with petroleum ether (bp 60–68°) gave 2.01 g of oil which was shown by glpc analysis (DC-710, 225°) to be >95% **3b** (100% recovery). Elution of the column with diethyl ether gave an oil (0.89 g, mp 30–37°) which crystallized to give 2-chloro-2-cyclotridecen-1-ol (**5**) as a colorless solid (mp 45–46°, 0.86 g, 93% yield based on *cis*-**3a**) upon recrystallization from pentane–ether.

Anal. Calcd for $C_{13}H_{23}ClO$: C, 67.66; H, 10.04; Cl, 15.36. Found: C, 67.95; H, 10.24; Cl, 15.19.

The infrared spectrum (Nujol mull) of **5** showed ν_{OH} (3300 cm^{-1}), $\nu_{C=C}$ (1658 cm^{-1}), and ν_{C-Cl} (845 cm^{-1}). The nmr spectrum (15%, CCl_4) showed C*H*=CCl (triplet, τ 4.19, 4.21, and 4.33; *J* = 7 cps, wt 1), C*H*OH (triplet, τ 5.68, 5.79, and 5.90; *J* = 7 cps, wt 1), allylic *H* (multiplet, τ 7.6–8.0, wt 2), CO*H* (singlet, τ 8.08, wt 1), CH_2 (complex singlet centered at τ 8.73, wt 18).

Oxidation of 2-Chloro-2-cyclotridecen-1-ol to 2-Chloro-2-cyclotridecen-1-one.—In a 25-ml flask filtered with a magnetic stirrer was placed a solution of **5** (0.69 g, 0.003 mole) in acetone (20 ml) and the solution was cooled to 0–5°. A solution of sodium dichromate (0.298 g, 0.001 mole), water (10 ml), and concentrated sulfuric acid (0.39 g, 0.004 mole) was added dropwise with stirring. The mixture was stirred for an additional 4 hr at ice-water temperature and was then poured into water (100 ml). The resulting mixture was extracted with three 50-ml portions of ether, and the combined ether extract was washed with saturated sodium bicarbonate (10 ml), water (25 ml), and was then dried (Na_2SO_4). The solution was filtered and concentrated to give 0.40 g of crude 2-chloro-2-cyclotridecen-1-one. The ketone was characterized by conversion to the 2,4-dinitrophenylhydrazone **7** [mp and mmp 131–132°, $\lambda_{max}^{95\%\ alcohol}$ 371 mμ (ϵ 24,000), lit.[13] $\lambda_{max}^{95\%\ alcohol}$ 372 mμ (ϵ 24,070)].

Reaction of 2-Chloro-2-cyclotridecen-1-ol with Sodium and Liquid Ammonia.—Liquid ammonia (25 ml) was added to a 100-ml flask fitted with a magnetic stirrer, Dry Ice–acetone condenser, dropping funnel, and gas inlet tube. Sodium (0.23 g, 0.01 g-atom) was added in small pieces. Upon solution of the sodium, a pentane solution of 2-chloro-2-cyclotridecen-1-ol (0.4 g, 0.0017 mole, 10 ml) was added dropwise. The mixture was stirred for 1 hr, and ammonium chloride (~10 g) and then water (50 ml) was added slowly. The mixture was extracted with ether (100 ml) and the ether extract was washed with water, aqueous sodium bicarbonate, and with water. The dried (Na_2SO_4) extract was filtered and concentrated. The yellow oil that was obtained (0.25 g) solidified on cooling and was recrystallized from pentane. The yield of *trans*-2-cyclotridecen-1-ol (**6**) was 0.2 g (mp 38–39°, 60% yield).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.80; H, 12.23.

The infrared spectrum (mull) of **6** showed ν_{OH} (3480 cm^{-1}), ν_{-CC} (1663 cm^{-1}), and ν_{CH-CH} (*trans*) (980 cm^{-1}). The nmr spectrum (15%, $DCCl_3$) showed C*H*=C*H* (multiplet, τ 4.42–4.26, wt 2), allylic *H* (multiplet, τ 7.2–8.18, wt 3), O*H* (singlet, τ 8.38, wt 1), CH_2, τ 8.72, wt 18).

Registry No.—**3a**, 5548-51-6; **3b**, 5775-08-6; **4**, 7732-06-1; **5**, 7732-07-2; **6**, 7732-09-4; **7**, 7732-08-3.

Reactions of Enol Ethers with Carbenes. VIII. Rearrangement of the Dichlorocyclopropane Derived from 1-Ethoxycyclododecene[1]

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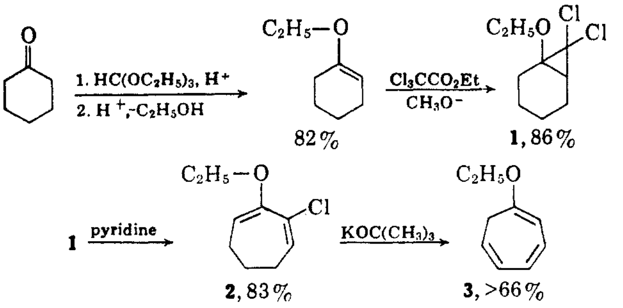
Received November 1, 1966

The dichlorocyclopropane prepared (96% yield) from the large-ring enol ether 1-ethoxycyclododecene (**4**) undergoes facile ring expansion to give 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**, 87% yield). This result is in sharp contrast to the analogous cyclopropanes derived from intermediate-ring enol ethers which resist expansion and give, under more vigorous conditions, products derived by transannular processes. The stereochemistry of **6** is discussed and a variety of chemical reactions is described. A new synthesis of heterocyclic *m*-cyclophanes is reported by reaction of **6** with hydrazine, or by reaction of the derived 1-ethoxy-1-cyclotridecen-3-eyne (**13**, 74% yield from **6**) with hydrazine or 2,4-dinitrophenylhydrazine. The conversion of cyclododecanone to cyclotridecanone constitutes a new method for ring homologation.

The conversion of cyclohexanone to 1-ethoxycycloheptatriene (**3**) (Scheme I), by a process involving reaction of the intermediate **1** with hot pyridine or quinoline, was described in an earlier communication.[3] It was also observed that dihalocyclopropanes derived from enol ethers of intermediate-sized rings, such as 1-ethoxycycloheptene and 1-ethoxycyclooctene, were more resistant to ring expansion and, under vigorous conditions (hot quinoline), gave products resulting from transannular reactions. It was anticipated that this reaction sequence might offer an attractive route for increasing by one the number of carbon atoms in cyclic systems of larger rings in which ring strain is diminished and transannular reactions are less likely. This has been shown to be the case, and this paper is concerned with the synthesis and reactions of 1-ethoxy-13,13-dichlorobicyclo[10.1.0]tridecane (**5**) (Scheme II) and the products derived from it by ring expansion.

