desired product. After several recrystallizations from nitromethane–ether, a small quantity of pure material was obtained, m.p. 131.5–133.5°.

Anal. Calcd. for $C_{11}H_{13}N_3O_9S_3$: C, 30.91; H, 3.07; N, 9.83. Found: C, 30.89; H, 3.10; N, 10.10.

1,2-Dideuterio-1-dimethylsulfonio-2-methylthioethene 2,4,6-Trinitrobenzenesulfonate.—Deuterated acetylene was prepared by adding deuterium oxide (99.5 mole % min.) to calcium carbide at a rate sufficient to maintain a constant slow flow of gas through a Drierite drying tube into a reaction vessel containing 2.0 g. (0.0050 mole) of **1** in approximately 15 ml. of nitromethane. Total reaction time was 8.5 hr. The reaction mixture was worked up as above to yield product, m.p. 128–129.5°, and trimethylsulfonium 2,4,6-trinitrobenzenesulfonate. A mixture melting point between the deuterated and undeuterated adducts showed no depression, and the n.m.r. of **8** was identical with that of **7** with the exception of the absence of the two doublets from the vinyl protons.

Synthesis of 1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6. Novel Lithium–Ammonia Reduction of the γ,δ-Diacetoxy α,β-Unsaturated Ketone System[1a]

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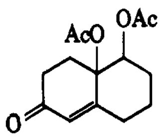
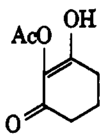
1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (III) has been synthesized *via* careful, stepwise Robinson annelation of dihydropyrogallol acetate with ethyl vinyl ketone, in a sequence analogous to the previously reported preparation of 1,9-*cis*-diacetoxy-$\Delta^{5,10}$-octalone-6 (I). Treatment of III and I with lithium in ammonia converted these substances to 1-methyl-$\Delta^{9,10}$-octalone-2 (XII) and $\Delta^{9,10}$-octalone-2 (XIV), respectively. A mechanism for this novel reduction, involving successive carbanionic elimination of the two acetoxyl groups, is presented and discussed.

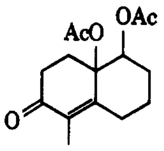
We have previously reported the synthesis of 1,9-*cis*-diacetoxy-$\Delta^{5,10}$-octalone-6 (I) by careful, stepwise Robinson annelation of dihydropyrogallol acetate (II) with methyl vinyl ketone.[2] In this paper the preparation of the ethyl vinyl ketone analog, 1,9-*cis*-diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (III), and the novel reduction of III and I with lithium in ammonia are described.



I



II



III

Synthesis of 1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (III).—The synthesis of III was undertaken as a continuation of our studies[2] of intermediates potentially useful for elaboration to diterpenoids of the rosenonolactone type and was accomplished by essentially the same path used for the synthesis of I. Michael addition of II to ethyl vinyl ketone smoothly afforded 80% of the adduct IV, m.p. 68.5–69.5°. Cyclization of IV with pyrrolidine and acetic acid was much slower than cyclization of the corresponding methyl vinyl ketone adduct.[2] However, upon treatment of IV with excess pyrrolidine and acetic acid at room temperature for 72 hr., a 67% yield of ketol V, m.p. 217–217.5°, was obtained. The hydronaphthalenic skeleton of the ketol was evident from its n.m.r. spectrum. It is assigned the *cis* ring fusion (as shown in V) by analogy to the corresponding ketol in the methyl vinyl ketone series, according to our postulate[2] of stereoselective cyclization of *cis*-fused ring systems when a bulky angular substituent is present.[3] Further work to substantiate this assignment is planned. No experimental evidence is available concerning the configuration of the C-5 methyl group.[4]

No bridged ketol isomeric to V was isolated, but 5% of a substance, m.p. 118–119°, with an analysis indicating a molecular formula $C_{11}H_{16}O_4$ was obtained. This material has been tentatively assigned the dioldione structure VI on the basis of its infrared and n.m.r. spectra, and its conversion, upon refluxing with *p*-toluenesulfonic acid in benzene, to 5-methyl-6-hydroxytetralone-1 (VII).[5] This structural assignment deserves to be the subject of further investigation. Although formation of VI from IV could result from displacement on the tertiary acetate carbonyl at any stage during the prolonged treatment with pyrrolidine and acetic acid, this result was not expected and is intriguing.

