Some Chemical Transformations and Conformations in the Cycloheptadecanone Series(1)

Sumner H. Burstein and Howard J. Ringold

The Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts

Received May 8, 1963

Cycloheptadec-9-en-1-one (I) was converted to cycloheptadeca-1,9-dione (VI) and to 2-bromocyclohepta-deca-1,10-dione (VIII). Dehydrobromination of the latter which was shown to have a quasi-axial conformation yielded a mixture of α,β- and β,γ-unsaturated diketones IX and X. The double bond was found to be *trans* in both IX and X while infrared data indicated that IX existed as an *S-cis, S-trans* mixture.

As part of an investigation of the conformation of large-ring unsaturated ketones we have studied the dehydrobromination of 2-bromocycloheptadeca-1,10-dione (VIII). Synthesis of this substance was effected by a straight-forward route (Chart I) involving the addition of hypobromous acid to civetone(2) (cycloheptadec-9-en-1-one)(I) followed by chromic acid oxidation of the intermediate bromohydrin (VII). The requisite bromo diketone VIII, which was obtained as an oil solidifying only below room temperature, was homogeneous on thin-layer chromatography (silica gel) and gave the proper elemental analysis, while its infrared spectrum (Table I) indicated a C—Br/C=O angle of about 90° (quasi-axial conformation)(3) in accord with the findings of Leonard and Owens(4) in 2-bromocycloalkanones containing 11–15 carbon atoms. The least strained conformation of VIII about C-1,2,3 would appear to be one with dihedral angles of 60° and 180° (pictured in Newman projection) which places the bromine atom and the polymethylene groups attached to the C-3 carbon at maximum distance from each other.

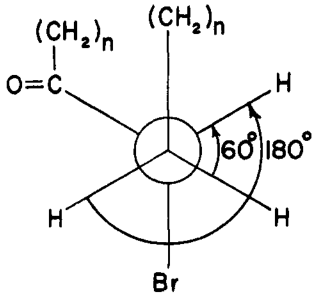


Table I

Infrared Spectra of Cycloheptadecane Derivatives[a]

Substituent	C=O	H–C=C–H	-CH₂-	CH₂—C=O	-(CH₂)ₙ-
1-Keto	1715		1458, 1442 (sh)[b]	1407	728
1-Keto-Δ^9 (I)	1710	972	1463, 1442	1417	722
1-Keto-9-Br-10-OH (VII)	1712		1457, 1445	1410	725
1,9-Diketo (VI)	1712		1460, 1442	1410	722
2-Br-1,10-diketo (VIII)	1714, 1711		1460, 1440	1410	725
Δ^2-1,10-Diketo (IX)	1710, 1692, 1667	1625, 985	1465, 1445	1412	725
Δ^3-1,10-Diketo (X)	1712	973	1463, 1440	1410	725

[a] Determined as a liquid film and reported as cm.$^{-1}$. Estimated accuracy of readings ±2 cm.$^{-1}$. [b] Poorly resolved in 1430–1450-cm.$^{-1}$ region. Ref. 13 reports bands at 1450 and 1438 cm.$^{-1}$ in carbon tetrachloride.

Dehydrobromination of the bromo ketone (VIII) with powdered calcium carbonate in boiling dimethylformamide yielded, in a number of runs, ratios of about 3:2 to 3:1 of the α,β-unsaturated ketone IX and an accompanying by-product which was shown to be the β,γ-unsaturated ketone X, as well as significant quantities of more polar materials which were not investigated further. The two unsaturated ketones, obtained as oils, were readily separable by thin-layer chromatography with the β,γ-isomer being the faste moving substance.

The α,β-unsaturated ketone IX gave a satisfactory elemental analysis and exhibited the anticipated mass number 264 as the principal molecular ion in the mass spectrum,(5) while catalytic reduction resulted in the uptake of just one mole of hydrogen with the formation of cycloheptane-1,9-dione (VI) in high yield. In the ultraviolet spectrum, determined in ethanol solution, a maximum appeared at 227 mμ (ϵ 13,800) which was shifted to 220 mμ in isooctane (ϵ 12,050). A bis-semicarbazone was obtained with λ_{max} 230 mμ (ϵ 24,400) and 263 mμ (ϵ 22,500), the higher wave-length maximum being due to the α,β-unsaturated semicarbazone moiety(6) while the 230-mμ maximum is clearly due to the saturated semicarbazone group.(6,7) The infrared spectrum of IX (Fig. 1), which was determined in carbon tetrachloride solution, showed a strong carbonyl band at

---

(1) Supported in part by Grant T-185, American Cancer Society.