SCHEME I



1-Ethoxycyclododecene (**4**) was prepared in 78% yield by the acid-catalyzed elimination of ethanol from cyclododecanone diethyl ketal (92% yield from cyclododecanone). The data observed [nuclear magnetic resonance (nmr) and gas–liquid partition chromatography (glpc)] for this enol ether established it to be essentially one[4] stereoisomer (>90%), and the chemical

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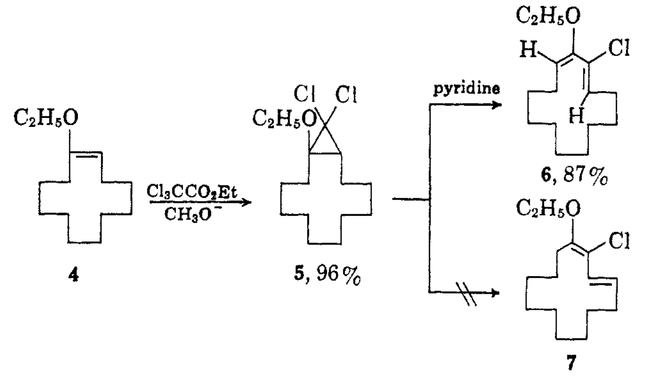
[1] This work was supported by Grants GP-3357 and GP-6169X from the National Science Foundation.

[2] From the Ph.D. Thesis of R. J. Sperley, the University of Minnesota, 1966.

[3] W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Am. Chem. Soc.*, **87**, 321 (1965).

[4] The parent hydrocarbon, cyclododecene, forms an equilibrium mixture of *trans–cis* isomers of about 60:40. *Cf.* M. Suoboda and J. Sicher, *Chem. Ind.* (London), 290 (1959).

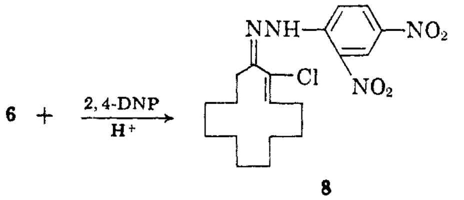
SCHEME II



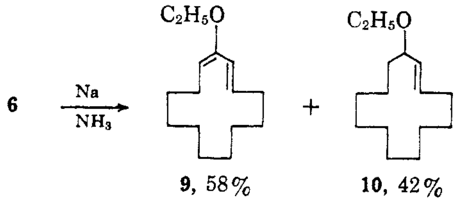
shift observed for the vinyl proton in the nmr spectrum[5] of **4** and the infrared spectrum[6] of the derived cyclopropane **5** suggest that **4** has the expected *trans* configuration.

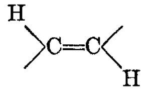
Reaction of *trans*-1-ethoxycyclododecene (**4**) with excess ethyl trichloroacetate and sodium methoxide gave the cyclopropane **5** in 96% yield. The cyclopropane **5**, unlike the analogous products derived from the intermediate-sized rings (C_7–C_8)[3] underwent facile ring expansion. Distillation of **5** at reduced pressure, or reaction of **5** with boiling pyridine, resulted in elimination of hydrogen chloride and formation of 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**) in 79 and 87% yield, respectively. The nmr 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 **6** but not for the isomer **7**.

The chlorodiene **6** was characterized by its conversion to the hydrazone **8** by reaction with 2,4-dinitrophenylhydrazine reagent, and by conversion to 1:1 adducts with tetracyanoethylene and with N-phenylmaleimide (>55 and 3.9% yield, respectively). These adducts appeared to be structurally similar (nmr spectra); however, their apparent resistance to mild acid hydrolysis (suggesting probable absence of enol ether) and the absence of vinyl hydrogens in nmr spectra (suggesting a normal 1,4-adduct) represented conflicting data which precluded definitive assignment of structure.[7]



The reaction of 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**) with sodium (6 equiv) in liquid ammonia gave a mixture of the replacement product **9** and the reduced diene **10** in good yield. The mixture was analyzed by glpc and found to be a mixture of two new components in the ratio 58:42. The product had the composition calculated for a mixture of **9** and **10** in the ratio 58:42, and the nmr spectrum was that expected for such a composition. The infrared spectrum of the mixture showed strong absorption for *trans*

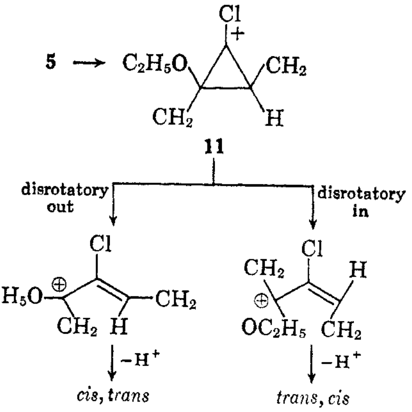




deformation near 975 cm^{-1}, but no absorption for *cis* deformation near 760 cm^{-1}. Since reaction of vinyl halides with sodium in liquid ammonia is thought to be stereospecific[8] (retention of configuration), this observation suggests that the C(—Cl)=(H—)C configuration is *trans* as shown in formula **6**.

The stereochemical configuration of the diene **6** was not established with certainty; however, it is probable that the structure 2-ethoxy-3-chloro-*cis,trans*-1,3-cyclotridecadiene is correct as shown in formula **6**. Reduction, as discussed above, suggests the *trans* configuration for the C(—Cl)=(H—)C group, and Hubert and Dale[9] have noted in a series of 1,3-cycloalkidines (C_{12}–C_{18}) that only the *cis,trans* stereoisomer is formed by isomerization of nonconjugated *cis*-cycloalkadienes with triethylborane at 200°. If the CCl=CH configuration in **6** is *trans*, as reduction indicates, then collapse of the cyclopropyl cation **11** (Scheme III) by a disrotatory outward process[10,11] would give *cis,trans* **6**; collapse by a disrotatory inward process would give **6** with the CCl=CH group *cis* which is inconsistent with the reduction data.

SCHEME III



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[5] The vinyl proton of **4** occurs as a triplet centered at τ 5.82, and this compares with τ 5.46 and 5.57 for the vinyl protons in 1-ethoxycyclohexene and 1-ethoxycycloheptene in which the vinyl hydrogen and ethoxy groups are *cis*. F. Bohlmann, C. Arndt, and V. Starnich [*Tetrahedron Letters*, No. 24, 1605 (1963)] report the nmr spectra of a series of vinyl ethers in which the vinyl hydrogen and ethoxy groups are both *cis* and *trans*, and observed the chemical shift for vinyl hydrogens *cis* to the ether group to be greater than for vinyl hydrogens *trans* to the ether group.

[6] *Cf.* H. E. Kenney, D. Komanowsky, L. L. Cook, and A. N. Wrigley, *J. Am. Chem. Soc.*, **41**, 82 (1964). A doublet, near 800 cm^{-1} assigned to carbon–chlorine stretch, was observed in the infrared spectrum of the *cis*-dichlorocyclopropanes derived from 1-ethoxycycloheptene, 1-ethoxycyclooctene, *cis*-9-octadecene, and methyl oleate. The dichlorocyclopropane **5** and the *trans*-cyclopropane derived from methyl elaidate show a singlet at 817 and 800 cm^{-1} (br), respectively.