Dehydration of ketol V to the desired α,β-unsaturated ketone VIII proved to be the most troublesome step in the synthesis of III. An extended study of dehydration conditions was necessary in order to find those which would effect formation of VIII without causing subsequent aromatization to VII. Heating with *p*-toluenesulfonic acid in benzene, the conditions which effected the desired dehydration successfully in the methyl vinyl ketone series,[2] yielded only VII plus recovered starting material. Very brief treatment of V with dilute hydrogen chloride in methanol gave 88% of 5-methyl-6-methoxytetralone-1 (IX).[6] However,

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[1] (a) A portion of this work was presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964. We wish to thank Dr. Morris Brown for making this presentation. (b) National Science Foundation Graduate Teaching Assistant Summer Fellow, 1963.

[2] T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963).

[3] J. A. Marshall and W. I. Fanta [*J. Org. Chem.*, **29**, 2501 (1964)] showed selective formation of a *cis*-fused ring system when the angular substituent was methyl, and selective formation of a *trans*-fused system when the angular substituent was hydrogen. These workers also presented n.m.r. evidence proving the hydronaphthalenic skeleton of a ketol previously prepared by McQuillin and assigned a *cis*-fused structure: R. Howe, F. J. McQuillin, and R. Temple, *J. Chem. Soc.*, 363 (1959), and references cited therein.

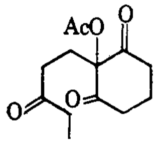
[4] Since V is a *cis*-decalin derivative, this methyl group can adopt an equatorial conformation in either configuration.

[5] A. J. Birch, J. A. K. Quartey, and H. Smith, *J. Chem. Soc.*, 1768 (1952); J. W. Ralls, W. C. Wildman, K. E. McCaleb, and A. L. Wilds, *Chem. Abstr.*, **49**, 1813 (1955).

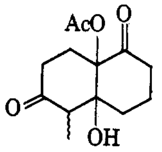
[6] R. H. Martin and R. Robinson, *J. Chem. Soc.*, 491 (1943).

with *p*-toluenesulfonic acid and calcium chloride[7] in refluxing acetone for 30 min., a 74% yield (based on unrecovered starting material) of VIII, m.p. 77–78°, was achieved.

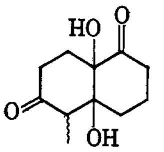
Reduction of VIII with 1 equiv. of purified sodium borohydride[8] afforded 44% of a crystalline α,β-unsaturated ketone, m.p. 98.5–99.5°. This substance was assigned structure X, in which the acetoxyl had migrated to the newly generated secondary hydroxyl group, on the basis of its n.m.r. spectrum which showed a quartet at 4.70 p.p.m. due to the hydrogen on the acetoxyl-bearing carbon of the product. This characteristic quartet was used[2] to assign the analogous structure XI to the corresponding sodium borohydride reduction product in the methyl vinyl ketone series. Acetylation of X with isopropenyl acetate and *p*-toluenesulfonic acid afforded III, m.p. 119–120°, in 74% yield.



