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

The Rearrangement of α,β-Epoxy Ketones. V. Rearrangements Resulting in Ring Contraction

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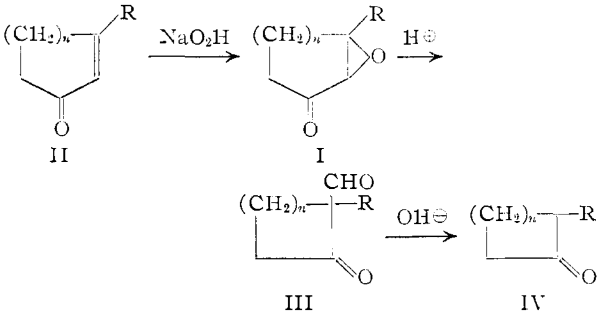
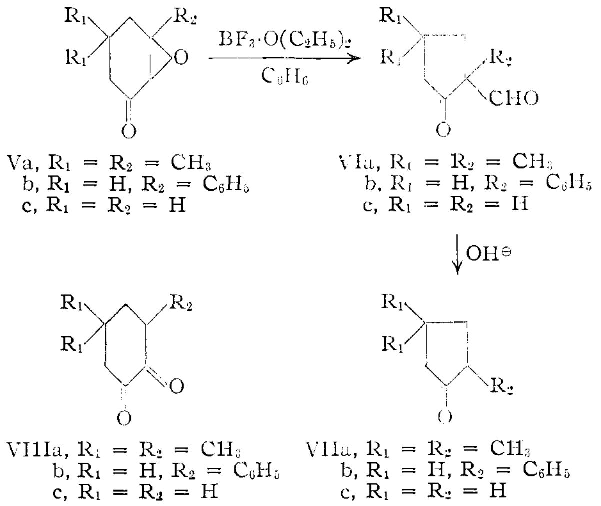
A method is described for the conversion of cyclohexenone derivatives to the corresponding cyclopentanone derivatives. The procedure involves the isomerization of 2,3-epoxycyclohexanone derivatives to the corresponding α-formyl- or α-acylcyclopentanones accompanied in certain instances by 1,2-cyclohexanediones. Isophorone oxide was converted to a mixture of 2,4,4-trimethylcyclopentanone, 2-formyl-2,4,4-trimethylcyclopentanone and 3,5,5-trimethyl-1,2-cyclohexanedione. 2,3-Epoxycyclohexanone yielded a mixture of cyclopentanone and 1,2-cyclohexanedione. 2,3-Epoxy-3-phenylcyclohexanone and 2,3-epoxy-2-methylcyclohexanone gave 2-phenylcyclopentanone and 2-acetylcyclopentanone, respectively. The isomerization of 3-methyl- and 3-phenyl-2,3-epoxycyclopentanone yielded the corresponding 3-substituted-1,2-cyclopentanediones.

Consideration of the normal course of the acid-catalyzed rearrangement of α,β-epoxy ketones (*i.e.*, acyl migration)[2] suggested that this reaction might provide a useful method for reducing the ring size of cyclic ketones. For example, rearrangement of an epoxy ketone of type I, which is readily accessible *via* the corresponding unsaturated ketone II, would be expected to yield the keto aldehyde III. Subsequent cleavage of the formyl group would yield the ketone IV, the over-all result being the loss of a carbon atom adjacent to the carbonyl group.



The series of compounds V was selected to test the applicability of the method for conversion of cyclohexanone derivatives to the corresponding derivatives of cyclopentanone. The isomerization of a benzene solution of isophorone oxide (Va) in the presence of boron trifluoride etherate produced the keto aldehyde VIa (33%) accompanied by the ketone VIIa (28%). The ketone VIIa was presumably formed by the deformylation of VIa during the isolation. A small amount (3%) of the enol form of the α-diketone VIIIa also was formed. Treatment of the keto aldehyde VIa with boiling, ethanolic sodium hydroxide produced the ketone VIIa in 90% yield. A more satisfactory procedure for the preparation of the ketone VIIa involved treatment of the crude reaction mixture from the isomerization with ethanolic sodium hydroxide. This procedure increased the yield of the desired ketone VIIa (70–75%) and facilitated separation of the alkali-soluble α-diketone VIIIa.