[7] Compare ref 3. The chlorodiene **2** gives adducts derived by prior isomerization of **2** to the conjugated diene related to **7**.

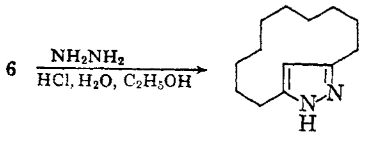
[8] M. C. Hoff, K. W. Greenlee, and G. E. Boord, *J. Am. Chem. Soc.*, **73**, 3329 (1951).

[9] A. J. Hubert and J. Dale, *J. Chem. Soc.*, 6674 (1965).

[10] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

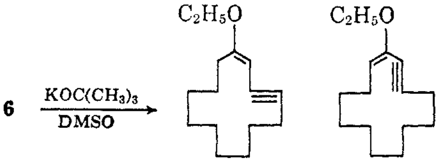
[11] C. H. DePuy, L. G. Schnack, J. W. Hausser, W. Wiedemann, *ibid.*, **87**, 4006 (1965).

The gross structure of **6** was established by a study of its reaction with hydrazine which gave 3,5-[10]-pyrazolophane (**12**) in 62% yield. The product **12** was identical with an authentic sample of **12** prepared by an independent procedure.[12] This reaction sequence appears to be a promising one for the synthesis of a variety of heterocyclic *m*-cyclophanes.



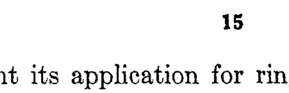
12

The reaction of 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**) with potassium t-butoxide in dimethyl sulfoxide gave 1-ethoxy-1-cyclotridecen-3-eyne **13** in 74% yield instead of ethoxytriene as formed in the analogous reaction with **2**. This observation was not unexpected since decrease strain in the larger ring would permit the conjugated enyne structure. The enyne **13** showed[13] $\lambda_{\max}^{95\%\ \text{alcohol}}$ 239 mμ (ε 12,300), $\nu_{C=C}$ 1630 cm^{-1}, and $\nu_{C\equiv C}$ 2200 cm^{-1} in the infrared, and strong $\nu_{C\equiv C}$ 2200 cm^{-1} and $\nu_{C=C}$ 1633 cm^{-1} in the Raman spectrum. That isomerization to the conjugated acetylene **13** had occurred was evident from the nmr spectrum of the olefin. If the enyne had structure **14** one would expect the vinyl proton to appear as a triplet with J_{A_2X} = 7–8 cps; for **13** the vinyl proton should appear as a singlet, or multiplet with $J \sim$ 1–2 cps caused by long-range splitting. The vinyl proton appeared as a triplet near τ 5.59 with J = 1.8 cps.



13, 74% **14**, not detected

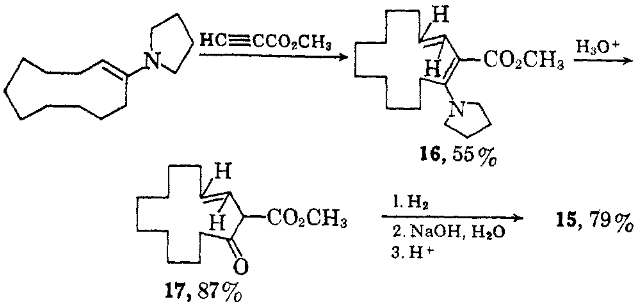
The structure of **13** was established by hydrolysis and reduction (69% over-all yield) to cyclotridecanone. The yields in this over-all sequence are sufficiently high to warrant its application for ring homologation of large-ring ketones. Authentic cyclotridecanone (**15**) was prepared from cycloundecanone by a new procedure based on the method suggested by Brannock, Burpitt, Goodlett, and Thweatt[14] as outlined in Scheme IV.



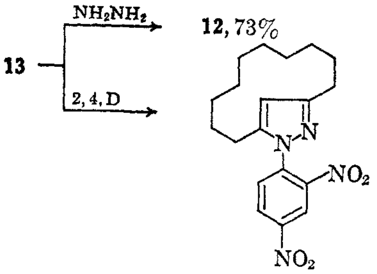
15

The reaction of 1-ethoxy-1-cyclotridecen-3-eyne (**13**) (Scheme V) with hydrazine in acid gave 3,5-[10]-pyrazolophane (**12**) in 73% yield; reaction with acidic 2,4-dinitrophenylhydrazine gave 1-(2,4-dinitrophenyl)-3,5-[10]-pyrazolophane (**18**) in >65% yield. The structure of **18** was assigned on the basis of (1) its composition; (2) its ultraviolet spectrum[15] ($\lambda_{\max}^{95\%\ \text{alcohol}}$ 232 mμ (ε 9650) and 311 (6000), and 320 (6050); (3) its infrared spectrum which showed no NH absorption, and (4) the nmr spectrum which was similar to **12** and consistent for **18**.

SCHEME IV



SCHEME V



18

Experimental Section[16–18]

Cyclododecanone diethyl ketal [bp 111–120° at 0.6–0.8 mm, 23.8 g from benzene–ethanol, 92.4% yield, mp 34–34.5° (lit.[19] mp 39–39.5° from ethanol)] was prepared by a procedure essentially identical with that described for cyclohexanone diethyl ketal.[20]

1-Ethoxycyclododecene (4). A.—The enol ether **4** was prepared in 79% yield (2.34 g, bp 119–120° at 1.2 mm, $n^{26.5}\mathrm{D}$ 1.4817–1.4819) from cyclododecanone diethyl ketal as previously described[21] for cyclohexanone diethyl ketal. The product contained 7% of cyclododecanone (glpc Apiezon L, 180°) which was removed by column chromatography (1.39-g sample, 30 g of alumina, petroleum ether with bp 60–68° as eluent). The pure enol ether was collected ($n^{26}\mathrm{D}$ 1.4820) at 100° (0.55 mm) (lit.[19] bp 133 at 15 mm, $n^{20}\mathrm{D}$ 1.4851).

Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 80.22; H, 12.46.

This product showed infrared spectrum $\nu_{C=C}$ 1658 cm^{-1}, ν_{C-OR} 1238 cm^{-1}, ν_{C-OR} 1125 cm^{-1}; nmr spectrum (20% CCl_4), $CH{=}C$ (triplet, τ 5.70, 5.82, 5.94, J = 7 cps, wt 1), OCH_2CH_3 (quartet, τ 6.25, 6.37, 6.49, 6.60, J = 7 cps, wt 2), allylic CH_2

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[12] W. E. Parham and J. F. Dooley, *J. Am. Chem. Soc.*, **89**, 985 (1967).

[13] This compares with $\lambda_{\max}^{95\%\ \text{alcohol}}$ 238 (ε 11,000) for 2-nonen-4-yn-1-ol. A. A. Petrov and G. I. Sermanov, *J. Gen. Chem. USSR*, **28**, 73 (1958).

[14] K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **29**, 818 (1964).

[15] The values compare favorably to those reported for 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazole. L. A. Jones and K. Hancock, *J. Am. Chem. Soc.*, **82**, 105 (1960). Lack of absorption in the 360–380-mμ region is incompatible with a hydrazone structure.