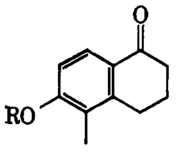
IV



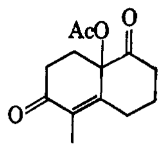
V



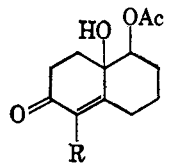
VI



VII, R = H
IX, R = CH$_3$



VIII



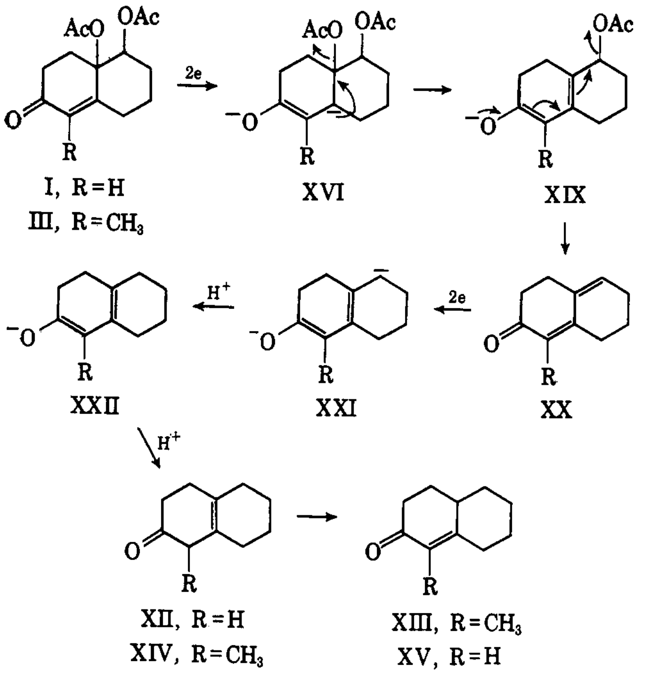
X, R = CH$_3$
XI, R = H

Lithium–Ammonia Reduction of III and I.—Among other potentially interesting reactions of III and I, their reduction with lithium in ammonia was investigated. Treatment of tetrahydrofuran solution of III with lithium in ammonia, followed by an ammonium chloride work-up, afforded an oily product whose only strong carbonyl absorption in the infrared was a single sharp band at 5.81 μ. Thus, both acetoxyls had been lost and only a saturated ketone group remained. Treatment of III with liquid ammonia alone gave a quantitative recovery of starting material.

The crude lithium–ammonia product was separated by v.p.c. into one principal constituent (at least 80% of the mixture) and several minor ones. The principal product was readily identified as 1-methyl-$\Delta^{9,10}$-octalone-2 (XII) by its isomerization in base to an α,β-unsaturated ketone, presumably 1-methyl-$\Delta^{1,9}$-octalone-2 (XIII), and by its conversion to the red 2,4-dinitrophenylhydrazone of XIII, which was compared with an authentic sample. The second most abundant product from the reduction was spectrally identified as XIII.

Similarly, the diacetate I derived from methyl vinyl ketone and dihydropyrogallol acetate suffered loss of all acetoxyl absorption on treatment with lithium in ammonia. The crude oily product (74%) showed only one peak (after a small peak apparently due to unremoved solvent) on v.p.c. analysis. This material proved to be a mixture of *ca.* 90% of $\Delta^{9,10}$-octalone-2 (XIV) and *ca.* 10% of $\Delta^{1,9}$-octalone-2 (XV). The crude product afforded a mixture of 2,4-dinitrophenylhydrazones (42% yield) from which the red derivative of XV could be isolated and was found to be identical with an authentic sample. Use of mild conditions for preparation of the 2,4-dinitrophenylhydrazone afforded a yellow derivative, presumably formed from XIV without isomerization to XV.[9]

Chart I



The reduction of I to XIV and III to XII can be interpreted as shown in Chart I. It is well known that the reduction of α,β-unsaturated ketones with lithium in ammonia proceeds *via* a species, *e.g.*, XVI,[10] which possesses carbanionic character at the β-position.[11] Elimination of acetate anion from XVI, presumably from the conformation in which the β-carbanion orbital is *trans* to the leaving group, is certainly reasonable. Lithium reduction of allylic acetates,[12] allylic ethers,[12] α-hydroxy ketones,[13] and the γ-hydroxy α,β-unsaturated ketone XVII to XVIII[14] can be interpreted as examples of the type of carbanionic elimination step depicted in XVI → XIX.

The derived species XIX is the enolate anion from an α,β-unsaturated ketone and could readily eliminate the remaining acetoxyl, as shown, to afford XX. This dienone would then be subject to further reduction by the lithium–ammonia medium *via* XXI to XXII.

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[7] E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, **78**, 2318 (1956).

[8] C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).

[9] A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953). Details of the melting point behavior observed and previously reported for 2,4-dinitrophenylhydrazones of XIV and XV are given in the Experimental part.

[10] Species XVI and XXI have been arbitrarily shown as dianions, implying addition of two electrons before elimination to XIX or protonation to XXII. It is more probable that XVI and XXI should be drawn as anion radicals, with addition of the second electron occurring after dispersal of the carbanionic charge, but depiction is abbreviated by use of dianions: *cf.* G. Stork and J. Tsuji, *J. Am. Chem. Soc.*, **83**, 2783 (1961).

