{25} 1.4593, b.p. 51–57° at 5.0 mm.) of vinyl ether. This product contained a trace of ketal (by v.p.c.) which was not removed by repeated fractionation.

Anal. Calcd. for C₉H₁₆O: C, 77.09; H, 11.50. Found: C, 76.44; H, 11.56.

1-Ethoxy-8,8-dichlorobicyclo[5.1.0]octane (16). The procedure used was essentially identical with that described for the preparation of **3**. From 1-ethoxycycloheptene (28 g., 0.20 mole), sodium methoxide (14 g., 0.28 mole), and ethyl trichloroacetate (46 g., 0.24 mole) in hexane (250 ml.), there was obtained 42 g. (94.2% yield) of 1-ethoxy-8,8-dichlorobicyclo[5.1.0]octane (b.p. 67–68° at 0.075 mm., n_{D}^{25} 1.4093, m.p. +12°).

Anal. Calcd. for C₁₀H₁₆Cl₂O: C, 53.86; H, 7.23. Found: C, 53.73; H, 7.29.

Reaction of 1-Ethoxy-8,8-dichlorobicyclo[5.1.0]octane with Quinoline. A solution of 1-ethoxy-8,8-dichlorobicyclo[5.1.0]octane (20 g., 0.090 mole) in quinoline (40 ml.) was heated until an exothermic reaction was noted (~130°). The resulting mixture was processed as described for the reaction with the heptane derivative; however, the ether layer was extracted with 4% hydrochloric acid until the aqueous layer was distinctly acid. The ether layer was dried (Na₂SO₄) and distilled. The fraction (2.8 g.) boiling at 48–56° (2.1 mm.), which represented the majority of distillable product, was examined.

The distillate was shown to contain three principal components by vapor phase chromatography in the approximate percentage (by peak weight): A (3–5%), B (10–13%), C (80–87%). The two principal components were subsequently identified as *acetophenone* (B), and *cis-bicyclo[3.3.0]oct-3-en-2-one* (C). The vapor phase chromatograms were run at a temperature of

145–160° on a column (0.25 in. × 10 ft.) packed with Dow silicone high-vacuum grease (20%) absorbed on Johns-Manville Chromosorb "W" (60–80 mesh). Helium at 30 p.s.i. was used as the carrier gas. Peaks B and C were collected on the same column using: 110°, shot 30–40 μ l., collected in an ice bath.

Identification of Acetophenone (19). The infrared spectrum of sample B was essentially identical with that of authentic acetophenone. The 2,4-dinitrophenylhydrazone prepared from this fraction melted at 249–250° (from benzene–ethanol) and was identical with the corresponding derivative prepared from authentic acetophenone.

Identification of cis-Bicyclo[3.3.0]oct-3-en-2-one (18). Microanalyses of fraction C (98% pure by v.p.c., $n_{\text{D}}^{27.5}$ 1.5016) gave erratic results.

Anal. Calcd. for C₈H₁₀O: C, 78.65; H, 8.25. Found: C, 77.26, 79.50; H, 8.60, 8.74.

The ultraviolet spectrum of C showed: $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 220–221 m μ (ϵ 9800). The infrared spectrum showed (in cm⁻¹) principal absorption at 2920 (C–H), 1704 (C=O), and 1585 cm⁻¹ (C=C). The n.m.r. spectrum showed (in τ -units): a quartet (2.48, 2.53, 2.58, and 2.63; $J_{3,4} = 6.0$ and $J_{4,5} = 2.81$ c.p.s.; wt. 1), a split doublet (3.92 and 4.02; $J_{3,4} = 6.0$ and $J_{3,1} = 2.1$ c.p.s.; wt. 1), a multiplet (6.71, wt. 1), a multiplet (7.47, wt. 1), and a multiplet (CH₂) (8.35 and 8.45, wt. 6).

The 2,4-dinitrophenylhydrazone of the ketone [$\lambda_{\text{max}}^{\text{HCCl}_3}$ 381 m μ (ϵ 25,700)] melted at 192–194° (from benzene–ethanol).