[16] Melting points are uncorrected.

[17] Nmr spectra (Varian A-60) were obtained from 6 to 25% solutions in carbon tetrachloride or deuteriochloroform using tetramethylsilane as internal standards. Peak weights were obtained by integration.

[18] Glpc analysis were run on a Beckman GC-4 using flame ionization detector and helium (20 cc/min) as carrier gas. The columns were 1/8 in. × 6 ft packed with DC 710 or Apiezon L on Chromosorb W (80–100 mesh), and peak areas were determined with a Disc integrator.

[19] V. Schmidt and P. Graffen, *Ann.*, **656**, 101 (1962).

[20] A. Johannissian and E. Akunian, *Bull. univ. état. R.S.S. Arménie*, **No. 5**, 245 (1931); *Chem. Abstr.*, **25**, 921 (1931).

[21] A. Johannissian and E. Akunian, *Bull. univ. état. R.S.S. Arménie*, **No. 5**, 235 (1930); *Chem. Abstr.*, **25**, 992 (1931).

(multiplet, τ 7.72–8.2, wt 4), $\mathrm{C}H_2$ (broad near τ 8.69, wt 12), $\mathrm{OCH_2C}H_3$ triplet, τ 8.69, 8.80, 8.91, J = 7 cps, wt 3).

B. To a 300-ml flask equipped with a reflux condenser and magnetic stirrer, were added cyclododecanone (36.4 g, 0.2 mole), ethyl orthoformate (37.0 g, 0.25 mole), absolute ethanol (40 ml), and *p*-toluenesulfonic acid (0.54 g). The mixture was refluxed for 1.5 hr, cooled, and equipped for distillation. The low-boiling components (60 g) were removed at atmospheric pressure (bp 55–80°) and the remaining oil was distilled at reduced pressure. The vinyl ether **4** (32 g, 78% yield, $n^{25.2}\mathrm{D}$ 1.4819) was collected at 127–134° (10–12 mm).

1-Ethoxy-13,13-dichlorobicyclo[10.1.0]tridecane (5).—The reaction of **4** (12.57 g, 0.059 mole), sodium methoxide (10.0 g, 0.18 mole, fresh), and olefin-free heptane (140 ml) was carried out for 3 hr at 0° as previously described for 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane.[3] The mixture was allowed to warm to room temperature and was stirred for an additional 4 hr. Petroleum ether (bp 60–68°) (100 ml) and water (200 ml) were added, the phases were separated, and the aqueous layer was extracted with petroleum ether (250 ml). The combined ether extract was washed with saturated saline solution (50 ml), dried ($\mathrm{MgSO_4}$), and concentrated on a rotary evaporator. The crude oil was chromatographed on alumina (500 g) using petroleum ether as eluent. There was obtained (combination of several fractions) 16.73 g (96% yield, $n^{25.5}\mathrm{D}$ 1.4994) of **5**.

Anal. Calcd for $\mathrm{C_{15}H_{26}Cl_2O}$: C, 61.43; H, 8.94; Cl, 24.74. Found: C, 61.68; H, 9.10; Cl, 24.69.

The infrared spectrum of **5** showed no C=C absorption, $\nu_{\text{cyclopropane}}$ 1020 cm^{-1}, and ν_{CCl} 817 cm^{-1}; nmr spectrum (20% in $\mathrm{CCl_4}$), $\mathrm{OC}H_2\mathrm{CH_3}$ (quartet, 6.08, 6.20, 6.32, 6.44, J = 7 cps, wt 2), $(\mathrm{C}H_2)_n$ (complex centered at τ 8.52, wt 21), $\mathrm{OCH_2C}H_3$ triplet, τ 8.69, 8.81, 8.93, J = 7 cps. wt 3).

Reactions of 1-Ethoxy-13,13-dichlorobicyclo[10.1.0]tridecane (5). A. With Pyridine.—A solution of **5** (7.0 g, 0.024 mole) and dry pyridine (24.0 g, 0.3 mole) was heated under nitrogen for 3 hr at 90–110° in a 50-ml flask equipped with a reflux condenser, a nitrogen inlet, and a magnetic stirrer. Dry ether (25 ml) was added to the cold reaction mixture and pyridine hydrochloride was removed (and rinsed with dry ether) by filtration. The filtrate was poured into water (200 ml) and the resulting mixture was extracted with three 50-ml portions of petroleum ether. The ether extract was dried ($\mathrm{Na_2SO_4}$) and concentrated. The crude oil (5.9 g, 96% yield) was fractionated to give 5.3 g (87% yield, $n^{26}\mathrm{D}$ 1.5070, bp 139–141° at 0.6–0.8 mm) of 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**).

Anal. Calcd for $\mathrm{C_{15}H_{25}ClO}$: C, 70.15; H, 9.81; Cl, 13.81. Found: C, 69.88; H, 10.08; Cl, 14.03.

The diene showed ultraviolet spectrum, $\lambda_{\max}^{95\%\ \text{alcohol}}$ 241 mμ (ϵ 2280); infrared spectrum, $\nu_{\mathrm{C=C}H}$ 3040 cm^{-1}, $\nu_{\text{C=C}}$ (1663 and 1633 cm^{-1}, and $\nu_{\text{C=COR}}$ 1235 and 1118 cm^{-1}. The nmr spectrum of **6** (20%, $\mathrm{CCl_4}$) showed $\mathrm{C}H\mathrm{{=}CCl}$ (triplet, τ 4.23, 4.34, 4.47, J = 7 cps, wt 1), $\mathrm{C}H\mathrm{{=}COR}$ (triplet, τ 5.23, 5.37, 5.52, J = 8 cps, wt 1), $\mathrm{OC}H_2\mathrm{CH_3}$ (quartet, τ 6.19, 6.31, 6.43, 6.54, J = 7 cps, wt 2), allylic $\mathrm{C}H_2$ (multiplet, τ 7.58–8.0, wt 4), $\mathrm{OCH_2C}H_3$ (triplet, τ 8.65, 8.77, 8.89, J = 7 cps, wt 3), and $\mathrm{C}H_2$ (complex centered at τ 8.70, wt 14).

B. Heat.—A sample of chromatographed (pure) **5** was heated at a pressure of 0.3 mm. At 100° vigorous bubbling occurred and hydrogen chloride was evolved. The liquid then distilled at 126–127° (0.3 mm) to give 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**, $n^{26}\mathrm{D}$ 1.5068) in 79% yield.

Reactions of 2-Ethoxy-3-chloro-1,3-cyclotridecadiene (6). A. With Tetracyanoethylene.—A solution of **6** (0.3 g, 0.0013 mole) and TCNE (0.15 g, 0.0013 mole) in benzene (25 ml) was stirred under nitrogen for 6 days at room temperature. The solution was concentrated and the residue was recrystallized from chloroform–petroleum ether and from diethyl ether. The weight of colorless adduct was 0.25 g (55% yield, mp 201–202°).

Anal. Calcd for $\mathrm{C_{21}H_{25}ClN_4O}$: C, 65.52; H, 6.55; N, 14.52. Found: C, 65.25; H, 6.64; N, 14.23.

