One-half of the benzene solution yielded 10.6 g. of semisolid which was warmed with carbon tetrachloride. Chilling and filtration separated 1.76 g. of material, m.p. 139–166°, which after recrystallization from 85–95% methanol gave 1.03 g. (14%) of α-(*p*-tolylsulfonyl)-propionanilide (XVI), m.p. 171–173°, constant m.p. 172.5–173.5°.

Anal. Calcd. for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65. Found: C, 63.66; H, 5.70.

Residual material in the carbon tetrachloride resisted purification. Solid obtained from the other half of the benzene solution was washed with petroleum ether–benzene and subjected to systematic fractional crystallization from methanol, but the yield of XVI was not improved.

In a similar experiment with the same quantities of reagents, but with anisole rather than benzene as the solvent, the ethylmagnesium bromide was mixed with 10 ml. of anisole and added to ethyl *p*-tolyl sulfone in 150 ml. of anisole. The seemingly homogeneous mixture was stirred and then heated during 1.7 hr. to 100°. The mixture was cooled and phenyl isocyanate in 5 ml. of anisole added. After 3 hr., hydrolysis followed by concentration of the anisole phase gave semisolid which was washed with ether–petroleum ether and chromatographed on alumina. Recrystallization of the fraction eluted using benzene–ethanol gave 2.24 g. (15%) of XVI, m.p. 172–173.5°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of α,β-Epoxy Ketones. IV. The Synthesis of Cyclic β-Diketones

BY HERBERT O. HOUSE AND RICHARD L. WASSON[1]

RECEIVED MARCH 19, 1956

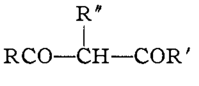
2-Benzalcyclopentanone oxide, 2-benzalcyclohexanone oxide and 2-benzalcycloheptanone oxide have been isomerized to 2-phenyl-1,3-cyclohexanedione, 2-phenyl-1,3-cycloheptanedione and 2-phenyl-1,3-cyclooctanedione, respectively, by treatment with boron trifluoride etherate in benzene solution. When the same cyclohexanone and cycloheptanone derivatives were treated with boron trifluoride in ether solution, the products were fluorohydrins. The thermal rearrangement of 2-cyclohexylidenecyclohexanone oxide produced spiro[5.6]dodecane-7,12-dione. Rearrangement of 3,4-epoxy-4-methyl-2-pentanone with boron trifluoride etherate in benzene solution formed 2,2-dimethyl-3-oxobutyraldehyde; the same oxide, when passed over alumina at 250°, yielded methyl isopropyl ketone.

The general preparative methods for β-dicarbonyl compounds,[2] the base-catalyzed acylation of ketones with esters (the Claisen condensation) and the acid-catalyzed acylation of ketones with acid anhydrides, are limited to compounds of the types I and II which can form stable enolates. Satisfactory synthetic procedures for compounds of type III have involved the alkylation of β-dicarbonyl compounds[2,3] and the acylation of the sodium enolates of mono-carbonyl compounds with acid chlorides.[2] The first of these synthetic methods is often complicated by O-alkylation of the β-diketone.[4] Similarly, the acylation of metallic enolates of carbonyl compounds with acid chlorides may lead to the formation of O-acyl derivatives (enol esters).[2] Our previous[5] and present studies have indicated that isomerization of the appropriate α,β-epoxy ketones can serve as a useful preparative method for dicarbonyl compounds of the types II and III.[6]

It was of interest to learn whether the same type of isomerization could be employed to prepare cyclic β-diketones of type IV. Five- and six-membered cyclic β-diketones (IV, n = 2 and 3) are readily accessible *via* intramolecular Claisen acylations[2]; the six-membered cyclic diketones (IV, n = 3) have also been prepared by the alkylation of dihydroresorcinol.[4] However, consideration of the difficulty with which seven-membered and larger carbocycles are formed and the reversible nature of the base-catalyzed acylations leads to the expectation that the Claisen reaction will be of little value for compounds of type IV in which n has values greater than three.[7] To explore the possibility that compounds of type IV could be prepared by isomerization of α-keto epoxides, a study of the 2-benzalcycloalkanone oxides (V) was undertaken.

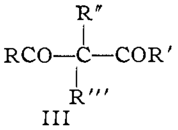
$RCO—CH_2—COR'$

I



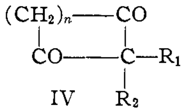
$$RCO—\overset{\overset{R''}{|}}{C}H—COR'$$

II



$$RCO—\underset{\underset{R'''}{|}}{\overset{\overset{R''}{|}}{C}}—COR'$$

III



IV

R_1 and R_2 = H, alkyl or aryl

2-Benzalcycloheptanone oxide (Va) and 2-benzalcyclohexanone oxide (Vb) were prepared by treatment of the corresponding unsaturated ketones VIa and VIb with alkaline hydrogen peroxide.[8] Repeated attempts to prepare 2-benzalcy-

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[1] Alfred P. Sloan Foundation Research Assistant, 1956.

[2] C. R. Hauser, F. W. Swamer and J. T. Adams, *Org. Reactions*, **8**, 59 (1954).

[3] H. Adkins, W. Kutz and D. D. Coffman, THIS JOURNAL, **52**, 3212 (1930); J. M. Sprague, L. J. Beckham and H. Adkins, *ibid.*, **56**, 2665 (1934).

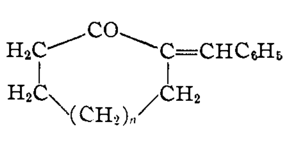
[4] For example see H. Setter and W. Dierichs, *Chem. Ber.*, **85**, 61 (1952).

[5] (a) H. O. House, THIS JOURNAL, **76**, 1235 (1954); (b) H. O. House and D. J. Reif, *ibid.*, **77**, 6525 (1955); (c) H. O. House, *ibid.*, **78**, 2298 (1956).

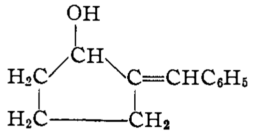
[6] Our investigations related to the preparation of compounds of the *type I will be reported in a subsequent paper of this series.*

[7] Cyclization of the appropriate keto esters for the preparation of diketones of type IV in which n = 4 or 5 yields instead of the α-acyl derivatives of cyclopentanone and cyclohexanone (reference 2). The related Dieckmann reaction has not been satisfactory for the preparation of carbocyclic ketones with more than six ring members [W. Dieckmann, *Ann.*, **317**, 27 (1901)]. Since such acylations are reversible, the use of high-dilution conditions would not be expected to favor medium- and large-ring formation unless the cyclic product could be removed from the reaction mixture as it was formed (*e.g.*, by means of the insolubility of the metal enolate of the product in the reaction solvent). The use of the Dieckmann reaction to prepare a heterocyclic ketone of medium ring size, reported by N. J. Leonard and R. C. Sentz [THIS JOURNAL, **74**, 1704 (1952)], appears to represent a case of this type.