By use of this procedure 2,3-epoxy-3-phenylcyclohexanone (Vb) was converted to 2-phenylcyclopentanone VIIb (68%), the intermediate keto aldehyde VIb not being isolated. None of the α-diketone VIIIb could be isolated from the reaction mixture. The rearrangement of 2,3-epoxycyclohexanone (Vc) followed by alkaline cleavage produced cyclopentanone VIIc (25%); however, the major product was the α-diketone VIIIc (56%). The yields of the two products VIIc and VIIIc were not altered significantly when the oxide Vc was isomerized in the presence of boron trifluoride rather than boron trifluoride etherate.



Va, $R_1 = R_2 = CH_3$
b, $R_1 = H, R_2 = C_6H_5$
c, $R_1 = R_2 = H$

VIa, $R_1 = R_2 = CH_3$
b, $R_1 = H, R_2 = C_6H_5$
c, $R_1 = R_2 = H$

VIIIa, $R_1 = R_2 = CH_3$
b, $R_1 = H, R_2 = C_6H_5$
c, $R_1 = R_2 = H$

VIIa, $R_1 = R_2 = CH_3$
b, $R_1 = H, R_2 = C_6H_5$
c, $R_1 = R_2 = H$

A possible explanation for the variation in the relative amounts of the rearrangement products VI and VIII is shown in the accompanying equations. It will be noted from the preceding results that as the stability of the carbonium ion IX, the presumed intermediate in the formation of the keto aldehyde X, decreases the proportion of α-diketone XI in the product increases. Such a result would be anticipated if the α-diketone XI was formed by an acid-catalyzed elimination reaction (represented by XII) which was competing with the formation of the intermediate IX.

The behavior of 2,3-epoxy-2-methylcyclohexanone (XIII), a compound which cannot undergo an elimination of the type XII, is in agreement with the foregoing hypothesis. Rearrangement of the oxide XIII was appreciably slower than had been the case with the cyclohexanone oxides V as would be anticipated if the formation of the secondary carbonium ion XIV was required. The only prod-

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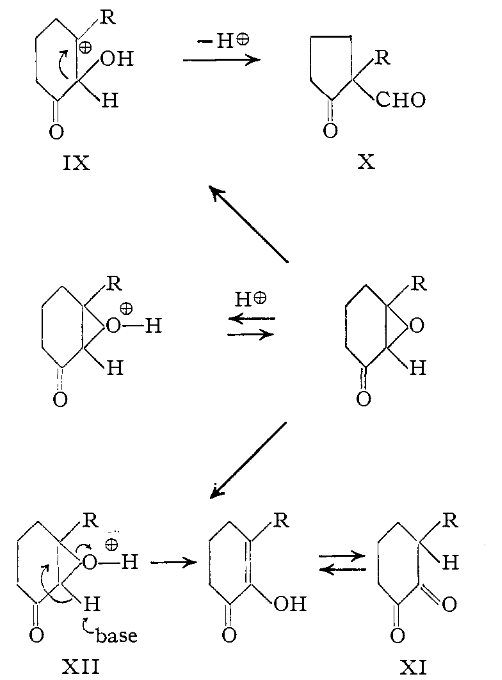
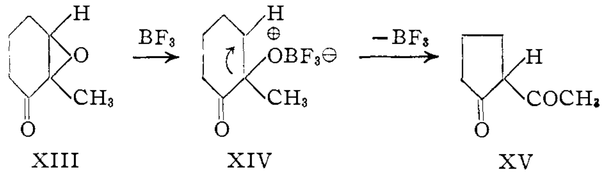
[1] Alfred P. Sloan Foundation Research Assistant, 1956.