The infrared spectrum of the 1:1 adduct (split mull, halocarbon oil, Nujol) showed $\nu_{\mathrm{C{\equiv}N}}$ 2250 and 2260 cm^{-1}, $\nu_{\text{C=C}}$ 1642 cm^{-1}, $\nu_{\text{C=COR}}$ 1240 and 1115 cm^{-1}. The ultraviolet spectrum of the adduct showed $\lambda_{\max}^{95\%\ \text{alcohol}}$ 226 mμ (ϵ 4660). The nmr spectrum of the adduct showed no vinyl proton absorption (τ 3.5–5.5), $\mathrm{OC}H_2\mathrm{CH_3}$ (split quintet, τ 5.54, 5.58, 5.66, 5.70, 5.78, 5.82, 5.88, 5.92, 6.0, 6.04, J_{large} = 7 cps, J_{small} = 2.5 cps, wt 2), methine H (complex singlets τ 6.35, 6.52, 6.72, 6.90, wt 2), $\mathrm{C}H_2$ (complex τ 7.8–8.9, wt 18), $\mathrm{OCH_2C}H_3$ (triplet τ 8.51, 8.63, 8.75, J = 7 cps wt 3).

Attempts to *hydrolyze the adduct* (0.1 g) in warm dioxane (5 ml) and water (2 ml) containing sulfuric acid (10 drops) for 10 hr led to recovery of 0.08 g of recovered adduct (mp 201–202°).

B. With N-Phenylmaleimide.—A solution of **6** (1.0 g, 0.0039 mole) and N-phenylmaleimide (0.67 g, 0.0039 mole) in dry benzene (10 ml) was heated at the reflux temperature for 1 week. The mixture was filtered and the filtrate was concentrated to a yellow semisolid (1.63 g). The product was recrystallized from ether to give 0.065 g of 1:1 adduct, mp 144–145°, 3.9% yield.

Anal. Calcd for $\mathrm{C_{25}H_{32}ClNO_3}$: C, 69.95; H, 7.50; Cl, 8.25; N, 3.26. Found: C, 70.23; H, 7.21; Cl, 8.13; H, 3.20.

The adduct had infrared spectrum, $\nu_{\text{C=O}}$ imide 1760 and 1697 cm^{-1}, $\nu_{\text{C=C}}$ 1642 cm^{-1}, ν_{aromatic}, 1595 and 1507 cm^{-1}, $\nu_{\text{C=COR}}$ 1238 and 1110 cm^{-1}; nmr spectrum, aromatic H (multiplet, τ 2.3–2.78, wt 5), $\mathrm{OC}H_2\mathrm{CH_3}$ (split quintet, τ 5.84, 5.88, 5.96, 6.0, 6.08, 6.12, 6.2, 6.24, 6.32, 6.36 J_{large} = 7 cps, J_{small} = 2.5 cps, wt 2), methine H, (complex singlets, τ 6.41, 6.50, 6.73, 7.0, wt 4, $\mathrm{C}H_2$ (complex τ 7.5–8.9, wt 18, $\mathrm{OCH_2C}H_3$ (triplet, τ 8.6, 8.72, 8.84, J = 7 cps, wt 3).

The adduct (0.01 g) was recovered unchanged after being stirred for 8 hr at room temperature in ethanol (5 ml) and water (2 ml) containing 3 drops of hydrochloric acid.

C. With Acidic Hydrazine.—A solution of 2-ethoxy-3-chloro-1,3-cyclotridecadiene (1.0 g, 0.003 mole) in ethanol–water (~75:25, 5 ml) and concentrated hydrochloric acid (0.3 ml, 0.0039 mole) was stirred for 30 min in a 25-ml flask fitted with a reflux condenser and magnetic stirrer. Ethanolic hydrazine (5 ml, 95%, 0.4 g, 0.0039 mole of hydrazine) was added dropwise and the mixture was stirred at room temperature for 30 min and at reflux for 2 hr. The solution was concentrated in a rotary evaporator, water (100 ml) was added, and the mixture was extracted with ether (100 ml). The ether extract was dried ($\mathrm{MgSO_4}$) and concentrated to give 0.7 g of solid melting at 50–78°. The yield of pure **12** (white needles from ether–pentane, mp 92–93° cor) was 0.5 g, 62%. The material was identical[12] (ultraviolet, infrared, nmr, and mixture melting point) with authentic 3,5-[10]-pyrazolophane (**12**).

D. With 2,4-Dinitrophenylhydrazine Reagent.—The reaction of **6** (0.3 g) in ethanol with 2,4-dinitrophenylhydrazine reagent[22] (containing 0.26 g, 0.0013 mole of the hydrazine) gave the 2,4-dinitrophenylhydrazone of 2-chloro-2-cyclotridodecene-1-one (**8**, 0.31 g from ethanol–ethyl acetate, mp 131–132°, 58% yield).

Anal. Calcd for $\mathrm{C_{19}H_{25}ClN_4O_4}$: C, 55.81; H, 6.16; N, 13.70. Found: C, 55.69; H, 6.15; N, 13.75.

The ultraviolet spectrum of the hydrazone **8** showed $\lambda_{\max}^{95\%\ \text{alcohol}}$ 372 mμ (ϵ 24,070); infrared spectrum (split mull), ν_{NH} 3220 cm^{-1}, $\nu_{\text{phenyl H}}$ 3070 cm^{-1}, $\nu_{\text{C=N}}$ 1620 and 1590 cm^{-1}, $\nu_{\text{RC(−H)=(Cl−)CR}}$ 835 cm^{-1}; nmr spectrum (10% $\mathrm{DCCl_3}$), $\mathrm{N}H$ (complex singlet, τ 0.2, wt 1), phenyl H (multiplet, τ 1.54–1.89, wt 3), $\mathrm{C}H\mathrm{{=}C(Cl)}$ (triplet, τ 3.3, 3.42, 3.54, J = 7 cps, wt 1), allylic $\mathrm{C}H_2$ (multiplet, τ 7.0–7.81, wt 4), $\mathrm{C}H_2$ (complex, near τ 8.59, wt 16).

E. With Sodium in Liquid Ammonia.—Liquid ammonia (200 ml) was placed in a 500-ml flask fitted with Dry Ice–acetone condenser, drying tube, magnetic stirrer, and dropping funnel. Metallic sodium (2.76 g, 0.12 mole in small pieces) was dissolved in the ammonia and a pentane solution (20 ml) of **6** (5.12 g, 0.02 mole) was added dropwise. The mixture was stirred for 1 hr, and ammonium chloride (25 g) and then water (200 ml) were added. The mixture was extracted with petroleum ether (150 ml), and the ether extract was washed with water (50 ml) and dried ($\mathrm{Na_2SO_4}$). Concentration of the ether solution gave 4.47 g of light yellow oil which, upon distillation, gave 3.07 g of colorless liquid (bp 87–89° at 0.05 mm, $n^{27.5}\mathrm{D}$ 1.4995). Analysis of this oil by glpc (Apiezon L, 150°) showed it to be a mixture of two components in the approximate ratio of 58:42. These products were assumed to be the expected olefins 2-ethoxy-1,3-cyclotridecadiene (**9**) and 3-ethoxycyclotridecene (**10**).