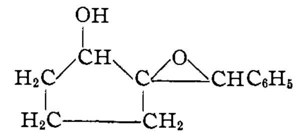
[8] The positions of maximum absorption (284–298 mμ) in the ultraviolet spectra of the 2-benzylcycloalkanones (VI) employed suggest that all of the unsaturated ketones have the *trans* configuration (see reference 9). However, the stereochemistry of the oxides V is



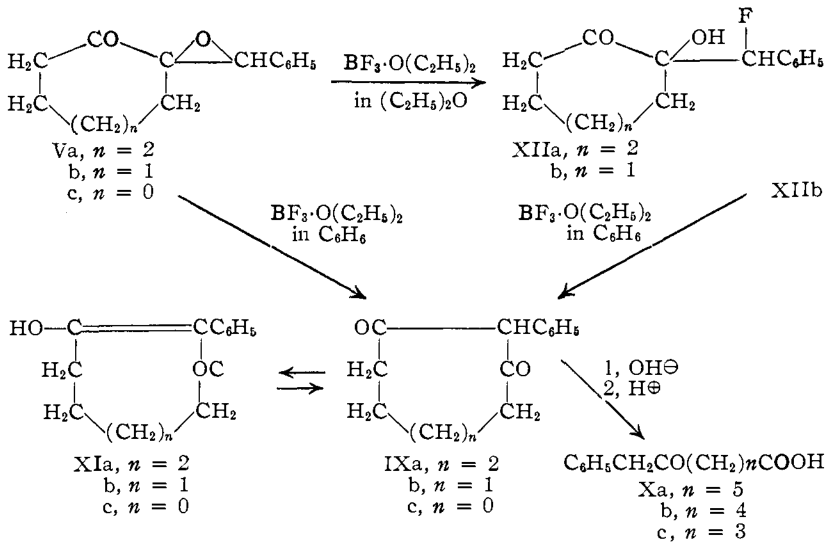
VIa, $n = 2$
b, $n = 1$
c, $n = 0$



VII



VIII



clopentanone oxide (Vc) from VIc in the same manner resulted either in the recovery of the starting material or in the isolation of benzoic acid. A related study[9] of the addition of amines to the 2-benzalcycloalkanones (VI) suggests that the first step of the epoxidation reaction, the addition of the hydroperoxide anion to the unsaturated ketone,[10] would be slow (or that the equilibrium involved in the first step would be unfavorable) with the cyclopentanone derivative VIc. The alternate synthetic method used for the oxide Vc involved the reduction of the unsaturated ketone VIc to the alcohol VII with lithium aluminum hydride. The same alcohol VII had been previously prepared by the oxotropic rearrangement of 1-cyclopentenylphenylcarbinol.[11] Epoxidation of VII with peracetic acid yielded the crystalline epoxy alcohol VIII. Of the oxidation procedures studied (including chromium trioxide in acetone and chromium trioxide in pyridine) for the conversion of the alcohol VIII to the ketone Vc, only oxidation with N-bromosuccinimide in acetone[12] yielded a crude product whose infrared and ultraviolet spectra were consistent with the structure Vc. Since all of our attempts to purify the crude product resulted in decomposition of the sample, it was necessary to study the rearrangement of the crude keto oxide Vc. The results of the rearrangement indicated that the crude product contained at least 50% of the desired ketone Vc.

Treatment of the oxides V with boron trifluoride etherate in benzene solution yielded the diketones IX, the products expected from the preferential migration of an acyl group.[5] Similar results were obtained when cyclohexane was employed as the medium for the rearrangement. Confirmation of the β-diketone structures for the isomerization products was obtained by the alkaline cleavage of the diketones IX to yield the corresponding keto acids X whose ultraviolet spectra lacked absorption attributable to a conjugated ketone grouping. The physical properties of the diketone IXc and the related acid Xc correspond to the values previously reported[13] for these compounds. Further verification of the symmetrical diketone structure IXb for the isomerization product of Vb was gained from the nuclear magnetic resonance spectrum of the isomerization product.

The properties of the seven- and eight-membered cyclic diketones IXb and IXa differed markedly from the properties of the cyclohexanedione IXc. Compounds IXa and IXb gave negative ferric chloride tests, absorbed only weakly in the ultraviolet region and had infrared spectra consistent with the non-enolized β-diketone structure IX. The six-membered cyclic diketone IXc had properties in much better agreement with the enolic structure XIc.[14] A possible interpretation for this variation in behavior may be found in the steric resistance to the presence of a planar, α,β-unsaturated ketone system in a seven- or eight-membered ring (*i.e.*, structures XIb and XIa). A study of molecular models suggests that appreciable steric strain would exist in structures XIa and XIb but not in XIc.[15]

Attempts to isomerize the 2-benzalcycloalkanone

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uncertain since it is not yet known whether the epoxidation of α,β-unsaturated ketones with alkaline hydrogen peroxide is stereospecific. Previous examples in which the reaction has not been stereospecific [see H. H. Wasserman, N. E. Aubrey and H. E. Zimmermann, THIS JOURNAL, **75**, 96 (1953) and W. B. Black and R. E. Lutz, *ibid.*, **75**, 5990 (1953)] have all involved oxides which were capable of base-catalyzed epimerization and, therefore, may not have been the initial products formed in the reaction.

[9] R. Baltzly, E. Lorz, P. B. Russell and F. M. Smith, THIS JOURNAL, **77**, 624 (1955).

[10] C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

[11] E. A. Braude and W. F. Forbes, *ibid.*, 1755 (1951).

[12] L. F. Fieser and S. Rajagopalan, THIS JOURNAL, **72**, 5530 (1950).

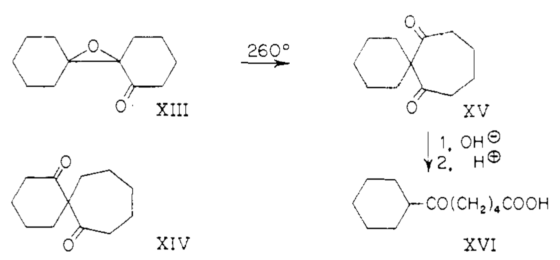
[13] H. Born, R. Pappo and J. Szmuszkovicz, *J. Chem. Soc.*, 1779 (1953).

[14] Since the position of the keto (IX)–enol (XI) equilibrium for the cyclic diketones was not determined, the above data, based on the single tautomer which was isolated in each case, suggest only that enolization is more favorable in the case of the six-membered cyclic diketone IXc than in the case of the seven- and eight-membered homologs IXa and IXb. The referee has suggested that the ultraviolet spectra of ethanolic solutions of the cyclic diketones indicate approximate values of 30% and 10% for the extent of enolization of the seven-membered cyclic diketone IXb and the eight-membered cyclic diketone IXa, respectively.