(2) Purchased from the Firmenich Co., Geneva, Switzerland, and stated by the manufacturer to consist of a mixture of *cis* and *trans* isomers in a 1:2 ratio.

(3) In liquid film and in carbon tetrachloride a split carbonyl peak with maxima at 1711 and 1714 cm.$^{-1}$ was observed, the higher frequency peak being assigned to the α-bromo ketone group. This small shift denotes that the C–Br bond possesses little if any *syn*-skew character (see ref. 4).

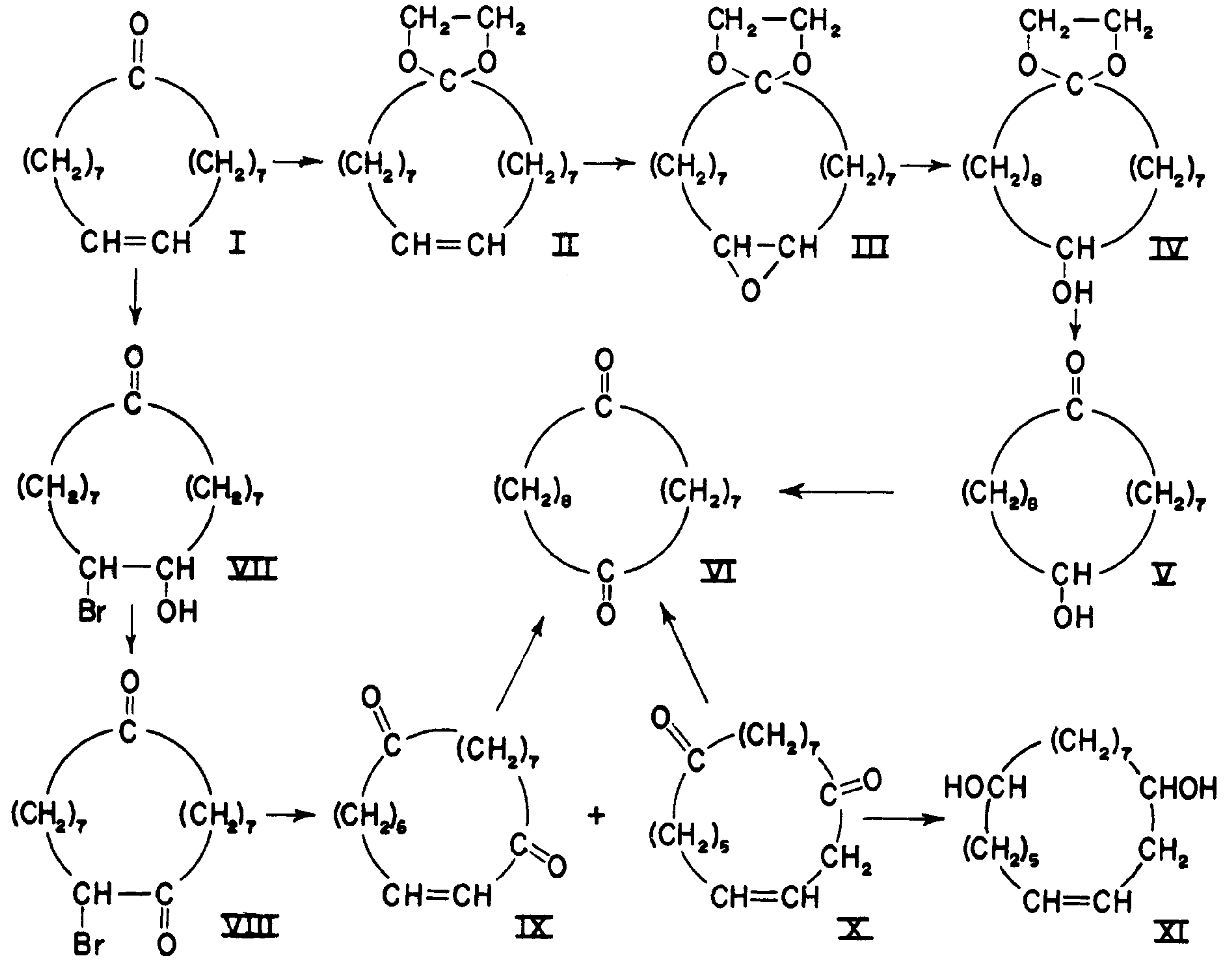
(4) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6039 (1958).