Anal. Calcd for 58% $\mathrm{C_{15}H_{26}O}$ and 42% $\mathrm{C_{15}H_{28}O}$: C, 80.4; H, 12.1. Found: C, 80.22; H, 12.24.

The infrared spectrum of the oil (neat) showed $\nu_{\text{C=O}}$ 1653 and 1612 cm^{-1}, $\nu_{\text{C=COR}}$ 1245 and 1120 cm^{-1}, $\nu_{\text{CH=CH}}$ (*trans*) 975 cm^{-1}, absence of $\nu_{\text{CH=CH}}$ (*cis*) near 760 cm^{-1}, nmr spectrum (20%, $\mathrm{CCl_4}$), vinyl H (multiplet τ 3.68–4.14), vinyl H (triplet, 5.49,

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[22] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., 1956, p 219.

5.62, 5.75, $J = 8$ cps), methine H (triplet, τ 5.69, 5.81, 5.92, $J = 7$ cps), $\mathrm{OC}H_2\mathrm{CH}_3$ (quartet, τ 6.13, 6.25, 6.37, 6.49, $J = 7$ cps, and quartet τ 6.21, 6.33, 6.45, 6.57, $J = 7$ cps), allylic H (multiplet τ 7.68–8.13), $\mathrm{OCH_2C}H_3$ (triplet, τ 8.59, 8.71, 8.83, $J = 7$ cps and triplet, τ 8.63, 8.75, 8.87, $J = 7$ cps), $\mathrm{C}H_2$ (complex singlet, τ 8.79).

F. With Potassium *t*-Butoxide in Dimethyl Sulfoxide.—A mixture of dimethyl sulfoxide (25 ml) and technical grade potassium *t*-butoxide (5.0 g, 0.044 mole) was stirred under nitrogen at 20° in a 100-ml flask fitted with a reflux condenser, dropping funnel, magnetic stirrer, and nitrogen inlet, until most of the alkoxide had dissolved. A solution of **6** (4.0 g, 0.015 mole) in anhydrous ether was added to the cooled mixture and the resulting mixture was stirred for 3 hr at a temperature below 20°. The mixture was then cooled to 0° and water (100 ml) was added. The mixture was extracted with three 50-ml portions of petroleum ether. The combined ether extract was washed with water (100 ml) and was dried ($\mathrm{Na_2SO_4}$) and concentrated to give 3.3 g of yellow oil. The oil was purified by chromatography on alumina (Woelm, activity 1, 100 g) using petroleum ether as eluent. There was obtained 2.58 g (74% yield) of pure 1-ethoxycyclotridecen-1-eyne-3 (**13**). Glpc analysis of this product (DC-710, 225°) showed only one peak.

Anal. Calcd for $\mathrm{C_{15}H_{24}O}$: C, 81.76; H, 10.98. Found: C, 81.78; H, 11.26.

The ultraviolet spectrum of **13** showed $\lambda_{\max}^{95\%\ \mathrm{alcohol}}$ 239 mμ (ϵ 12,300); infrared spectrum (neat), $\nu_{\mathrm{C=CH}}$ 3005 cm^{-1}, $\nu_{\mathrm{C\equiv C}}$ 2200 cm^{-1}, $\nu_{\mathrm{C=C}}$ 1633 cm^{-1}, $\nu_{\mathrm{C=COR}}$ 1240 cm^{-1}, ν_{COR} 1100 cm^{-1}; Raman spectrum (2.13%, $\mathrm{CCl_4}$), $\nu_{\mathrm{C\equiv C}}$ 2119–2200 cm^{-1}, $\nu_{\mathrm{C=C}}$ 1633 cm^{-1}; nmr spectrum (20%, $\mathrm{CCl_4}$), $=\mathrm{C}H$ (triplet, τ 5.56, 5.59, 5.62, $J = 1.8$ cps, wt 1), $\mathrm{OC}H_2\mathrm{CH}_3$ (quartet τ 6.18, 6.29, 6.41, 6.52, wt 2), allylic H (multiplet, τ 7.5–7.85 wt 4), $\mathrm{C}H_2$ (complex singlet, τ 8.6, wt 14), $\mathrm{OCH_2C}H_3$ (triplet, τ 8.65, 8.75, 8.85, wt 3).

Reactions of 1-Ethoxycyclotridecen-1-enyne-3 (**13**). **A. With Hydrazine.**—A mixture of **13** (0.3 g, 0.0014 mole), 95% alcohol (5 ml), and concentrated hydrochloric acid (0.13 ml, 0.0014 mole) was cooled (20°) and stirred for 30 min, and then hydrazine (95%, 0.13 g, 0.0039 mole) in ethanol (5 ml) was added. The resulting mixture was stirred for 30 min at room temperature and heated at the reflux temperature for 1.5 hr.. The mixture was poured into water (100 ml) and extracted with petroleum ether (50 ml). The crude solid (mp 78–86°, 0.23 g) obtained by evaporation of the dried petroleum ether extract was dissolved in ether and treated with decolorizing charcoal. Pentane was added to the filtered solution and the mixture was cooled. There was obtained 0.21 g (73% yield) of 3,5-[10]-pyrazolophane (**12**, mp and mmp[12] 92–93° cor).

B. With 2,4-Dinitrophenylhydrazine.—A freshly prepared solution of acidic 2,4-dinitrophenylhydrazine reagent[22] (0.45 g of hydrazine, 0.0023 mole, 25 ml) was added to a solution of **13** (0.5 g, 0.0023 mole) in ethanol (~5 ml). A tarry red material formed immediately and the orange supernatant was decanted. The red semisolid residue was dissolved in hot ethanol (5 ml) and filtered, and water (2 ml) was added. This ethanol solution was cooled and an orange-yellow solid (0.2 g, mp 116–121°) was collected. The original supernatant was treated with water (5 ml) and the yellow solid that formed was collected and recrystallized from ethanol–water. There was obtained 0.54 g (65% yield) of 1-(2,4-dinitrophenyl)-3,5-[10]-pyrazolophane (**18**), mp 120–121°.

Anal. Calcd for $\mathrm{C_{19}H_{24}N_4O_4}$: C, 61.27; H, 6.48; N, 15.05. Found: C, 61.55; H, 6.25; N, 15.13.

The ultraviolet spectrum of **18** showed $\lambda_{\max}^{95\%\ \mathrm{alcohol}}$ 232 mμ (ϵ 9650), 311 (6000), 320 (6050). The infrared spectrum showed $\nu_{\mathrm{aromatic}\ H}$ 3070 cm^{-1}, ν_{NH} none, $\nu_{\mathrm{C=C}}$ 1608 cm^{-1}, $\nu_{\mathrm{NO_2}}$ 1540 and 1350 cm^{-1}. The nmr spectrum (20%, $\mathrm{DCCl_3}$) showed aromatic H (multiplet, τ 1.22–2.44, wt 3), $=\mathrm{CH}$ (singlet, τ 3.75, wt 1), allylic H (multiplet, τ 7.23–7.50, wt 4), $\mathrm{C}H_2$ (complex, τ 8.13–9.13, wt 16).