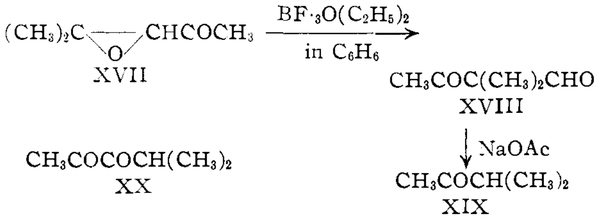
[15] The authors are indebted to Professor E. J. Corey for a helpful discussion of this point. The ready interconversion of 2-cycloheptenone and 3-cycloheptenone [E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 607 (1954)] lends support to the idea that an α,β-unsaturated ketone system is destabilized when located in a seven-membered ring.

oxides Va and Vb with boron trifluoride in ether solution resulted in the formation of fluoro alcohols. The formation of β-fluoro-α-hydroxy ketones from other keto oxide systems under comparable conditions[5c] suggests that the fluoro alcohols isolated in the present investigation have the structures XIIa and XIIb; the conversion of XIIb to the diketone IXb is also in agreement with this formulation. As in the previous cases[5c] the question as to whether the fluorohydrins XII are intermediates in the isomerization of the oxides V to the diketones IX cannot be answered until kinetic data for the isomerization are available.

In a study of 2-cyclohexylidenecyclohexanone and its derivatives, Reese found that the distillation of 2-cyclohexylidenecyclohexanone oxide (XIII) produced a dicarbonyl compound, isolated as its monosemicarbazone, which was tentatively assigned the structure XIV.[16] Since this thermal isomerization process[17] appeared to yield a product different from the structure XV expected from an acid-catalyzed process, the thermal isomerization of several α,β-epoxy ketone systems was investigated. When the oxide XIII was heated to 260° for 15 minutes and then distilled under reduced pressure, an isomeric diketone, subsequently found to have the structure XV, was isolated in 65% yield. The diketone XV formed the same monosemicarbazone which had previously been described by Reese. Alkaline cleavage of the diketone XV formed the known[16] keto acid XVI. All of our attempts to isomerize the oxide XIII in the presence of a benzene or ether solution of boron trifluoride etherate resulted in the formation of an unstable red oil from which no pure product or crystalline carbonyl derivative could be isolated. The thermal isomerization of 2-benzalcyclohexanone oxide (Vb) produced the diketone IXb (15% yield) accompanied by benzaldehyde (11% yield).



The failure of the boron trifluoride etherate–benzene system to yield an isolable isomerization product of 2-cyclohexylidenecyclohexanone oxide (XIII) prompted us to study the behavior of a simpler aliphatic keto oxide system, 3,4-epoxy-4-methyl-2-pentanone (XVII). Treatment of the oxide XVII with boron trifluoride etherate in benzene solution produced 2,2-dimethyl-3-oxobutyraldehyde (XVIII), isolated as its bis-*p*-nitrophenylhydrazone in 58% yield. Deformylation of the crude keto aldehyde XVIII with sodium acetate in boiling ethanol yielded methyl isopropyl ketone (XIX), isolated as its 2,4-dinitrophenylhydrazone. Also isolated from the deformylation reaction mixture was a small amount (1%) of the mono-2,4-dinitrophenylhydrazone of a diketone isomeric with the oxide XVII. The product is not the mono-2,4-dinitrophenylhydrazone of 4-methylpentane-2,3-dione (XX)[18] and may be the mono-2,4-dinitrophenylhydrazone of XVIII. Attempts to effect thermal isomerization of the oxide XVII by distillation at atmospheric pressure resulted in decomposition, but no volatile products could be distilled from the mixture. If the initial product of thermal isomerization was the keto aldehyde XVIII, such a result would be expected since our attempts to distil the crude dicarbonyl compound XVIII, prepared by acid-catalyzed isomerization, resulted in decomposition (apparently accompanied by polymerization), necessitating the isolation of the keto aldehyde XVIII as its bis-*p*-nitrophenylhydrazone.


$(CH_3)_2C\overset{O}{—}CHCOCH_3 \xrightarrow[\text{in } C_6H_6]{BF_3 \cdot O(C_2H_5)_2} CH_3COC(CH_3)_2CHO$

XVII XVIII

$CH_3COC(CH_3)_2CHO \xrightarrow{NaOAc} CH_3COCH(CH_3)_2$

XIX

$CH_3COCOCH(CH_3)_2$

XX

3,4-Epoxy-4-methyl-2-pentanone (XVII) has been reported to yield 4-methylpentane-2,3-dione (XX), isolated as its mono-2,4-dinitrophenylhydrazone, when the vaporized oxide was passed over alumina heated to 250°.[19] Since this result also appeared to represent a mode of rearrangement different from the predominant reaction path with the acid-catalyzed process, the isomerization of the oxide XVII over alumina at 250° was reinvestigated. The product, isolated as its 2,4-dinitrophenylhydrazone, was found to be the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone (XIX).[20] The formation of this ketone XIX would appear to involve the initial isomerization of the oxide XVII to the keto aldehyde XVIII followed by deformylation over the basic alumina.

Experimental[21]

The 2-Benzalcycloalkanones (VI).—The preparative method used for the 2-benzalcycloalkanones, a modification of previous procedures[22-24] consisted of stirring equivalent amounts of the cycloalkanone and benzaldehyde with aqueous sodium hydroxide at steam-bath temperatures. 2-Benzalcyclohexanone crystallized from hexane as light yellow prisms, m.p. 56–56.5° (lit. 51–53°,[23] 53–54°,[24] 56.5°[25]). The ultraviolet spectrum of the ketone has absorption peaks at 223 mμ (ε 6,700) and 290 mμ (ε 16,200) [lit.[9] 290 mμ (ε

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[16] J. Reese, *Ber.*, **75**, 384 (1942).

[17] The possibility that the initial decomposition of the oxide yields acidic products with the resultant acid-catalyzed isomerization of the remaining oxide has not been excluded.

[18] The authors are indebted to Professor J. W. Baker who kindly supplied an authentic sample of the diketone derivative.

[19] E. G. E. Hawkins, *J. Chem. Soc.*, 3288 (1955).

[20] The physical properties and composition previously reported (reference 19) for this product are in much better agreement with the values for the derivative of methyl isopropyl ketone (XIX) than with the values for the derivative of the α-diketone XX.

[21] All melting points are corrected and all boiling points are uncorrected. The ultraviolet spectra were determined in ethanol solution with a Cary recording spectrophotometer, Model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

[22] R. Poggi and V. Guastalla, *Gazz. chim. ital.*, **61**, 405 (1931); *C. A.*, **26**, 104 (1932).

[23] W. S. Emerson, G. H. Birum and R. I. Longley, Jr., This Journal, **75**, 1312 (1953).

[24] J. D. Billimoria, *J. Chem. Soc.*, 1126 (1955).

[25] G. Vavon and J. M. Conia, *Compt. rend.*, **234**, 526 (1952).

18,000)]; the infrared spectrum[26,27] has a band at 1685 cm.$^{-1}$ (conjugated C=O). After the removal of the crude 2,5-dibenzalcyclopentanone, m.p. 155–167° (lit.[28] 189°), 2-benzalcyclopentanone was isolated as light yellow prisms, m.p. 70–71° (lit. 71–72°[25]), ultraviolet maxima 224 mμ (ϵ 7,500), 230 mμ (ϵ 7,000) and 298 mμ (ϵ 22,400) [lit.[9] 298 mμ (ϵ 22,600)], infrared absorption[26,27] at 1710 cm.$^{-1}$ (conjugated C=O in a five-membered ring). 2-Benzalcycloheptanone crystallized from hexane as white prisms, m.p. 40–40.5° (lit. 37.5°,[29] 45°[9]); three additional recrystallizations did not alter the melting point of our sample. The ultraviolet spectrum of the unsaturated ketone has maxima at 222 mμ (ϵ 7,200) and 284 mμ (ϵ 15,100) [lit.[9] 285 mμ (ϵ 15,000)]; absorption in the infrared[26,27] occurs at 1680 cm.$^{-1}$ (conjugated C=O). Because of the discrepancy in melting point values for the ketone, the composition of our sample was also determined.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.83; H, 8.11.