(5) We are grateful to Dr. H. Budzikiewicz and Prof. Carl Djerassi, Stanford University, for the mass spectrometric analyses.

(6) L. Dorfman, *Chem. Rev.*, **53**, 85 (1953).

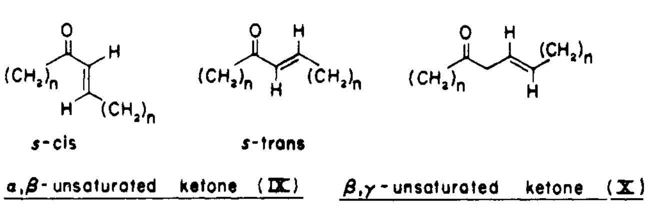
(7) The abnormally high ϵ at 230 mμ, instead of the expected(6) 13,000–14,000, may be attributed to the contribution of the unsaturated semicarbazone at that wave length. Testosterone semicarbazone, for example, (λ_{max} 270 mμ, ϵ 22,700) exhibits an ϵ-value of 7,200 at 230 mμ.

CHART I



1714 (saturated ketone), a considerably weaker band at 1670 (unsaturated ketone), an intense band at 1624 of about one-half the area of the 1670 band (C=C stretching), and a strong band at 987 cm.$^{-1}$ characteristic of a *trans* double bond. Neither in film nor in carbon disulfide was a band characteristic of a *cis* olefin found, which is in accord with the finding of Leonard and Owens[4] that in rings of greater than ten carbon atoms the *trans* olefin is greatly favored over the *cis* compound.

In the carbonyl region, apart from the bands described, a weaker but definite band appeared at 1695 (CCl_4 $CHCl_3$), 1693 (film), and 1692 cm.$^{-1}$ (CS_2). This band does not appear to be due to an impurity since all samples of IX as well as a sample of the monoketone cycloheptadec-2-en-1-one exhibited a peak at this position. It is probable that IX exists as a mixture of *S-cis* and *S-trans* isomers and the peak at 1695 cm.$^{-1}$ is due to the *S-cis* conformation while the 1670 cm.$^{-1}$ band may be assigned to the *S-trans* unsaturated ketone. These two conformations are



The propensity of *S-cis* unsaturated ketones to rearrange to the β,γ-unsaturated isomers has been noted by Noack and Jones[8] and would account for the presence of significant quantities of X in the crude dehydrobromination mixture. However, it must be noted that the extinction coefficient of IX in the ultraviolet (ε 13,800) is unusually high[9] if a significant portion of compound is present in an *S-cis* configuration. Additional support for the presence of *S-cis* isomer comes from the pronounced intensity of the C=C stretching frequency band at 1624 cm.$^{-1}$ in the infrared, which is consistent[10] for an *S-cis* and not for an *S-trans* ketone. The C=C stretching frequency band for the *S-trans* compound may be concealed beneath this 1624 cm.$^{-1}$ band, or a shoulder appearing at about 1640 cm.$^{-1}$ may be due to the *S-trans* compound. The possibility cannot be excluded, however, that the 1695-cm.$^{-1}$ peak is not, in fact, a carbonyl band and is instead a combination band or a Fermi resonance band due to the absorption at 987 and 725 cm.$^{-1}$.[11]

The principal features of interest in the n.m.r. spec-

---

[8] K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

[9] The extinction coefficient of *S-cis* α,β-unsaturated ketones is reported to range between 4700–7200; R. B. Turner, D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951), and references therein.

[10] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960); K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

[11] The broad band appearing at 725 cm.$^{-1}$ was also found in cycloheptadecanone and in cycloheptadecane-1,9-dione and may be attributed to a rocking mode of the $(CH_2)_n$ groups.

trum of IX (Fig. 2) were the vinylic proton peaks, the C-2 proton appearing as a doublet at 357 and 372.5 c.p.s., while the C-3 proton appeared as a sextet spaced between 393 and 422.5 c.p.s.[12] The coupling constant of the doublet, $J = 15.5$ c.p.s., is the order that would be expected for a pair of *trans* protons.