Anal. Calcd. for C₁₄H₁₄N₄O₄: C, 55.62; H, 4.67; N, 18.54. Found: C, 55.48; H, 4.80; N, 18.22.

Hydrogenation of cis-Bicyclo[3.3.0]octan-3-en-2-one. The reduction of the ketone (0.1919 g.) was carried out in ethyl acetate (10 ml.) using 10% Pd–C (0.0229 g.) as catalyst. The catalyst and solvent were removed and the residue was converted to the corresponding semicarbazone (m.p. 177.5–179° from water–ethanol, lit. for *cis*-bicyclo[3.3.0]octan-2-one: m.p. 178.8–180°,^{13a} 180°,^{13b} 181°,^{13c} and 197–198°^{13d}).

Anal. Calcd. for C₉H₁₅N₃O: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.39; H, 8.43; N, 22.99.

1,1-Diethoxycyclooctane. The procedure used was essentially identical with that described for the preparation of 1,1-diethoxycyclohexane. From 82.5 g. (0.655 mole) of cyclooctanone there was obtained 42.6 g. (32.5% yield) of 1,1-diethoxycyclooctane (b.p. 55–66° at 1 mm., $n_{\text{D}}^{25.5}$ 1.4539).

Anal. Calcd. for C₁₂H₂₄O₂: C, 71.95; H, 12.08. Found: C, 71.69; H, 12.05.

1-Ethoxycyclooctene. A mixture of 1,1-diethoxycyclooctane (42.6 g., 0.213 mole) and *p*-toluenesulfonic acid (~0.5 g.) was heated at a pot temperature of about 135° for 3.5 hr. Some ethanol distilled during this period. The residue was distilled (b.p. 120–196°), and the distillate was redistilled. The olefin (n_{D}^{31} 1.4652, 25.5 g., 77% yield, 95% pure by v.p.c.) was collected at b.p. 54–58° (3.0 mm.). The small amount of impurity, identified as 1,1-diethoxycyclooctanone by thin layer chromatography, was not removed by repeated distillation or by vapor phase chromatography.

Anal. Calcd. for C₁₀H₁₈O: C, 77.86; H, 11.76. Found: C, 77.16; H, 11.85.

(22) Reported m.p. 148°: O. L. Brady, *J. Chem. Soc.*, 756 (1931).

1-Ethoxy-9,9-Dichlorobicyclo[6.1.0]nonane (24). The reaction of 1-ethoxycyclooctene (25.5 g., 0.166 mole) with ethyl trichloroacetate (38.2 g., 0.195 mole) and sodium methoxide (13.5 g., 0.25 mole) in hexane (250 ml.), under nitrogen was carried out as previously described for the preparation of 3. There was obtained 10 g. of recovered vinyl ether and 4.3 g. (10.9% of yield) impure 1-ethoxy-9,9-dichlorobicyclo[6.1.0]nonane (b.p. 74–76° at 0.075 mm.).

Anal. Calcd. for C₁₁H₁₈Cl₂O: C, 55.68; H, 7.63. Found: C, 56.82; H, 8.05.

The yield of cyclopropane was raised to 28% by employing twice the described quantity of ethyl trichloroacetate and sodium methoxide. The material was refractionated but had the same boiling point and refractive index and essentially the same composition (Found: C, 56.92; H, 8.05). No further purification was attempted.

Reaction of 1-Ethoxy-9,9-dichloro[6.1.0]nonane with Quinoline. A solution of 24 (10.2 g., 0.043 mole) in quinoline (pure, 30 ml.) was heated at the reflux temperature for 25 min.; no strongly exothermic reaction was noted. The mixture was cooled and extracted with a mixture of water and ether. The ether layer was washed with 4% hydrochloric acid until the aqueous wash was distinctly acidic. The ether layer was dried (Na₂CO₃) and distilled. Two principal fractions were collected: (A) b.p. 45–65° at 1 mm., 2.3 g., and (B) 65–67° at 1.0 mm., 0.8 g.