The infrared spectrum of the orange solid (mp 116–121°) was almost identical with that of pure **18**. Analysis of the orange solid by tlc [alumina, ether–petroleum ether (10:90) as eluent] showed at least four components the major component having an R_f identical with **18**.

C. With Hydrogen.—A solution of **13** (1.02 g, 0.0046 mole) in ethanol (95%, 50 ml) was treated in a Parr apparatus with hyrogen (36 psi) and platinum oxide (0.01 g). After 18 hr the mixture was filtered and concentrated. The yellow oil (1.03 g) was chromatographed on alumina (20 g). Elution of the column with petroleum ether gave 0.72 g of cyclotridecyl ethyl ether ($n^{26.5}\mathrm{D}$ 1.4792). The oil was redistilled (bp 97–101° at 0.8–1.0 mm, $n^{26.5}\mathrm{D}$ 1.4791, 0.70 g, 69% yield).

Anal. Calcd for $\mathrm{C_{15}H_{30}O}$: C, 79.57; H, 13.36. Found: C, 79.31; H, 13.10.

The nmr spectrum of cyclotridecyl ethyl ether (20%, $\mathrm{CCl_4}$) showed $\mathrm{OC}H_2\mathrm{CH}_3$ (quartet, τ 6.43, 6.55, 6.67, 6.79, $J = 7$ cps, wt 2), $\mathrm{C}H\mathrm{OR}$ (singlet, τ 8.48, wt 1), $\mathrm{CH_2}$ (complex singlet centered at τ 8.64, wt 24); $\mathrm{OCH_2C}H_3$ (triplet, τ 8.78, 8.89, 9.01, $J = 7$ cps, wt 3).

Elution of the column with petroleum ether–diethyl ether (90:10) gave 0.14 g (15.4% yield) of cyclotridecanone, identified by comparison glpc with authentic cyclotridecanone and by conversion to the 2,4-dinitrophenylhydrazone (mp and mmp 113–114°).

D. Hydrolysis and Hydrogenation to Cyclotridecanone.—A solution of **13** (10 g, 0.0045 mole), ethanol (95%, 20 ml), water (3 ml), and perchloric acid (concentrated, 5 drops) was hydrogenated over platinum oxide (0.01 g) in a Parr shaker with hydrogen (38 psi) for 8 hr. The mixture was filtered, poured into water (10 ml), and the resulting mixture was extracted with ether (50 ml). The ether extract was dried ($\mathrm{Na_2SO_4}$) and concentrated and the residue was distilled. There was obtained 0.60 g of cyclotridecanone (bp 94–96° a 0.12 mm, mp 26–29°). This product and the derived 2,4-dinitrophenylhydrazone (mp 113–114°) were identified by comparisons with authentic materials.

Cylotridecanone (**15**).—The conversion of cycloundecanone to cyclotridecanone was effected by a procedure described by Brannock, Burpitt, Goodlett, and Thweatt[14] for conversion of cyclic ketones to higher homologs containing two more carbon atoms. The method is general but had not previously been applied to the synthesis of cyclotridecanone.

Methyl 2-(1-Pyrrolidenyl)-1,12-cyclotridecadiene-1-carboxylate (**16**).—The reaction of 1-(1-cycloundecen-1-yl)pyrrolidine (prepared in 80% yield by the general procedure of Stork,[23] *et al.*, bp 140–141° at 0.9 mm, 8.87 g, 0.04 mole) with an ethereal solution of methyl propiolate (3.4 g, 0.04 mole) was carried out as described[14] for 1-(1-cycloocten-1-yl)pyrrolidine. The yellow-white solid was washed with cold ether and the resulting solid was recrystallized from heptane to give methyl 2-(1-pyrrolidenyl)-1,12-cyclotridecadiene-1-carboxylate (6.78 g, 55.6% yield, mp 81–83°). This product was unstable and rapidly turned yellow in air at room temperature.

Anal. Calcd for $\mathrm{C_{19}H_{31}NO_2}$: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.20; H, 9.78; N, 4.41.

The infrared spectrum of the adduct (Nujol mull) showed: $\nu_{\mathrm{C=O}}$ 1680 cm^{-1}, $\nu_{\mathrm{C=CN}}$ 1543 cm^{-1}, $\nu_{\mathrm{CH=CH}}$ (*trans*) 978 cm^{-1}. The nmr spectrum showed $=\mathrm{C}H$ (two doublets, τ 3.22, 3.27 and 3.38, 3.43, $J_{\mathrm{large}} = 14$ cps, $J_{\mathrm{small}} = 8$ cps, wt 1), $\mathrm{OC}H_3$ (singlet, τ 6.36, wt 3), $=\mathrm{CH}$ (doublet, τ 6.48, 6.60, $J = 14$ cps, wt 1), allylic H (multiplet, τ 6.91–7.24, wt 4), pyrrolidine $\mathrm{C}H_2$ (multiplet τ 7.84–8.42 wt 8), $\mathrm{C}H_2$ (complex singlet near τ 8.74, wt 14).

Methyl 2-Oxo-12-cyclotridecene-1-carboxylate (**17**).—A mixture of methyl 2-(1-pyrrolidinyl)-1,12-cyclotridecadiene-1-carboxylate (3.05 g, 0.01 mole) and hydrochloric acid (10%, 15 ml) was heated on a steam bath for 45 min. The mixture was cooled and extracted with ether (50 ml), and the ether extract was washed with water (15 ml) and dried ($\mathrm{Na_2SO_4}$). The colorless solid obtained from the ether was recrystallized from hexane to give 2.2 g (87% yield) of product melting at 47–48°.

Anal. Calcd for $\mathrm{C_{15}H_{24}O_3}$: C, 71.39; H, 9.59. Found: C, 71.62; H, 9.63.

The infrared spectrum (Nujol mull) of methyl-2-oxo-12-cyclotridecene-1-carboxylate showed $\nu_{\mathrm{C(=O)O}}$ 1740 cm^{-1}, $\nu_{\mathrm{C=O}}$ 1705 cm^{-1}, $\nu_{\mathrm{CH=CH}}$ (*trans*) 978 cm^{-1}. The nmr spectrum (20% $\mathrm{CCl_4}$) showed $\mathrm{C}H{=}\mathrm{C}H$ (multiplet, τ 4.33–4.55, wt 2), $\mathrm{C}H\mathrm{C}(=\mathrm{O})\mathrm{OR}$ (doublet, τ 6.0, 6.12, wt 1), $\mathrm{OC}H_3$ (singlet, τ 6.44, wt 3), allylic H (multiplet, τ 7.38–8.03, wt 4), $\mathrm{C}H_2$ (complex singlet centered, τ 8.74, wt 14).