2-Benzalcyclohexanone Oxide (Vb).—To a mixture of 25 g. (0.134 mole) of 2-benzalcyclohexanone, 50 ml. (0.52 mole) of 30% aqueous hydrogen peroxide and 350 ml. of methanol was added 25 ml. (0.15 mole) of 6 *N* aqueous sodium hydroxide. The resulting mixture was stirred for 2 hr., the reaction flask being cooled in a bath of cold water. The reaction mixture was diluted with two volumes of cold water and the product collected on a filter. The crude epoxy ketone (21 g. or 77.5%, m.p. 115–120°) was recrystallized from hexane to give pure 2-benzalcyclohexanone oxide as white needles, m.p. 124–125.5°, yield 20.7 g. (76.4%). The ultraviolet spectrum of the product has a band at 224 mμ (ϵ 10,600); the infrared spectrum[26,30] exhibits a band at 1715 cm.$^{-1}$ attributable to an unconjugated carbonyl group (the corresponding band was found at 1730 cm.$^{-1}$ when the spectrum was determined in carbon tetrachloride solution).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.92; H, 7.01.

2-Benzalcycloheptanone Oxide (Va).—A solution of 13.5 g. (0.0675 mole) of 2-benzalcycloheptanone and 30 ml. (0.312 mole) of 30% aqueous hydrogen peroxide in 200 ml. of methanol was treated with 15 ml. (0.09 mole) of 6 *N* aqueous sodium hydroxide, and the resulting solution was stirred for 22 hr. at room temperature. The reaction mixture, after dilution with 400 ml. of water, was extracted with ether, and the extract was washed with water, dried over magnesium sulfate and distilled through a Holtzman column. The 2-benzalcycloheptanone oxide, b.p. 108–111° (0.08 mm.), n^{25}D 1.5487, amounted to 9.0 g. (61.5%), ultraviolet maximum 226 mμ (ϵ 10,400), infrared absorption[26,27] 1710 cm.$^{-1}$ (unconjugated C=O).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.44.

2-Benzalcyclopentanol (VII).—A solution of 20 g. (0.116 mole) of 2-benzalcyclopentanone in 175 ml. of ether was added, dropwise and with stirring, to a suspension of 1.5 g. (0.04 mole) of lithium aluminum hydride in 75 ml. of ether. The resulting mixture was stirred for 1 hr. at room temperature, chilled in an ice-bath and treated with a slight excess of cold, 10% aqueous sulfuric acid. The organic layer was separated and combined with an ether extract of the aqueous phase. The ether solution was washed with water, dried over magnesium sulfate and concentrated. The residual oil crystallized from pentane as colorless needles, m.p. 78–79.5°, yield 15.13 g. (74.5%). Recrystallization gave the pure 2-benzalcyclopentanol, m.p. 83–83.5° (lit.[11] 86°). The infrared spectrum[26,27] of the alcohol has no absorption in the 6 μ region attributable to a carbonyl group and exhibits bands at 3500 cm.$^{-1}$ (unassociated O–H) and 3250 cm.$^{-1}$ (associated O–H); the ultraviolet spectrum has a maximum at 257 mμ (ϵ 21,500) [lit.[11] 251 mμ (ϵ 19,100) and 256 mμ (ϵ 19,100)] with a point of inflection at 252 mμ (ϵ 20,400).

2-Benzalcyclopentanol Oxide (VIII).—A mixture of 15 g. (0.086 mole) of 2-benzalcyclopentanol, 15 g. of sodium acetate trihydrate and 200 ml. of chloroform, cooled to 0°, was treated with a solution containing 7.6 g. (0.1 mole) of peracetic acid in acetic acid. After the resulting mixture had been stirred for 5 hr. at 0° and an additional 21 hr. at room temperature, the chloroform solution was washed with water, with aqueous sodium bicarbonate and, finally, with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue crystallized from an ether–hexane mixture as colorless plates, m.p. 44–46°, yield 12.16 g. (74.4%). Recrystallization from hexane raised the melting point of the 2-benzalcyclopentanol oxide to 47–47.5°; infrared absorption[26,27] at 3400 cm.$^{-1}$ indicated the presence of a hydroxyl group and the lack of absorption in the 6 μ region excluded the presence of a carbonyl function. The ultraviolet spectrum of the alcohol has a maximum at 219 mμ (ϵ 9,800).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.43.

Oxidation of 2-Benzalcyclopentanol Oxide (VIII).—A solution of 2 g. (0.0105 mole) of 2-benzalcyclopentanol oxide, 1.96 g. (0.011 mole) of N-bromosuccinimide, 1 ml. of acetic acid and 10 ml. of water in 100 ml. of acetone was allowed to stand at room temperature for 24 hr. The resulting mixture was diluted with aqueous sodium bicarbonate and extracted with three portions of ether. The combined extracts were washed, first with aqueous sodium bicarbonate and then with water, dried over magnesium sulfate and concentrated under reduced pressure. The infrared spectrum[26,27] of the residual yellow oil (1.31 g.) has a strong band at 1730 cm.$^{-1}$ attributable to an unconjugated carbonyl group in a five-membered ring; a second weak band at 3350 cm.$^{-1}$ suggests that some unchanged 2-benzalcyclopentanol oxide was present in the mixture. The ultraviolet spectrum of the oil has maxima at 229 mμ (ϵ 5,200) and 309 mμ (ϵ 130). Since repeated attempts to purify the epoxy ketone were unsuccessful, the crude oil was isomerized without further purification.

Rearrangement of Crude 2-Benzalcyclopentanone Oxide (Vc).—A solution of 0.30 g. of the crude 2-benzalcyclopentanone oxide in 15 ml. of benzene was treated with 0.2 ml. of boron trifluoride etherate, and the resulting mixture was allowed to stand for 5 minutes at room temperature. The reaction mixture was diluted with ether, washed with water, dried over magnesium sulfate and concentrated under reduced pressure. The crude product separated as a white solid, m.p. 159–161°, yield 0.15 g. (50% based on the theoretical yield if the starting material had been pure). Recrystallization from benzene afforded the pure **enol of 2-phenyl-1,3-cyclohexanedione (XIc)** as white plates, m.p. 160.5–161° (lit.[13] 160–161°), which gave a violet color with aqueous ferric chloride and deteriorated rapidly on standing. The infrared spectrum[26,30] of the compound has both a sharp band at 3400 cm.$^{-1}$ (unassociated O–H) and a broad band at about 3000 cm.$^{-1}$ (strongly associated O–H) in the 3 μ region; in the 6 μ region is found a broad band with its center at 1615 cm.$^{-1}$ (enolized β-diketone) accompanied by a second, slightly less intense band at 1590 cm.$^{-1}$ (phenyl group or conjugated C=C). The ultraviolet spectrum of the product has a maximum at 265 mμ (ϵ 9,300) with a plateau at 230–237 mμ (ϵ 6,200) and a minimum at 219 mμ (ϵ 5,700).