The β,γ-unsaturated diketone X, which had no strong selective absorption in the ultraviolet, exhibited in the infrared a single intense carbonyl band at 1718 cm.$^{-1}$ (CCl_4) and a band at 971 cm.$^{-1}$ characteristic of a *trans* olefin (Fig. 1). As in the case of IX no evidence was found for the presence of a *cis* olefin. Both the α,β- and β,γ-isomers showed a band at 1410 cm.$^{-1}$ due to the methylene groups adjacent to the carbonyl functions[13] with the more pronounced peak being present in the spectrum of X. Although a satisfactory elemental analysis could not be obtained for X, a crystalline bissemicarbazone with correct analysis was prepared. The derivative had only a single maximum at 229 mμ (ϵ 20,800) which demonstrated that the double bond had not conjugated. Catalytic reduction of X gave an almost quantitative yield of cycloheptadeca-1,9-dione which established that no skeletal rearrangement had occurred during dehydrobromination and left the β,γ-structure as the only reasonable one. The n.m.r. spectrum (Fig. 3), which was confirmatory for this structure, exhibited the olefinic protons as a series of at least six lines centered at 313 c.p.s. with the outer peaks separated by 10 c.p.s. The doubly activated methylenic protons appeared as a doublet (containing additional unresolved fine structure) at 171 and 176 c.p.s. while broad absorption centered at 137.5 c.p.s. is attributed to the balance of methylene groups adjacent to the carbonyl functions. Base-catalyzed exchange carried out in methanol-d_4 supported these assignments since the peaks in the 171–176-c.p.s. region disappeared the most rapidly, as would be expected for the doubly activated methylene position, followed then by diminution of absorption in the 137 c.p.s. region. The deuterated material was reisolated after sixteen hours of deuterium exchange and showed, in the infrared, complete disappearance of the aforementioned α-methylene absorption at 1410 cm.$^{-1}$ and appearance of the anticipated C–D bands in the 2000–2200-cm.$^{-1}$ region. The β,γ-isomer X is schematically depicted with no conformational implications since it is not known whether or not the carbonyl and double bond are coplanar.

The mass spectrum[5] of X was anomolous. In two different analyses the compound demonstrated a molecular ion peak at the anticipated position of mass 264, but the major peak appeared at mass 250 in one run and at 262 in the second run. Since in each case the samples were stored in glass for approximately one month prior to the mass spectral determination it is not known whether chemical modification occurred on storage or if the differences are due to some variation in analytical procedure. For additional mass spectral investigation, X was reduced with lithium aluminum hydride to the unsaturated diol XI which exhibited a principal mass peak at 250. The loss of mass 18 is almost certainly due to the elimination of water, a behavior not unexpected for a β,γ-unsaturated alcohol.

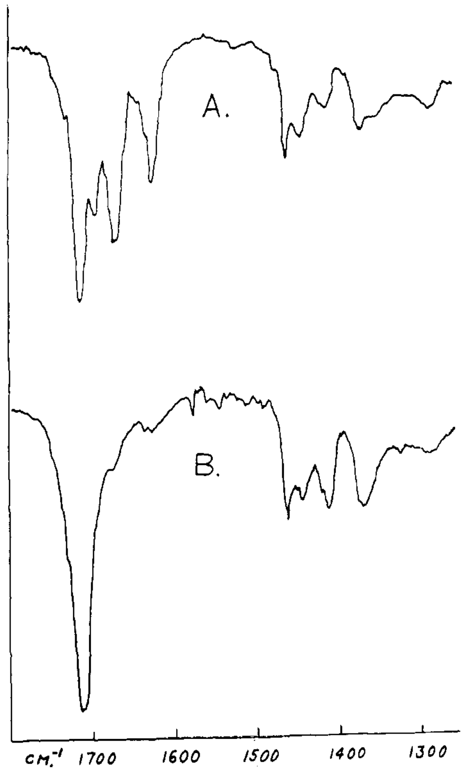


Fig. 1.—The infrared spectrum of A, cycloheptadec-2-ene-1,10-dione (IX); and B, cycloheptadec-3-ene-1,10-dione (X) determined in carbon tetrachloride.