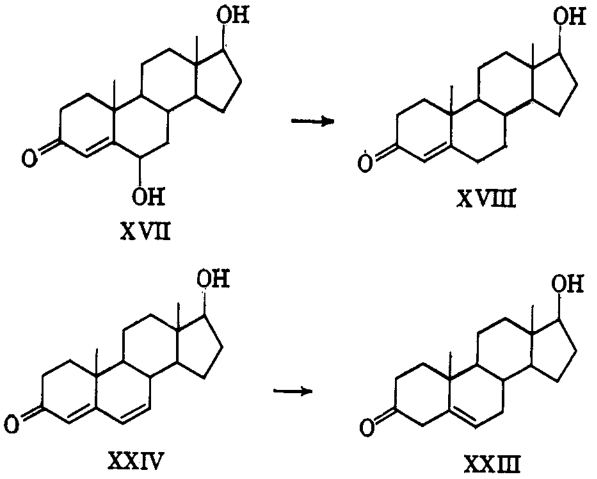
[11] G. Stork and S. D. Darling, *ibid.*, **82**, 1512 (1960); G. Stork and J. Tsuji, ref. 10; M. Tanabe, J. W. Chamberlin, and P. Y. Nishiura, *Tetrahedron Letters*, 601 (1961).

[12] A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *J. Chem. Soc.*, 1969 (1957). In this work the reducing medium was lithium in ethylamine.

[13] P. A. Mayor and G. D. Meakins, *ibid.*, 2800 (1960).

[14] C. Amendolla, G. Rosenkranz, and F. Sondheimer, *ibid.*, 1226 (1954).

Ammonium chloride quenching of a mixture containing an enolate anion like XXII has been observed to afford the β,γ-unsaturated ketone XXIII from the reduction of XXIV.[15] It will be of interest to see whether similar carbanionic elimination, and subsequent reduction of the newly generated unsaturated ketone, will occur in other systems with suitably situated leaving groups.



XVII XVIII

XXIV XXIII

Experimental

Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken either in an open capillary or on a micro hot stage; those of analytical samples are corrected. Boiling points are uncorrected. Ultraviolet spectra were determined in 95% ethanol solution on a Bausch and Lomb Spectronic 505 recording spectrophotometer. Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam recording spectrophotometer. N.m.r. spectra were determined on 20% solutions in carbon disulfide (unless otherwise stated) containing 1% tetramethylsilane, on a Varian DP-60 spectrometer. Spectra were calibrated by the audio side-band method with subsequent interpolation. V.p.c. was done on a Wilkens A-90-P2 chromatograph.

2-Acetoxy-2-(3-oxopentyl)cyclohexane-1,3-dione (IV).—To 5.00 g. (0.0294 mole) of 2-acetoxycyclohexane-1,3-dione[2] (II), m.p. 154–156°, were added 2.68 g. (0.0319 mole) of ethyl vinyl ketone, b.p. 100–102° (prepared by condensation of propionyl chloride with ethylene,[16] followed by distillation from sodium benzoate[17]), and 1 ml. of a solution of one pellet of sodium hydroxide in 10 ml. of absolute methanol. This mixture was heated on the steam bath for 45 min., cooled, and neutralized with 0.025 ml. of acetic acid. Evaporation of excess methanol and ethyl vinyl ketone under reduced pressure afforded a residue which crystallized from ether to give 5.97 g. (80%) of IV, m.p. 59–61°. Recrystallization from hexane containing a little acetone afforded material with m.p. 68.5–69.5°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.75 (sh) and 5.82 μ; n.m.r., triplet centered at 0.93 ($\mathrm{CH_2C}H_3$), 1.94 ($\mathrm{C}H_3\mathrm{COO}$), quartet $-\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{C}H_2-\mathrm{CH_3}$ obscured among other bands in the 2–2.5-p.p.m. region.

Anal. Calcd. for $\mathrm{C_{13}H_{18}O_5}$: C, 61.40; H, 7.13. Found: C, 61.46; H, 7.15.

5-Methyl-9-acetoxy-10-hydroxydecalin-1,6-dione (V).—To a magnetically stirred solution of 42.3 g. (0.167 mole) of Michael adduct IV in 850 ml. of dry benzene was added 33.3 ml. (0.40 mole) of pyrrolidine, and then 25 ml. (0.44 mole) of glacial acetic acid was added dropwise (noticeable heating occurred). The yellow solution was stirred at room temperature for 72 hr. The entire reaction mixture was poured onto a column of 900 g. of acid-washed alumina. Elution with 2:3 acetone–hexane afforded 28.42 g. (67%) of nearly pure ketol V, m.p. 216–218°, after crude fractions were washed with ether. Recrystallization from acetone and acetone–hexane gave an analytical sample with m.p. 217–217.5°; $\lambda_{\max}^{\mathrm{Nujol}}$ 2.96, 5.73, and 5.82 μ; n.m.r. [in $\mathrm{(CD_3)_2C{=}O}$], doublet at 0.95 and 1.07 ($\mathrm{H}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{C}H_3$), 2.23 ($\mathrm{C}H_3\mathrm{COO}$), and 4.18 p.p.m. ($\mathrm{O}H$).