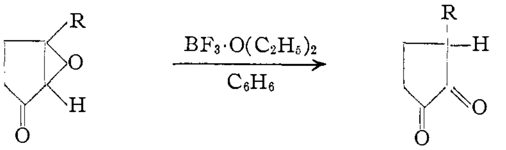
[2] For previous papers in this series see THIS JOURNAL, **76**, 1235 (1954); **77**, 6525 (1955); **78**, 2298, 4394 (1956).

uct which could be isolated was the β-diketone XV, the product expected from the reaction path represented by XIV.



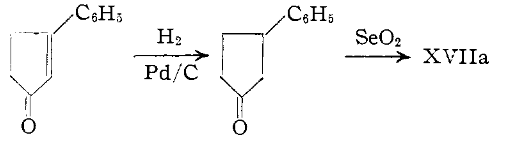


In order to learn whether similar ring contractions could be achieved in the cyclopentanone series, the isomerization of the cyclopentenone oxides XVI was investigated. However, the only products which could be isolated were the enol forms of the α-diketones XVII. These products could arise either by the formation of a carbonium ion analogous to IX followed by hydrogen migration or by a concerted elimination reaction analogous to XII. The structure of the diketone XVIIa was established by hydrogenation of the unsaturated ketone XVIII to the ketone XIX which was oxidized to the diketone XVIIa with selenium dioxide.



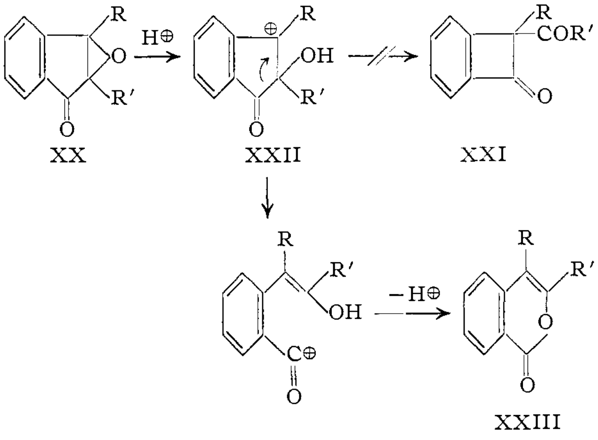
XVIa, R = C_6H_5
b, R = CH_3

XVIIa, R = C_6H_5
b, R = CH_3



XVIII XIX

Studies[3–7] of the isomerization of 2,3-disubstituted indenone oxides XX and related compounds have similarly established that ring contraction (*i.e.*, XXI) does not occur[8]; instead the presumed intermediates XXII are converted to lactones XXIII.



We conclude, therefore, that the isomerization of α,β-epoxy ketones provides a satisfactory method for the contraction of six-membered (and presumably larger) cyclic ketones, particularly if the α,β-epoxycyclohexanone derivative has an additional substituent at the β-position. The method is not applicable to the preparation of cyclobutanone derivatives from the corresponding cyclopentanones.

Experimental[9]

Preparation of the Epoxy Ketones.—All of the unsaturated ketones (Table I) except commercially available isophorone were prepared by previously described procedures. The reaction time for each epoxidation was determined by the periodic measurement of the optical density of the reaction mixture at the wave length corresponding to the maximum of longest wave length for the unsaturated ketone being oxidized. In each case the reaction was stopped when the optical density of the reaction mixture had fallen to approximately 1% of its initial value. If shorter reaction times were employed a difficultly separable mixture of the epoxy ketone and the unchanged unsaturated ketone resulted; longer reaction times reduced the yield of the epoxy ketone. The procedure for isophorone oxide is illustrative.

A solution of 55.2 g. (0.4 mole) of isophorone and 115 ml. (1.2 moles) of 30% aqueous hydrogen peroxide in 400 ml. of methanol was cooled to 15° and 33 ml. (0.2 mole) of 6 *N* aqueous sodium hydroxide was added, dropwise and with stirring, over a period of 1 hour. During the addition the temperature of the reaction mixture was maintained at 15–20°. The resulting mixture was stirred for 3 hours, the temperature of the reaction mixture being kept at 20–25°, then poured into 500 ml. of water. The product was extracted with ether and dried over magnesium sulfate. Distillation afforded 43.36 g. (70.4%) of isophorone oxide.