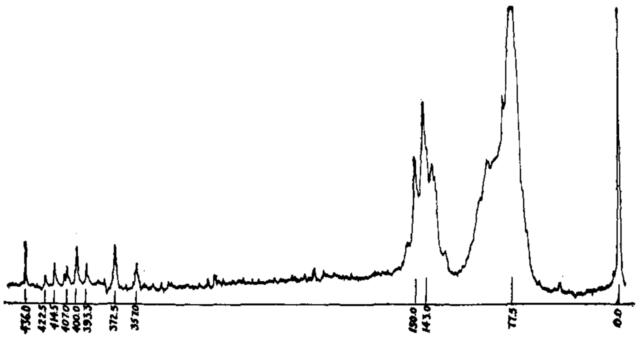


Fig. 2.—N.m.r. spectrum[12] of cycloheptadec-2-ene-1,10-dione (IX) determined in deuteriochloroform (c.p.s.).

The partial conversion of IX to X was readily demonstrable by treating the α,β-unsaturated ketone with calcium carbonate in dimethylformamide or by stirring an ether or benzene solution of the substance with alkaline alumina. The α,β-unsaturated ketone remained the predominant isomer in each case but because of low recovery due to the formation of polar by-products it is not possible to state whether or not this is a reflection of the true stability of the two isomers. It was also possible to effect the partial conversion of the β,γ-unsaturated to the α,β-unsaturated isomer under identical conditions but with extremely low product recovery.

It would appear to be pertinent to comment on the structure of the large-ring α,β-unsaturated monoketones (C_{10} to C_{14}) which have been reported[4] to exhibit unusually low ϵ-values in the ultraviolet and whose infrared spectra indicate the presence of both satu-

---

[12] We wish to thank Mr. Thomas Wittstruck for the n.m.r. determinations which were carried out in deuteriochloroform solution with tetramethylsilane as internal standard, utilizing a Varian 4302 60 Mc./sec. spectrometer. Peak positions are reported in c.p.s. downfield from the standard.

[13] G. Chiurdoglu, Th. Doehard, and B. Tursch, *Bull. soc. chim. France*, 1322 (1960).

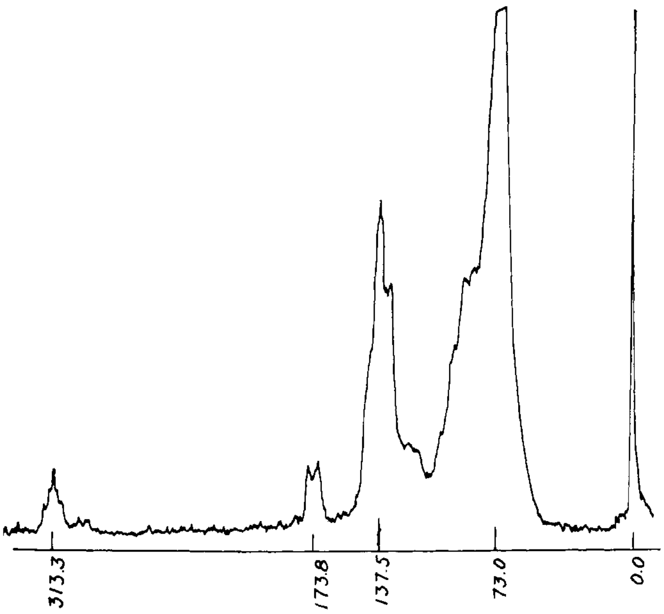


Fig. 3.—N.m.r. spectrum[12] of cycloheptadec-3-ene-1,10-dione (X) determined in deuteriochloroform (c.p.s.).

rated and unsaturated carbonyl functions, while semicarbazones derived from these substances possess ultraviolet spectral maxima characteristic of saturated rather than unsaturated carbonyl derivatives. These results, which have been explained[4] on the basis of steric inhibition of resonance, are probably due to a preponderance of β,γ-unsaturated isomer in the unsaturated ketone mixture.