6-Phenyl-5-ketohexanoic Acid (Xc).—A solution of 0.2 g. (0.0011 mole) of 2-phenyl-1,3-cyclohexanedione and 3 ml. (0.0018 mole) of 6 *N* aqueous sodium hydroxide in 20 ml. of ethanol was boiled under reflux for 30 minutes, diluted with water, acidified with hydrochloric acid and extracted with ether. The extract was dried over magnesium sulfate and concentrated to leave the crude acid as a white solid, m.p. 260–265°, yield 0.11 g. (53.4%). The pure acid crystallized from petroleum ether as white needles, m.p. 264–265° (lit.[13] 265°). The infrared spectrum[26,31] of the acid exhibits a broad band with its center at 1690 cm.$^{-1}$ (C=O of an acid and a ketone) as well as a very broad band in the 3 μ region (O–H stretching of a carboxylic acid); the ultraviolet spectrum has maxima at 253 mμ (ϵ 240) and 260 mμ (ϵ 245).

Rearrangement of 2-Benzalcyclohexanone Oxide (Vb). A. In Cyclohexane.—A suspension of 1 g. (0.005 mole) of 2-benzalcyclohexanone oxide and 4 ml. (0.032 mole) of boron trifluoride etherate in 50 ml. of cyclohexane was stirred for

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(26) Determined with a Baird double beam infrared recording spectrophotometer, Model B, fitted with a sodium chloride prism.

(27) Determined in carbon tetrachloride solution.

(28) D. Vorländer and K. Hobohm, *Ber.*, **29**, 1836 (1896). See also H. W. Wanzlick and W. Menz [*Chem. Ber.*, **87**, 475 (1954)] for a discussion of the nature of the isomers present.

(29) E. A. Braude, W. F. Forbes and E. A. Evans, *J. Chem. Soc.*, 2202 (1953).

(30) Determined in chloroform solution.

(31) Determined as a suspension in a potassium bromide pellet.

15 minutes and then worked up as described previously. The crude product, when sublimed *in vacuo* (100° at 0.5 mm.) afforded 0.71 g. (71%) of crude **2-phenyl-1,3-cycloheptanedione (IXb)**, m.p. 72–77°. The pure diketone separated from hexane as white needles, m.p. 76.5–77.5°. The infrared spectrum[26,27] of the product has a band at 1695 cm.$^{-1}$ with a shoulder at 1720 cm.$^{-1}$, attributable to a non-enolized β-diketone[32]; the spectrum lacks absorption in the 3 μ region attributable to a hydroxyl group. The ultraviolet spectrum of the diketone has a maximum at 266 mμ (ε 3,100). The diketone, which deteriorated when allowed to stand at room temperature, gave a negative ferric chloride test; no color developed when the test solution was allowed to stand overnight. The infrared spectrum[26,27] of the crude isomerization product (before sublimation) did not differ appreciably from the spectrum of the pure diketone. The nuclear magnetic resonance spectrum[27] of the diketone, determined with a Varian Associates high-resolution nuclear magnetic resonance spectrometer, Model V4300B, has absorption peaks (expressed as cycles per second relative to the proton resonance of water) at +95 sec.$^{-1}$ (hydrogen atoms of an aromatic system), −8 sec.$^{-1}$ (hydrogen atom bonded to a tertiary carbon atom, which is adjacent to three electronegative groups), −89 sec.$^{-1}$ (hydrogen atoms of methylene groups adjacent to carbonyl groups) and −100 sec.$^{-1}$ (hydrogen atoms of methylene groups); the areas under the four peaks are in an approximate ratio of 5:1:4:4.[33]

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.93; H, 6.84.

When treated with 2,4-dinitrophenylhydrazine and hydrochloric acid in ethanol, the diketone yielded the **bis-2,4-dinitrophenylhydrazone of 2-phenyl-1,3-cycloheptanedione**, m.p. 202–203° (dec.), in 59% yield. The pure derivative separated from a dioxane–water mixture as fine, yellow needles, m.p. 205.5–206.5° (dec). The infrared spectrum[26,34] of the derivative has a band at 3000 cm.$^{-1}$ (N–H) but lacks absorption in the 6 μ region attributable to a carbonyl group.

Anal. Calcd. for $C_{25}H_{22}N_8O_8$: C, 53.39; H, 3.94; N, 19.93. Found: C, 53.57; H, 4.21; N, 19.78.

B. **In Benzene**.—A solution of 0.5 g. (0.0025 mole) of 2-benzalcyclohexanone oxide and 2.0 ml. (0.016 mole) of boron trifluoride etherate in 15 ml. of benzene was allowed to stand at rooom temperature for 5 minutes and then worked up as described earlier. The yield of 2-phenyl-1,3-cycloheptanedione, m.p. 74–75.2°, isolated by crystallization from hexane, was 0.39 g. (78%). When reaction times of 2 and 15 minutes were employed, the yields of diketone were 70 and 32%, respectively.

C. **Thermal Rearrangement**.—A 1-g. (0.005 mole) sample of the oxide was heated to 280° for 15 minutes. When the resulting red oil was distilled *in vacuo* the only volatile product was 0.1 g. of crude benzaldehyde isolated as its 2,4-dinitrophenylhydrazone, m.p. 230–235° (lit.[35] 236–238°), yield 0.15 g. (10.5%); the compound was identified by a mixed melting point determination with an authentic sample. The residue from the distillation, when sublimed under reduced pressure, afforded 0.15 g. (15%) of 2-phenyl-1,3-cycloheptanedione, m.p. 72–76°, whose identity was established by a mixed melting point determination with the sample described previously.

2-(α-Fluorobenzyl)-2-hydroxycyclohexanone (XIIb).—A solution of 1 g. (0.005 mole) of 2-benzalcyclohexanone oxide and 5 ml. (0.04 mole) of boron trifluoride etherate in 40 ml. of ether was stirred for 30 minutes and then worked up as in the previous cases. The fluorohydrin crystallized from hexane as white plates, m.p. 119–121°, yield 0.44 g. (40%). Recrystallization from hexane raised the melting point to 129.5–130°. The infrared spectrum[26,30] of the fluoro alcohol has bands at 3320 cm.$^{-1}$ (associated O–H) and 1700 cm.$^{-1}$ (unconjugated C=O).

Anal. Calcd. for $C_{13}H_{15}FO_2$: C, 70.27; H, 6.76; F, 8.56. Found: C, 70.24; H, 6.98; F, 8.27.

Rearrangement of 2-(α-Fluorobenzyl)-2-hydroxycyclohexanone (XIIb).—A solution of 50 mg. (0.002 mole) of the fluorohydrin and 0.05 ml. (0.0004 mole) of boron trifluoride etherate in 10 ml. of benzene was allowed to stand at room temperature for 5 minutes and then worked up in the usual manner. The product, 2-phenyl-1,3-cycloheptanedione, identified by a mixed melting point determination with the previous sample, crystallized from hexane as white needles, m.p. 76–77°, yield 25 mg. (62.5%).