The two fractions were analyzed by vapor phase chromatography using a temperature of 160° on a column (0.25 in. × 10 ft.) packed with Dow Silicon high-vacuum grease (20%) absorbed on Johns-Manville Chromosorb "W" (60–80 mesh). Helium at 45 p.s.i. was used as the carrier gas. The principal component of both fraction A (61.7%) and fraction B (61.3%) was subsequently identified as 1-acetyl-1,3-cycloheptadiene (25) (total 1.91 g., 32.7% yield). The other major component of A was cyclooctanone (by infrared and by m.m.p. 32–34°).

Identification of 1-Acetyl-1,3-cycloheptadiene (25). The mixture was purified by preparative gas chroma-

tography on the column described in the preceding section. Minor products, including cyclooctanone, were easily resolved; however, the purest sample of ketone [$\lambda_{\text{max}}^{95\% \text{ EtOH}} 287 \text{ m}\mu$ (ϵ 12,070)] showed a shoulder on the v.p.c. curve which was not resolved. The amount of this impurity could not be determined; however, it was a minor one representing approximately 10–15% of the sample.

The n.m.r. spectrum (in CCl₄, τ -units) showed: 3.18 and 3.30 (doublet $J = 6.3$ c.p.s.; wt. ~1; 2H), 3.72–4.29 (multiplet; wt. ~2; 3 and 4H), 7.92 (singlet, wt. ~3; CH₃—C(=O)—), multiplet centered at 7.57 (wt. ~4, 5 and 7 —CH₂—), multiplet centered at 8.24 (wt. ~2; 6 —CH₂—).

The 2,4-dinitrophenylhydrazone of the ketone [$\lambda_{\text{max}}^{\text{CHCl}_3} 391.5 \text{ m}\mu$ (ϵ 29,200)] melted at 188.5–189.5° (from ethanol–benzene).

Anal. Calcd. for C₁₅H₁₆N₄O₄: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.67; H, 5.22; N, 17.67.

1-Acetylcycloheptane. A sample of the ketone 28 (103 mg.) was reduced in ethyl acetate (10 ml.) using 10% Pd–C (8.6 mg.) as catalyst. The catalyst and solvent were removed and the residue was converted to the semicarbazone (m.p. 175–176.5°, from ethanol–water).

Authentic 1-acetylcycloheptane was prepared¹⁷ as previously described. The semicarbazone prepared from the authentic ketone was identical (m.p. and m.m.p. 175–176°) with that prepared from 25.

Tropone. Reaction of 1-Ethoxy-1,3,5-cycloheptatriene with Selenious Acid. A mixture of 5 (0.50 g., 0.0037 mole) and selenious acid (0.50 g., 0.0039 mole) in absolute ethyl alcohol (15 ml.) was heated at the reflux temperature for 21 hr. The solution was filtered and then methanol was removed to leave 0.47 g., $n_D^{25} 1.5605$ of crude tropone (reported²³ $n_D^{25} 1.6070$). The ultraviolet spectrum of the residue showed the characteristic spectrum of tropone.²⁴ The yield of tropone was ~38% based on absorbance at 228, 231.5, 224, and 312.5 m μ .

(23) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, 73, 877 (1951).

(24) H. J. Dauben, H. J. Ringold, *ibid.*, 73, 876 (1951).

Organic Fluoronitrogens. II.

The Reductive Defluorination Reaction¹

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The reductive defluorination of perfluoramines with dicyclopentadienyliron or dicumenechromium is described. Difluoramino compounds are converted either to the perfluorimine or perfluoronitrile by the proper selection of organometallic reducing agent. High conversions to

perfluoroazomethines can also be realized by reaction of perfluoroacyclic or -cyclic secondary fluororamines with dicyclopentadienyliron.

Introduction

The increased interest in the fluorocarbons in the last decade has led to the discovery of several new and im-

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