Cyclotridecanone (**15**).—A methyl alcohol solution of methyl 2-oxo-12-cyclotridecene-1-carboxylate (1.25 g, 0.005 mole) was hydrogenated in a Parr shaker at 45 psi over 0.05 g of palladium on alumina until a pressure drop of 1 psi was observed. The mixture was filtered and concentrated, and the oil was treated with 5 ml of 50% aqueous potassium hydroxide solution. The resulting mixture was heated at the reflux temperature for 1 hr,

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[23] G. Stork, A. Brizzolara, H. Landerman, J. Szmuszkovicz, and R. Terell, *J. Am. Chem. Soc.*, **85**, 216 (1963).

and the cooled mixture was extracted with ether (50 ml). The extract was washed with water (20 ml) and dried (Na_2SO_4). The solid obtained from the ether was distilled to give 0.76 g (79% yield) of cyclotridecanone (bp 106–107° at 0.4 mm, mp 29–31°, lit.[24] mp 30–31°). The 2,4-dinitrophenylhydrazone of cyclotridecanone melted at 113–114°, lit.[25] mp 113–114°); the semicarbazone melted at 208–209°, lit.[25] mp 208°.

Registry No.—**5**, 7777-75-5; **4**, 7777-76-6; **17**, 7777-77-7; **16**, 7777-78-8; **6**, 7777-79-9; **6** adduct with tetracyanoethylene, 7777-80-2; **6** adduct with N-phenylmaleimide, 7777-81-3; **8**, 7777-82-4; **9**, 7777-83-5, **10**, 7777-84-6; **13**, 10026-26-3; **18**, 7777-85-7; cyclotridecyl ethyl ether, 7777-86-8.

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[24] N. J. Leonard and C. W. Schimelpfenig, Jr., *J. Org. Chem.*, **23**, 1708 (1958).

[25] H. Nozaki, S. Kato, and R. Noyori, *Can. J. Chem.*, **44**, 1021 (1966).

The Structure of Kaltwasser's Acid. A Novel Cyclopropane Formation

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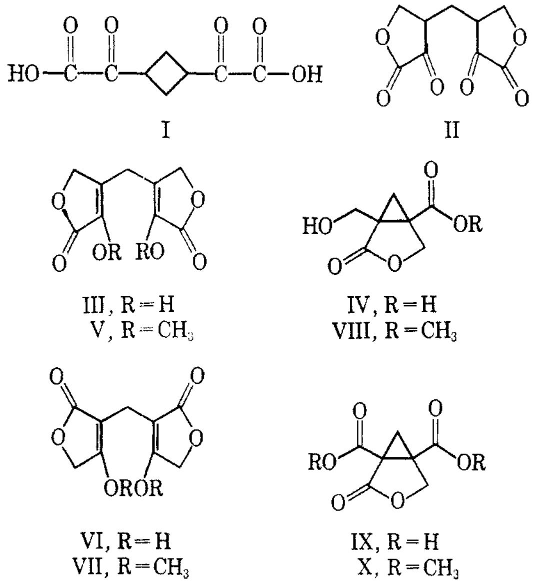
Received October 7, 1966

The structure of the acidic enol (Kaltwasser's acid) obtained by condensation of pyruvic acid with formaldehyde is confirmed as III. Silver oxide oxidation of III to the cyclopropyl lactone IV is also confirmed. The remarkable proposals made previously are thus essentially correct.

The condensation of formaldehyde and pyruvic acid in sulfuric acid was reported by Kaltwasser[1] to give a $C_8H_8O_6$ diacid (I) (Chart I). A reinvestigation of this work by Asahina and Terada[2] resulted in a revision of the molecular formula to $C_9H_8O_6$ and a proposal of structure II.[3] In support of this structure these authors report a remarkable oxidative degradation of II to IV, which was effected by silver oxide. The assignment of structure IV to the oxidation product rested on the carbon-hydrogen analysis and reduction (hydrogen iodide and phosphorous) to α,α′-dimethylglutaric acid. A few years after the publication of this work, Feofilaktov[4] repeated the silver oxide oxidation of II and found that product IV was further oxidized by alkaline permanganate to 1,1,2,2-cyclopropanetetracarboxylic acid. The identity of this latter compound was established by comparison with an authentic sample, synthesized from methylenebismalonic ester.[5]

CHART I


I

II

III, R=H
V, R=CH_3

IV, R=H
VIII, R=CH_3

VI, R=H
VII, R=CH_3

IX, R=H
X, R=CH_3

Since these early structural assignments are tenuous by present day standards, the unusual cyclopropane ring formation described above must be viewed with skepticism. Indeed, carbon–carbon bond formation seldom occurs during an oxidation reaction; the only well-substantiated examples are found in the oxidative coupling of phenolic compounds.[6]

Kaltwasser's acid, prepared according to Feofilaktov's procedure,[4] was obtained as white crystals, mp 236–238 dec, after several crystallizations from water. The infrared spectrum of this material exhibited strong absorptions at 3310 and 1725 cm^{-1}, indicating that if structure II is to remain as a reasonable representation of Kaltwasser's acid it must exist predominantly as the dienol III. In agreement with this conclusion, Kaltwasser's acid was observed to react rapidly with ethereal diazomethane yielding the dimethyl derivative V. The structure of V rested on classical analysis, the infrared spectrum (carbonyl stretching at 1740 cm^{-1}), and the nuclear magnetic resonance spectrum (three singlets at τ 6.47, 6.00, and 5.33 having an area ratio of 1:3:2, respectively). Unfortunately, Kaltwasser's acid is not uniquely characterized by these measurements, since the bistetronic acid (VI) and its dimethyl derivative VII fit the data equally well. Even more disturbing is the fact that VI has been unambiguously synthesized[7] and is reported to have a melting point of 235–238°, identical with that of Kaltwasser's acid. It is more difficult to formulate a rational mechanism for the synthesis of VI from pyruvic acid and formaldehyde than for the formation of III; however, this is insufficient reason to reject the former structure. A decision in this matter can be reached by considering changes in the ultraviolet absorption spectra of α-hydroxybutenolides and β-hydroxybutenolides upon the addition of base. An unexpected variation is observed in the data presented in Table I. Although the two classes of hydroxybutenolides have essentially the same high intensity absorption in neutral solution (λ_{max}^{EtOH} ~235 mμ for a

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[1] O. Kaltwasser, *Ber.*, **29**, 2273 (1896).

[2] E. Asahina and S. Terada, *J. Pharm. Soc. Japan*, **502**, 855 (1923).

[3] An analogous structure was proposed for the product from the condensation of benzaldehyde and pyruvic acid: E. Erlenmeyer, *Ber.*, **32**, 1450 (1899). Other products from the formaldehyde condensation reaction have been identified by S. Olsen and G. Havre, *Acta Chem. Scand.*, **8**, 47 (1954).

[4] V. Feofilaktov, *J. Russ. Phys. Chem. Soc.*, **61**, 1145 (1929).

[5] O. Dressel, *Ann.*, **256**, 174 (1890).

[6] A. I. Scott, *Quart. Rev.* (London), **19**, 1 (1965).

[7] L. Wolff, *Ann.*, **315**, 145 (1901).