7-Phenyl-6-ketoheptanoic Acid (Xb).—A solution of 0.25 g. (0.0012 mole) of 2-phenyl-1,3-cycloheptanedione and 2 ml. (0.012 mole) of 6 *N* aqueous sodium hydroxide in 20 ml. of ethanol was boiled for 10 minutes and then allowed to stand for 19 hr. The reaction mixture was worked up as in the previous case except that the aqueous solution was continuously extracted with ether for 3.5 hr. The keto acid crystallized from a hexane–benzene mixture at Dry Ice temperatures as white needles, m.p. 48–52°, yield 0.15 g. (57%). Recrystallization raised the melting point to 51–53°. The infrared spectrum[26,27] of the product has a very broad band in the 3 μ region (O–H stretching of a carboxyl group) as well as a broad band at 1705 cm.$^{-1}$ (C=O of a carboxyl group and a ketone); the ultraviolet spectrum has maxima at 253 mμ (ε 309) and 259 mμ (ε 319).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.06; H, 7.14.

Rearrangement of 2-Benzalcycloheptanone Oxide (Va).—A solution of 0.5 g. (0.0023 mole) of the oxide and 0.5 ml. (0.004 mole) of boron trifluoride etherate in 15 ml. of benzene was allowed to stand at room temperature for 2 minutes and then worked up as in the previous cases. The product, **2-phenyl-1,3-cycloöctanedione (IXa)**, crystallized from petroleum ether as white plates, m.p. 43–45.5°, yield 0.29 g. (58%). Recrystallization raised the melting point of the diketone to 45.5–46°. Extension of the reaction time to 5 minutes lowered the yield to 50%; the use of additional boron trifluoride etherate (1 ml., 0.008 mole) with a 2-minute reaction time lowered the yield to 30%. The infrared spectrum of the oil obtained from the mother liquors of the diketone crystallizations did not differ appreciably from the spectrum of the pure diketone. When the isomerization was done in cyclohexane, as described earlier, the yield of diketone was 45%. The ultraviolet spectrum of the product has maxima at 259 mμ (ε 673) and 265 mμ (ε 643); the infrared spectrum[26,27] has a band at 1680 cm.$^{-1}$ with a shoulder at 1705 cm.$^{-1}$ (non-enolized β-diketone[32]) and lacks absorption in the 3 μ region attributable to a hydroxyl group. The diketone, which gave a negative ferric chloride test, deteriorated rapidly on standing. A sample of the diketone was successfully stored for two weeks under nitrogen in a refrigerator.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.91; H, 7.41.

The diketone, when treated with an ethanolic solution of 2,4-dinitrophenylhydrazine and hydrochloric acid, formed the **bis-2,4-dinitrophenylhydrazone of 2-phenyl-1,3-cyclooctanedione**, m.p. 195–197° (dec.). in 40% yield. Recrystallization from an ethanol–ethyl acetate mixture afforded the pure derivative as orange needles, m.p. 204–206.5° (dec.). The infrared spectrum[26,31] of the derivative has a band at 3200 cm.$^{-1}$ (associated N–H) but lacks absorption in the 6 μ region attributable to a carbonyl group.

Anal. Calcd. for $C_{26}H_{24}N_8O_8$: C, 54.16; H, 4.20; N, 19.44. Found: C, 54.23; H, 4.33; N, 19.13.

2-(α-Fluorobenzyl)-2-hydroxycycloheptanone (XIIa).—A solution of 0.5 g. (0.0023 mole) of 2-benzalcycloheptanone oxide and 3 ml. (0.024 mole) of boron trifluoride etherate in 30 ml. of ether was allowed to stand at room temperature for 40 minutes and then worked up in the usual manner. The fluorohydrin crystallized from an ethanol–water mixture as white plates, m.p. 93–95°, yield 0.24 g. (45%). Recrystallization from hexane raised the melting point of the fluoro alcohol to 95.5–96°. The infrared spectrum[26,30]

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(32) Although the carbonyl groups of structure IX are equivalent, the presence of twin carbonyl peaks would be expected since the two acyl groups are bonded to the same atom. A similar splitting of the carbonyl band occurs with the structurally analogous acid anhydrides and imides.

(33) The values reported [B. P. Dailey and J. N. Shoolery, THIS JOURNAL, **77**, 3977 (1955)] for the proton chemical shifts (after conversion to make the values relative to the proton resonance of water) of $-CH_2-CO-$ (2-butanone), cyclic-CH_2- (cyclohexane) and $C_6H_5CH_2-$ (ethylbenzene) are 98, 117 and 86 cycles per second, respectively. There are no available data relating to the chemical shifts observed for a proton bonded to a carbon atom which is bonded to three electronegative groups.

(34) Determined as a Nujol mull.

(35) C. H. Hassall and A. F. Lippman, *J. Chem. Soc.*, 1059 (1953).

has bands at 1685 cm.$^{-1}$ attributable to an unconjugated carbonyl group and at 3300 cm.$^{-1}$ attributable to an associated hydroxyl group.

Anal. Calcd. for $C_{14}H_{17}FO_2$: C, 71.20; H, 7.20; F, 8.04. Found: C, 70.97; H, 7.50; F, 8.06.

8-Phenyl-7-ketoöctanoic Acid (Xa).—A solution of 0.23 g. (0.00106 mole) of 2-phenyl-1,3-cycloöctanedione and 2 ml. (0.012 mole) of 6 *N* aqueous sodium hydroxide in 20 ml. of ethanol was boiled under reflux for 30 minutes and worked up as previously described. The acid crystallized from hexane as white needles, m.p. 51–53°, yield 0.12 g. (49%). Recrystallization raised the melting point to 52.5–53°. The infrared spectrum[26,27] of the keto acid has a broad band in the 3 μ region (O–H stretching of a carboxyl group) and a broad band at 1695 cm.$^{-1}$ (C=O of a carboxyl group and a ketone); the ultraviolet spectrum has maxima at 253 mμ (ε 245) and 259 mμ (ε 284).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.60; H, 7.88.

2-Cyclohexylidenecyclohexanone Oxide (XIII).—A sample of 2-cyclohexylidenecyclohexanone, m.p. 56–56.5° (lit.[16] 57°), infrared spectrum[26,27] 1670 cm.$^{-1}$ (conjugated C=O) and 1610 cm.$^{-1}$ (conjugated C=C), ultraviolet maximum 255 mμ (ε 7,100) (calculated value[36] 259 ± 5 mμ), was converted to the oxide, m.p. 96.5–97° (lit.[16] 98°), infrared spectrum[26,27] 1700 cm.$^{-1}$ (unconjugated C=O), ultraviolet maximum 294 mμ (ε 45), according to the procedure of Reese.[16]

Thermal Rearrangement of 2-Cyclohexylidenecyclohexanone Oxide (XIII).—A 2-g. (0.0103 mole) sample of the oxide was heated to 260° for 15 minutes. Distillation of the resulting dark oil afforded 1.3 g. (65%) of **spiro[5.6]-dodecane-7,12-dione (XV)**, b.p. 125–126° (10 mm.), $n^{25}\mathrm{D}$ 1.5000 (lit.[16] b.p. 260–270°). The diketone gave a negative ferric chloride test; the infrared spectrum[26,27] of the product has a band at 1680 cm.$^{-1}$ with a shoulder at 1700 cm.$^{-1}$ (non-enolized β-diketone)[32] and lacks absorption in the 3 μ region attributable to a hydroxyl group.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: 74.00; H, 9.51.