Anal. Calcd. for $\mathrm{C_{13}H_{18}O_5}$: C, 61.40; H, 7.13. Found: C, 61.52; H, 7.24.

From chromatographic fractions previously eluted with 1:3 acetone–hexane was obtained 1.885 g. (5%) of **5-methyl-9,10-dihydroxydecalin-1,6-dione** (VI), m.p. 117–119°. Recrystallization from benzene–hexane afforded material with m.p. 118–119°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.85, 2.92, and 5.82 μ; n.m.r., doublet at 0.94 and 1.07 ($\mathrm{H}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{C}H_3$) and 4.45 p.p.m. ($\mathrm{O}H$).

Anal. Calcd. for $\mathrm{C_{11}H_{16}O_4}$: C, 62.25; H, 7.60. Found: C, 62.41; H, 7.66.

Conversion of VI to 5-Methyl-6-hydroxytetralone-1 (VII).—A mixture of 0.191 g. (9.02×10^{-4} mole) of VI, 0.065 g. of *p*-toluenesulfonic acid monohydrate, and 8 ml. of benzene was refluxed for 12 hr. The red-brown solution was cooled and poured onto a column of 5 g. of acid-washed alumina. Elution with 1:3 acetone–hexane gave 0.059 g. (37%) of 5-methyl-6-hydroxytetralone-1 (VII), m.p. 197–199°. Recrystallization from acetone–water afforded material with m.p. 200–201° (lit.[5] m.p. 199–201°); $\lambda_{\max}^{\mathrm{Nujol}}$ 3.25 (broad), 6.05, 6.24, and 6.32 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 232 mμ (ϵ 13,800) and 289 mμ (ϵ 14,300) [lit.[5] $\lambda_{\max}^{\mathrm{EtOH}}$ 231 mμ (ϵ 13,200) and 287.5 mμ (ϵ 13,500)].

5-Methyl-9-acetoxy-$\Delta^{5,10}$-octalin-1,6-dione (VIII).—To a solution of 2.00 g. (7.87×10^{-3} mole) of ketol V in 100 ml. of refluxing reagent grade acetone was added 2.0 g. of calcium chloride[7] and 1.0 g. of *p*-toluenesulfonic acid monohydrate. The mixture was refluxed for 30 min., cooled, and filtered. The filtrate was reduced in volume under reduced pressure to *ca.* 20 ml. and then diluted with 200 ml. of hexane and poured onto a column of 60 g. of acid-washed alumina. Some precipitate formed upon addition of the hexane; this was poured onto the column with the rest of the mixture. Elution with 3:17 acetone–hexane afforded fractions containing 1.154 g. of crude VIII contaminated with a small amount of tetralone VII, m.p. 198–200°, which could be conveniently removed by extracting VIII from it with hot hexane. The residue from these extracts gave 1.097 g. of crude crystalline VIII. Recrystallization from acetone–hexane afforded the analytical sample with m.p. 77–78°; $\lambda_{\max}^{\mathrm{EtOH}}$ 247 mμ (ϵ 12,800); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.73, 5.96, and 6.12 μ.

Anal. Calcd. for $\mathrm{C_{13}H_{16}O_4}$: C, 66.08; H, 6.83. Found: C, 66.19; H, 6.97.

Elution with 1:1 acetone–hexane afforded 0.397 g. (20%) of recovered ketol V. Thus the yield of VIII, based on unrecovered starting material, was 74%.