The synthesis of cycloheptadeca-1,9-dione (VI) and an unsuccessful attempt to prepare the requisite bromo diketone VIII *via* this compound are also briefly documented (Chart I). Civetone (I) was converted by conventional means to the cycloethylene ketal[14] II which on treatment with monoperphthalic acid gave the 9,10-oxido ketal III. Reduction of III with lithium aluminum hydride in ether solution produced the hydroxyketal IV, and acid hydrolysis of the ketal moiety yielded the ketol V as a *d,l*-pair. It should be noted that attack of hydride on the oxide at either C-9 or C-10 yields the same compound. Chromic acid oxidation of the ketol gave cycloheptadecane-1,9-dione (VI) as a crystalline solid.[15] Attempts to monobrominate VI led invariably to polyhalogenated substances.

Experimental[16]

1-Ethylenedioxycycloheptadec-9-ene (II).—A sample of civetone[3] (I) (10.0 g.) was dissolved in benzene (200 ml.) containing ethylene glycol (20.0 ml.) and *p*-toluenesulfonic acid (200 mg.), and the solution was boiled for 20 hr. with continuous separation of water. The cooled solution, after washing with dilute bicarbonate and water, was taken to dryness, leaving a crystalline residue of II, m.p. 36–41°[17]; yield, 12.0 g.; no carbonyl absorption in the infrared.

1-Ethylendioxy-9-hydroxycycloheptadecane (IV).—The ketal from the foregoing procedure (11.9 g.) in ether (100 ml.) at 0° was treated with a cold solution of monoperphthalic acid (2 equiv.) in ether (300 ml.), and the mixture was stored in a refrigerator for 25 hr. Titration indicated the uptake of 1 equiv. of peracid. The solution was washed with sodium bicarbonate solution, then water, and dried over sodium sulfate. Evaporation gave 1-ethylenedioxy-9,10-oxidocycloheptadecane (III) (12.5 g.) as an oil solidifying below room temperature. Without purification, III was taken up in dry ether (100 ml.) and added to a suspension of lithium aluminum hydride (5.0 g.) in ether (200 ml.). The mixture was boiled for 7 hr. and then allowed to stand for 16 hr. at room temperature. Saturated sodium sulfate solution was cautiously added dropwise until solid adhered to the sides of the reaction vessel, and then solid sodium sulfate was added. The ether solution was decanted, the residue was thoroughly washed with ether, and the combined solutions were evaporated yielding 11.5 g. of IV, m.p. 50–52°. An analytical sample was obtained by recrystallization from pentane, m.p. 51–52°.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61. Found: C, 73.30; H, 11.71.

9-Hydroxycycloheptadecanone (V).—The hydroxyketal IV (2.0 g.) was allowed to stand in a mixture of acetone (30 ml.), water (2.0 ml.), and 10% hydrochloric acid (1.0 ml.) for 5 hr. at room temperature. Dilution with water and ether extraction gave V, 1.28 g., m.p. 76–77°. The melting point was unchanged on further crystallization from pentane.

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.20; H, 12.12.

Cycloheptadecane-1,9-dione (VI).—A solution of V (0.2 g.) in 5 ml. of acetone (previously distilled from potassium permanganate) was cooled in an ice bath and treated dropwise with Jones' reagent[18] (8 *N* chromic acid in sulfuric acid) until the color of the reagent persisted. The mixture was allowed to stand at 0° for 5 min. before the addition of water and isolation of product by ether extraction; yield, 0.18 g., m.p. 62–64°. Crystallization from aqueous acetone gave the analytical sample of VI, m.p. 63–65°.[15] The infrared bands of interest are listed in Table I (see p. 3103).

Anal. Calcd. for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.46; H, 11.37.

9-Bromo-10-hydroxycycloheptadecanone (VII).—Civetone (0.25 g.) was dissolved in a mixture of purified dioxane (3.0 ml.) and dilute perchloric acid (0.4 ml., 0.5 *N*). N-Bromoacetamide (0.18 g.) was added in one portion, and the resulting clear solution was left for 1.5 hr. at room temperature. The excess N-bromo reagent was destroyed by the addition of dilute sodium bisulfite and the product isolated by ether extraction. The extract was washed with water, dried over sodium sulfate, and evaporated leaving the bromohydrin (VII) as a colorless oil; yield, 0.3 g. The analytical sample, obtained as an oil, was prepared by chromatography on a silica gel thin-layer plate utilizing 97% benzene–3% ethyl acetate as solvent. Apart from the infrared bands listed in Table I, hydroxyl absorption was seen at 3540 cm.$^{-1}$ (film).