The diketone formed a **mono-semicarbazone** which crystallized from ethanol as white plates, m.p. 223–224° (lit.[16] 224°), yield 88%. The infrared spectrum[26,31] of the derivative has a band at 1670 cm.$^{-1}$ (C=O of an amide) with a shoulder at 1690 cm.$^{-1}$ (C=O of an unconjugated ketone) as well as bands at 3100 cm.$^{-1}$ (associated N–H) and 3300 cm.$^{-1}$ (unassociated N–H).

6-Cyclohexyl-6-ketohexanoic Acid (XVI).—A solution of 1 g. (0.005 mole) of spiro[5.6]dodecane-7,12-dione and 5 ml. (0.03 mole) of 6 *N* aqueous sodium hydroxide in 30 ml. of ethanol was boiled under reflux for 30 minutes and then worked up as in the previous cases. The keto acid crystallized from petroleum ether as colorless plates, m.p. 56.5–58° (lit.[16] 57–58°), yield 0.7 g. (65%). The infrared spectrum[26,27] of the keto acid has a broad band in the 3 μ region (O–H stretching of a carboxyl group) and a broad band at 1695 cm.$^{-1}$ (C=O of a carboxyl group and a ketone). The keto acid was converted to its semicarbazone which crystallized from ethanol as colorless plates, m.p. 270–271° (lit.[16] 270–272°), yield 87%. The infrared spectrum[26,31] of the derivative has bands at 3380 cm.$^{-1}$ (unassociated N–H) and 3150 cm.$^{-1}$ (associated N–H) superimposed upon a very broad band in the 3 μ region (O–H stretching of a carboxyl group). In addition bands are present at 1700 cm.$^{-1}$ (C=O of a carboxyl group) and at 1660 cm.$^{-1}$ (C=O of an amide).

3,4-Epoxy-4-methyl-2-pentanone (XVII).—4-Methyl-3-penten-2-one was converted to its oxide, b.p. 70–75° (20 mm.), $n^{25}\mathrm{D}$ 1.4200 (lit. b.p. 44–48° (15 mm.),[37] $n^{20}\mathrm{D}$ 1.4223[38]) according to the procedure of Weitz and Scheffer.[37]

Rearrangement of 3,4-Epoxy-4-methyl-2-pentanone (XVII). A. With Boron Trifluoride Etherate.—A solution of 0.50 g. (0.0044 mole) of the oxide and 1 ml. (0.008 mole) of boron trifluoride etherate in 50 ml. of benzene was allowed to stand at room temperature for 5 minutes. Since attempts to isolate the isomerization product by distillation under reduced pressure resulted in decomposition of the sample, the reaction mixture was diluted with ethanol and treated directly with *p*-nitrophenylhydrazine and acetic acid. The crude derivative obtained was recrystallized from hexane, the **bis-*p*-nitrophenylhydrazone of 2,2-dimethyl-3-oxobutyraldehyde** separated as yellow needles) m.p. 147–147.5°, yield 0.4 g. (58%). The infrared spectrum[30,39] of the derivative has a band at 3410 cm.$^{-1}$ (N–H, but lacks absorption in the 6 μ region attributable to a carbonyl function.

Anal. Calcd. for $C_{18}H_{20}N_6O_4$: C, 56.24; H, 5.24; N, 21.87. Found: C, 56.04; H, 5.26; N, 21.63.

Attempts to prepare a derivative of the crude keto aldehyde with 2,4-dinitrophenylhydrazine resulted in the formation of an impure bis-2,4-dinitrophenylhydrazone which crystallized from nitrobenzene as orange needles, m.p. 300–302° (dec.). The infrared spectrum[26,31] of the material lacked absorption in the 6 μ region attributable to a carbonyl function. Although repeated recrystallization did not alter the decomposition point of the derivative, an analytically pure sample could not be obtained (*Anal.* Found: C, 43.13; H, 3.35; N, 24.28. Calcd. for $C_{18}H_{18}N_8O_8$: C, 45.57; H, 3.82; N, 23.62.).

In a second experiment the reaction mixture was boiled with an ethanolic solution of 1.6 g. (0.012 mole) of sodium acetate trihydrate for 30 minutes and then treated with 2,4-dinitrophenylhydrazine and hydrochloric acid in the usual manner. Under these conditions none of the bis-2,4-dinitrophenylhydrazone described above could be isolated. Instead the **2,4-dinitrophenylhydrazone of methyl isopropyl ketone** was isolated as orange needles, m.p. 110–115°, yield 0.55 g. (47%). Three recrystallizations from ethanol raised the melting point of the derivative to 120–121°, yield 0.50 g. (45%).[40] The product was shown to be identical with an authentic sample of the methyl isopropyl ketone derivative both by a mixed melting point determination and by comparison of the infrared spectra[26,30] of the two samples. The product was also shown not to be acetone 2,4-dinitrophenylhydrazone; the melting point of a mixture of the two samples was depressed and the infrared spectra[30,39] of the two samples differ significantly. Concentration of the mother liquors from the above recrystallization afforded a small amount (30 mg. or 1%) of the mono-2,4-dinitrophenylhydrazone of a diketone, m.p. 126–127.5°. The infrared spectrum[26,30] of the product, which has bands at 3220 cm.$^{-1}$ (associated O–H) and at 1700 cm.$^{-1}$ (unconjugated C=O), differs significantly from the spectrum[26,30] of 4-methylpentane-2,3-dione 2,4-dinitrophenylhydrazone.[41]

Anal. Calcd. for $C_{12}H_{14}N_4O_5$: C, 48.98; H, 4.80. Found: C, 49.08; H, 5.06.

B. Thermal Rearrangement.—A 6-g. (0.0526 mole) sample of the oxide was added dropwise to the top of a 5-cm. column of Merck acid-washed alumina which was maintained at 250°. The pyrolysis products were swept out of the system and into a cold trap with a stream of nitrogen. The material collected in the cold trap afforded, upon distillation, 2.68 g. of a yellow liquid, b.p. 90–95°. A 0.2-g. aliquot of the liquid was converted to its 2,4-dinitrophenylhydrazone in the manner previously outlined. The 2,4-dinitrophenylhydrazone of methyl isopropyl ketone

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[36] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

[37] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

[38] I. N. Nazaron and A. A. Akhrem, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 2183 (1950); *C. A.*, **45**, 7062 (1950).

[39] Determined with a Perkin–Elmer double beam infrared recording spectrophotometer, Model 21, fitted with a sodium chloride prism.