1β-Acetoxy-5-methyl-9β-hydroxy-$\Delta^{5,10}$-octalone-6 (**X**).—To a solution of 2.418 g. (0.01024 mole) of dione VIII, m.p. 77–78°, in 60 ml. of absolute ethanol, cooled in an ice bath, was added a solution of 0.102 g. (0.0108 equiv.) of purified[18] sodium borohydride in 60 ml. of absolute ethanol, with stirring, over a 20-min. period. After 15 min. more, at room temperature, the volume was reduced *in vacuo* to *ca.* 40 ml. The yellow solution was acidified with dilute hydrochloric acid, 30 ml. of saturated sodium chloride solution was added, and the solution was extracted with three 100-ml. portions of chloroform. The organic layers were dried and evaporated, and the residue was chromatographed on 30 g. of acid-washed alumina. Elution with 3:7 acetone–hexane gave 1.064 g. (44%) of crude X, m.p. 73–87°. Recrystallization from acetone–hexane gave 0.877 g. (36%), m.p. 92–99°; the analytical sample had m.p. 98.5–99.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ 244 mμ (ϵ 13,200); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.85, 5.73, 5.96, and 6.12 μ; n.m.r., 1.72 ($\mathrm{C}H_3\overset{|}{\mathrm{C}}{=}\overset{|}{\mathrm{C}}-$), 2.05 ($\mathrm{C}H_3\mathrm{COO}$), and a quartet at 4.70 p.p.m. ($\overset{|}{\underset{|}{H\mathrm{C}}}\mathrm{OAc}$).

Anal. Calcd. for $\mathrm{C_{13}H_{18}O_4}$: C, 65.53; H, 7.61. Found: C, 65.58; H, 7.67.

1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (**III**).—To a solution of 0.393 g. (1.65×10^{-3} mole) of hydroxyketoacetate X, m.p. 98.0–99.5°, in 10 ml. of redistilled isopropenylacetate, b.p.

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(15) R. E. Schaub and M. J. Weiss, *Chem. Ind.* (London), 2003 (1961).

(16) According to an unpublished procedure of A. L. Wilds, *et al.*

(17) S. Archer, W. B. Dickinson, and M. J. Unser, *J. Org. Chem.*, **22**, 92 (1957).

(18) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

97–98°, was added a solution of 0.020 g. of *p*-toluenesulfonic acid monohydrate in 3 ml. of isopropenyl acetate, and the mixture was refluxed for 2 hr. Then *ca.* 10 ml. of the isopropenyl acetate was removed by distillation and replaced by 10 ml. of hexane. The resulting mixture was allowed to stand overnight in the refrigerator, whereupon a precipitate formed. Another 10 ml. of hexane was added, and the 0.181 g. of solid, m.p. 118–120°, was collected by decantation and washed with hexane. Chromatography of the supernatant liquid on 10 g. of acid-washed alumina afforded (with 3:17 acetone–hexane) an additional 0.161 g. of III, m.p. 116–118°, for a total yield of 0.342 g. (74%). The analytical sample was prepared by recrystallization from ether–hexane and had m.p. 119.5–120.0°; $\lambda_{\max}^{\mathrm{EtOH}}$ 247 mμ (ϵ 13,700); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.73, 5.96, and 6.12 μ; n.m.r., 1.71 $(\mathrm{C}H_3\overset{|}{\mathrm{C}}{=}\overset{|}{\mathrm{C}})$, 2.04 $(\mathrm{C}H_3\mathrm{COO})$, and a quartet at 4.89 p.p.m. $(H\underset{|}{\overset{|}{\mathrm{C}}}\mathrm{OAc})$.

Anal. Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.16; H, 7.08.

Lithium–Ammonia Reduction of III.—To 150 ml. of liquid ammonia was added *ca.* 0.12 g. (3 cm. of $^1/_8$-in. wire) of lithium. To the resulting blue solution was added 0.516 g. (1.84×10^{-3} mole) of diacetate III, m.p. 119–120°, dissolved in 12 ml. of anhydrous tetrahydrofuran (distilled from lithium aluminum hydride). The mixture was magnetically stirred for 5 min. and then crystalline ammonium chloride was added, discharging the dark blue color. The mixture was allowed to evaporate, and the residual material was washed thoroughly with three 150-ml. portions of anhydrous ether. Evaporation of the ether yielded 0.377 g. of oily product, which v.p.c. analysis (silicone SE-30 column at 200°) indicated to contain one major component (at least 80% of the material detected by the column) and five minor components. The major component was collected from the chromatograph and exhibited $\lambda_{\max}^{\mathrm{film}}$ 5.81 μ. This material decolorized potassium permanganate solution, and, when it was treated with ethanolic sodium hydroxide, strong ultraviolet absorption at 245 mμ developed, consistent with XII → XIII.

The v.p.c.-purified XII yielded a red 2,4-dinitrophenylhydrazone (prepared with heating), m.p. 177.5–178.5°. This derivative was compared with the 2,4-dinitrophenylhydrazone, m.p. 178.5–179.5° (lit.[19] m.p. 177°), of 1-methyl-$\Delta^{1,9}$octalone-2 (XIII) prepared from ethyl vinyl ketone and the pyrrolidine enamine of cyclohexanone,[20] and these were found to be identical in all respects. The mixture melting point was 178.5–179.5°.