Anal. Calcd. for $C_{17}H_{31}BrO_2$: C, 58.79; H, 9.00. Found: C, 59.01; H, 8.82.

2-Bromocycloheptadeca-1,10-dione (VIII).—Crude bromohydrin (VII) (0.3 g.) was dissolved in acetone (15 ml.) and treated with 0.8 ml. of Jones' reagent.[18] After 5-min. reaction at room temperature a few drops of methanol were added to destroy the excess chromic acid, and the mixture was diluted with water. The bromo diketone was extracted with ether, and the extract was washed, dried, and evaporated *in vacuo*, leaving 0.24 g. of VIII as an oil which crystallized only upon cooling below room temperature. The material was essentially homogeneous on thin-layer chromatography with 97% benzene–3% ethyl acetate as solvent. An analytical specimen was obtained as an oil by column chromatography on silica gel with benzene as the eluting solvent: ultraviolet, $\lambda_{max}^{CH_3OH}$ 299 mμ; infrared, see Table I; n.m.r., quartet centered at 243 c.p.s.[12] due to coupling of the C-2 proton with the two protons at C-3. A first-order analysis indicates coupling constants of J = 8.7 and 6.2 c.p.s.

Anal. Calcd. for $C_{17}H_{29}BrO_2$: C, 59.13; H, 8.47. Found: C, 59.38; H, 8.61.

Cycloheptadec-2-ene-1,10-dione (IX).—The bromo diketone VIII (0.3 g.) was heated for 6 hr. in a boiling, stirred mixture of finely powdered calcium carbonate (0.4 g.) and dimethylformamide (10 ml.). The cooled mixture was filtered and, after the

---

[14] M. Stoll, J. Hulstkamp, and A. Rouve, *Helv. Chim. Acta*, **31**, 543 (1948).

[15] M. Stoll, M. Hinder, and L. Ruzicka, *ibid.*, **31**, 1176 (1948), reported VI as a liquid.

[16] Melting points are uncorrected. We are very grateful to Mr. Neville Bacon for infrared determinations which were carried out on a Beckman IR-7 with Bausch and Lomb replica grating.

[17] Lit.[14] m.p. of *cis* isomer, 19–21°; *trans* isomer, 49–50°.

[18] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

addition of water to the filtrate, the dehydrobromination products were extracted with ether. The washed and dried ether solution was taken to dryness leaving a yellow oil which was purified by chromatography on silica gel plates[19] with 18% ethyl acetate–82% benzene as developing solvent. Apart from traces of starting bromo compound and polar material remaining at the origin, two major zones were detected. The more polar zone, which had moved about 50% of the length of the plate, was eluted with ether yielding 90 mg. of α,β-unsaturated diketone IX as an oil. Rechromatography in the same system gave an analytical specimen: $\lambda_{\max}^{\mathrm{EtOH}}$ 227 mμ (ε 13,800); $\lambda_{\max}^{\mathrm{isooctane}}$ 220 mμ (ε 12,050); mass spectrum, principal peak 264. The infrared spectrum peaks are shown in Fig. 1 and Table I, while the n.m.r. spectrum is shown in Fig. 2.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.05; H, 10.41.

A bissemicarbazone of IX was prepared by treatment with excess semicarbazide hydrochloride in aqueous alcohol containing sodium acetate. The semicarbazone, after recrystallization from methanol–water melted at 225° dec.; $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (ε 24,400) and 263 mμ (ε 22,500).

Anal. Calcd. for $C_{19}H_{34}N_6O_2$: C, 60.29; H, 9.05; N, 22.20. Found: C, 60.54; H, 9.19; N, 21.16.

Cycloheptadec-3-ene-1,10-dione (X).—The less polar zone from the dehydrobromination of VIII had moved about 60% of the length of the silica gel plate. Elution of this zone with ether gave 65 mg. of the β,γ-unsaturated ketone X as an oil which showed no strong selective absorption in the ultraviolet. The infrared spectrum peaks are shown in Fig. 1 and Table I and the n.m.r. spectrum in Fig. 3. The mass spectral determination is noted in the discussion section. A satisfactory elemental analysis could not be obtained with carbon values consistently running about 2% low.