[40] As we have noted with the 2,4-dinitrophenylhydrazone derivatives of other unsymmetrical, aliphatic ketones [THIS JOURNAL, **77**, 5083 (1955)], the derivative initially obtained is apparently an equilibrium mixture of the *syn* and *anti* geometrical isomers. The melting point of the derivative is therefore dependent on the number of times the derivative is recrystallized (*i.e.*, the relative amounts of the two geometrical isomers present). The wide variation in melting-point values reported for methyl isopropyl ketone 2,4-dinitrophenylhydrazone is in agreement with this idea: G. D. Johnson [THIS JOURNAL, **75**, 2720 (1953)] reported 124–125°; J. H. Ross [*Anal. Chem.*, **25**, 1288 (1953)] reported 119°; J. R. Coley and V. I. Komarewsky [THIS JOURNAL, **68**, 716 (1946)] reported 116–117°; S. Winstein and L. L. Ingraham [*ibid.*, **74**, 1160 (1952)] reported 122–122.5°.

[41] An authentic sample of this derivative, m.p. 120–121°, was prepared according to the directions of J. W. Baker [*J. Chem. Soc.*, 1302 (1950)]. Comparison of our sample with the product prepared by Baker (reference 18) established the identity of the two materials.

separated as orange needles, m.p. 112–118°, yield 0.36 g. (60% based on the original oxide employed). Recrystallization from ethanol raised the melting point of the derivative to 120–121°. The product was shown to be identical with an authentic sample of methyl isopropyl ketone 2,4-dinitrophenylhydrazone and to differ from the corresponding derivative of acetone by the criteria previously described. We were unable to isolate any other product from the crude pyrolysis product.

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[Contribution from the Department of Chemistry, Duke University]

The Chlorination of 3-Phenanthrol

By Charles K. Bradsher, Frances C. Brown and Preston H. Leake[1]

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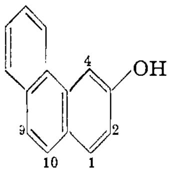
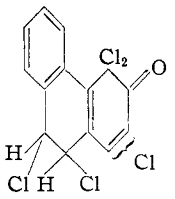
The chlorination of 3-phenanthrol with one equivalent of sulfuryl chloride yielded 4-chloro-3-phenanthrol, while with two equivalents, 4,9-dichloro-3-phenanthrol was produced. Four equivalents afforded a neutral compound believed to be 1,2,4,4,9-pentachloro-3-keto-1,2,3,4-tetrahydrophenanthrene (XIII). Reductive dehydrohalogenation of XIII yielded 2,4,9-trichlorophenanthrol. None of the chlorinated 3-phenanthrols proved superior to the parent substance in activity toward *A. niger* or *E. coli*.

Of more than eighty phenanthrene derivatives tested for fungistatic activity against *Aspergillus niger*, Steinberg[2] found 3-phenanthrol to be most effective. Subsequently[3] it was demonstrated that comparable fungitoxicity was shown by several congeners including related fluorenols and hydroxybiphenyls. The observation that the fungitoxicity of phenol[4] and of 2-naphthol[5] was increased by the introduction of one or more chlorine atoms suggested that it might be of interest to prepare and test some chlorinated 3-phenanthrols.

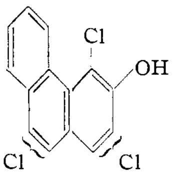
The chlorination of 3-phenanthrol (I) has been investigated in a preliminary way by Fieser and Dunn[6] using an excess of elementary chlorine. The product was described as probably 1,4,4-trichloro-3-keto-3,4-dihydrophenanthrene-9,10-dichloride (II) since on reductive dehydrohalogenation with stannous chloride it yielded an acidic compound which on the basis of its reactions was described as "1(?),4,9(or 10)-trichloro-3-phenanthrol" (III).



I



II



III

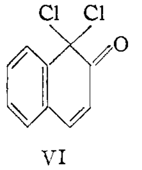
For greater convenience, sulfuryl chloride was used in our studies. When one equivalent was allowed to react with I, a monochlorination product was obtained. By analogy with the chlorination of 2-naphthol[7] it would be anticipated that the chlorine was at position 4. Strong support for this formulation was afforded by the failure of the chlorophenanthrol to undergo diazonium coupling when treated with diazotized sulfanilic acid. The characteristic ease with which 1-halo-2-naphthols undergo reductive dehalogenation when treated with tin and hydrochloric acid,[8] was likewise shown by our new chlorophenanthrol which under the same conditions, afforded 3-phenanthrol in 91% yield. It was shown that 3-methoxyphenanthrene gave similar orientation in the chlorination reaction with sulfuryl chloride. The new ether, when subjected to the conditions of the Rosenmund–von Braun reaction, yielded a nitrile IV. Refluxing the nitrile with 35% potassium hydroxide solution

$$\text{3-CH}_3\text{O-4Cl-C}_{14}\text{H}_8 \xrightarrow{\text{CuCN}}$$

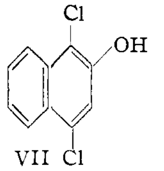
$$\underset{\text{IV}}{\text{3-CH}_3\text{O-4CN-C}_{14}\text{H}_8} \xrightarrow{\text{KOH}} \underset{\text{V}}{\text{3-OH-4-CN-C}_{14}\text{H}_8}$$

gave the hydroxy nitrile V[9] rather than the amide or acid. The unreactivity of the nitrile group can be explained in terms of the steric hindrance expected at the 4-position of a 3-substituted phenanthrene.

Chlorination of 3-phenanthrol with two equivalents of sulfuryl chloride or of 4-chloro-3-phenanthrol with one equivalent yielded a dichloro-3-phenanthrol. In this instance analogy with 2-naphthol is not particularly helpful. In the latter case the consensus is that the dichlorination product is 1,1-dichloro-2(1H)-naphthalenone (VI).[10]



VI



VII

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[1] Allied Chemical and Dye Corporation Fellow 1953–1954. This work was supported in part by the Chemical Corps, Fort Detrick, Maryland, under contract with Duke University.

[2] R. A. Steinberg, *J. Agr. Research*, **60**, 765 (1940).

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[7] Position 4 of 3-phenanthrol is structurally related to position 1 of 2-naphthol. It was demonstrated by T. Zincke that 2-naphthol chlorinates in the 1-position; *Ber.*, **21**, 1027 (1888).

[8] *E.g.*, H. Franzen and G. Stauble, *J. prakt. Chem.*, [2] **103**, 352 (1921–22); K. Fries and K. Schimmelschmidt, *Ber.*, **58**, 2835 (1925).

[9] Other instances of ether cleavage by alkali are known, *e.g.*, E. C. Dodds, *Proc. Roy. Soc. (London)*, **B132**, 88 (1944), although the present case might be considered a nucleophilic displacement by hydroxide ion, to be compared with the displacement of *ortho* methoxyl groups from sterically hindered ketones by the Grignard reagent; R. C. Fuson and S. B. Speck, This Journal, **64**, 2446 (1942).

[10] (a) T. Zincke, *Ber.*, **21**, 3378, 3540 (1888); (b) K. Fries and K. Schimmelschmidt, *Ann.*, **484**, 245 (1930); (c) P. M. James and D. Woodcock, *J. Chem. Soc.*, 1931 (1951).