One of the minor components of the reduction mixture (the second fraction, eluted directly after XII) was judged from its spectral properties [$\lambda_{\max}^{\mathrm{film}}$ 5.97 and 6.15 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 249 mμ (ϵ 9500); lit.[21] $\lambda_{\max}^{\mathrm{EtOH}}$ 249 mμ (ϵ 12,500)] to be XIII.

Lithium–Ammonia Reduction of I.—A solution of 0.200 g. (7.5×10^{-4} mole) of diacetate I in 4.9 ml. of dry tetrahydrofuran was added to a magnetically stirred solution of 0.05 g. of lithium in 60 ml. of liquid ammonia over a 4-min. period. The resulting solution was stirred for 8 min. before solid ammonium chloride was added to discharge the blue color. The ammonia was evaporated, and the mixture was partitioned between saturated sodium chloride solution and ether. The ether extracts were dried over magnesium sulfate and stripped to afford 0.084 g. of a light yellow oil (74% of the theoretical amount of XIV). V.p.c. analysis showed only one constituent after material of very low retention time (presumably solvent). The product peak had an infrared spectrum with $\lambda_{\max}^{\mathrm{film}}$ 5.82 (strong), 5.99 (weak), and 6.15 μ (weak), and other bands consistent with XIVcontaining a small amount of XV. On the basis of v.p.c. peak areas, the yield of XIV + XV was 55–60%. The crude product exhibited $\lambda_{\max}^{\mathrm{EtOH}}$ 238 mμ (ϵ 1600), which indicated that, of the mixture of XIV and XV contained therein, *ca.* 12% was XV [lit.[20] $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ (ϵ 17,400)].

Treatment of the product with base caused isomerization of XIV to XV, as indicated by an increase in absorption at 238 mμ. When the reduction product was treated with 2,4-dinitrophenylhydrazine reagent under the nonisomerizing conditions of Wilds and Nelson,[9] a yellow derivative with m.p. 163.0–163.5° was obtained; $\lambda_{\max}^{\mathrm{KBr}}$ 6.14, 6.27, 6.53, 6.66, 7.49, and 7.60 μ (lit.[9] m.p. 173.0–173.5° for the 2,4-DNP of XIV). When the reduction product was derivatized under the isomerizing conditions of Wilds and Nelson,[9] a mixture of 2,4-dinitrophenylhydrazones was obtained in 42% yield. The pure, red 2,4-DNP derivative of XV was separated by thin layer chromatography on silica gel G with chloroform and had m.p. 168–169° (lit. m.p. 168°,[22] 168–170°,[20] 180–181°[9]). The infrared spectrum of this derivative ($\lambda_{\max}^{\mathrm{KBr}}$ 6.18, 6.27, 6.57, 6.66, 7.51, and 7.66 μ) was identical with that of a red 2,4-DNP, m.p. 179–180°, of XV prepared by reaction of the pyrrolidineenamine of cyclohexanone with methyl vinyl ketone.[20]

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Hydrolysis of Alicyclic Perhalo Olefins[1]

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The reaction of several cyclic fluoro olefins (I) with hydroxide ion in solvents such as diglyme, dimethylformamide, and dimethyl sulfoxide gave high yields of salts of the corresponding 3-hydroxyperhalo-2-cycloalken-1-ones. The hydrogen analogs (II) of these salts were found to be extremely strong acids. The mechanism of the reaction and physical properties of the products are discussed.

In the course of preparing organofluoro compounds, we studied the reaction of several cyclic fluoro olefins (I)[2] with potassium hydroxide and observed unusual solvent effects.

Although no reaction was reported to occur between 1,2-dichlorohexafluorocyclopentene-1 (Ic) and potassium hydroxide in aqueous dioxane,[6] we found that 4 equiv. of base were consumed in diglyme or aprotic dipolar solvents, such as dimethyl sulfoxide. The product was the potassium salt of IIc. The same salt was also obtained by treating 1-chloro-2-methoxyhexafluorocyclopentene-1 (If) or 1-chloro-2-phenoxyhexa-

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(2) All of these compounds are known except Ig and Ih. These are prepared by the standard method of adding 1 equiv. of the anion to the appropriate olefin. See ref. 3–5.

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