A bissemicarbazone of X, prepared as described under IX, underwent gradual decomposition when heated above 250° and exhibited $\lambda_{\max}^{\mathrm{EtOH}}$ 229 mμ (ε 20,800).

Anal. Calcd. for $C_{19}H_{34}N_6O_2$: C, 60.29; H, 9.05; N, 22.20. Found: C, 59.80; H, 9.44; N, 22.03.

Equilibration of IX and X. A.—A solution of α,β-unsaturated ketone IX (45 mg.) in dimethylformamide (3 ml.) was treated with calcium carbonate (0.1 g.) and boiled for 5 hr. Conventional work-up and thin-layer chromatography yielded 6.2 mg. of β,γ-unsaturated compound X and 25 mg. of IX.

B.—A solution of 25 mg. of IX in 5 ml. of benzene was stirred for 25 hr. with 0.25 g. of Woelm alumina, activity grade I. Removal of alumina, followed by thin-layer chromatography gave 4.0 mg. of X and 7.1 mg. of IX.

C.—The equilibration of a small sample of β,γ-unsaturated isomer X as described in B led to the formation of the α,β-unsaturated isomer which was characterized by thin-layer chromatography and by infrared spectrum. While quantitative data was not obtained, the two isomers appeared to be present in about equal quantities but recovery was extremely low.

Reduction of IX to Cycloheptadecane-1,9-dione (VI).—The reduction of 24 mg. of IX was carried out in 2 ml. of absolute ethanol over 25 mg. of 5% palladium-on-barium sulfate at 20 p.s.i. and 25°. After 2 hr. the catalyst was removed and washed with acetone, and the combined solutions were treated with water to the point of turbidity. Chilling afforded 15 mg. of VI, m.p. 63–65°,[5] which was identical in all respects with the sample prepared by the oxidation of V.

Reduction of X to Cycloheptadecane-1,9-dione.—The catalytic reduction of 20 mg. of X carried out exactly as described in the preceding section, gave 11 mg. of VI, m.p. 64–65°, whose infrared spectrum chromatographic behavior and mass spectral pattern were identical with an authentic sample. The crystalline, but low melting mother liquors, were shown by chromatography and mass spectrum to consist almost exclusively of VI with only small amounts of impurities.

Cycloheptadec-3-ene-1,10-diol (XI).—A solution of 24 mg. of cycloheptadec-3-ene-1,9-dione (X) in 5 ml. of dry ether was added to 25 mg. of lithium aluminum hydride in 5 ml. of ether, and the mixture was stirred for 1 hr. at room temperature. The work-up was carried out with sodium sulfate as described under the preparation of IV. Crystallization of the residue from pentane yielded 20 mg. of the crystalline diol, m.p. 73–75°, $\nu_{\max}^{\mathrm{KBr}}$ 3 70 (OH), 989 cm.$^{-1}$ (HC=CH). Although XI is undoubtedly a mixture of 1,10-*cis* and -*trans* diols, only one spot appeared on thin-layer chromatography. An analytical specimen, from pentane, melted at 78° and exhibited the main peak in the mass spectrum at 250.

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 75.67; H, 11.96.

Deuterium Exchange of X.—A 25-mg. sample of X was dissolved in 0.25 ml. of methanol-d_4 and the n.m.r. spectrum traced in the conventional manner and also scanned on an oscilloscope. The C-2 methylene group appeared in the 175-c.p.s.[2] region while the balance of methylene groups adjacent to ketonic functions appeared in the 135-c.p.s. region. A drop of sodium deuteriomethoxide solution was added and the spectrum followed on the oscilloscope. Exchange was seen to occur most rapidly in the 175-c.p.s. region while protons in the 135-c.p.s. region exchanged more slowly. Partial isomerization to the α,β-unsaturated ketone was seen to be a much slower process. After standing for 16 hr. the deuterated X was reisolated by thin-layer chromatography. The infrared (film) demonstrated complete disappearance of the 1410-cm.$^{-1}$ band (CH_2—C=O), saturated carbonyl absorption at 1700 cm.$^{-1}$ and *trans* double bond absorption at 975 cm.$^{-1}$.

---

[19] For spotting, the silica gel layer was 0.25 mm. thick, while for preparative purposes a 1-mm. layer was utilized.