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[3] E. Weitz and A. Scheffer, *Ber.*, **54**, 2334 (1921).

[4] C. F. Koelsch and C. D. LeClaire, THIS JOURNAL, **65**, 754 (1943).

[5] C. F. H. Allen and J. W. Gates, Jr., *ibid.*, **65**, 1230 (1943).

[6] A. Banchetti, *Gazz. chim. ital.*, **81**, 419 (1951); *C. A.*, **46**, 5022 (1952).

[7] H. O. House, E. A. Chandross and B. J. Puma, *J. Org. Chem.*, **21**, 1256 (1956).

[8] The one example of ring contraction initially reported has subsequently been found to be incorrect (see ref. 7).

[9] All melting points are corrected and all boiling points are uncorrected. The ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

TABLE I

Unsaturated ketone	Physical constants	Infrared absorption, cm.$^{-1}$	Ultraviolet absorption, mμ (ε)
Isophorone	B.p. 72° (4.9 mm.) $n^{25}\mathrm{D}$ 1.4760[a]	1670 (conj. C=O)[17,18] 1638 (conj. C=C)	235 (13,300)
3-Phenyl-2-cyclohexenone	M.p. 61-61.5°[b]	1660 (conj. C=O)[19,20]	221 (10,200) 283 (19,200)
2-Cyclohexenone	B.p. 58.5° (13 mm.) $n^{25}\mathrm{D}$ 1.4826[c]	1670 (conj. C=O)[20,21] 1625 (conj. C=C)	225 (8,650)
2-Methyl-2-cyclohexenone	B.p. 92–95° (60 mm.) $n^{25}\mathrm{D}$ 1.4830[d]	1670 (conj. C=O)[17,20] 1615 (conj. C=C)	235 (9,600)[d]
3-Phenyl-2-cyclopentenone	M.p. 83-84°[e]	1690 (conj. C=O)[19,20]	218 (12,000)[e] 223 (11,900) 283 (24,100)
3-Methyl-2-cyclopentenone	B.p. 74–76° (15 mm.) $n^{25}\mathrm{D}$ 1.4870[f]	1710 (conj. C=O)[17,20] 1630 (conj. C=C)	226 (15,000)[f]

[a] Lit.[10] 99° (14 mm.), $n^{25}\mathrm{D}$ 1.47613. [b] Lit.[11] m.p. 64.5-66°. [c] Lit.[12] b.p. 67° (25 mm.), $n^{20}\mathrm{D}$ 1.4879. [d] Lit.[13] b.p. 98–101° (77 mm.), $n^{25}\mathrm{D}$ 1.4836, $\lambda_{\max}$ 234 mμ (ε 9660). [e] Lit.[14] m.p. 83–84°, $\lambda_{\max}$ 217.5 mμ (ε 11,500), 222 mμ (ε 10,730) and 281 mμ (ε 23,000). [f] Lit.[15] b.p. 74° (15 mm.), $n^{20}\mathrm{D}$ 1.4893, $\lambda_{\max}$ 225 mμ (ε 18,150).

TABLE II

Epoxy ketone	Total reacn. time, hr.	Yield, %	Physical constants	Molecular formula	Analyses, % Calcd.	Found	Infrared absorption, cm.$^{-1}$	Ultraviolet absorption, mμ (ε)
Va	4	70.4	B.p. 70–73° (5 mm.) $n^{25}\mathrm{D}$ 1.4510[a]	$C_9H_{14}O_2$	C, 70.10 H, 9 15	C, 69.99 H, 9.16	1720 (C=O)[17,18]	292 (43)
Vb	3	60	M.p. 55–55.5°[b]	$C_{12}H_{12}O_2$	C, 76.57 H, 6.43	C, 76.58 H, 6.59	1715 (C=O)[17,18]	260 (290), 267 (200), 302 (120)
Vc	4	30	B.p. 75–78° (10 mm.) $n^{25}\mathrm{D}$ 1.4725	$C_6H_8O_2$	C, 64.27 H, 7.19	C, 64.51 H, 6.96	1710 (C=O)[17,20]	299 (20)
XIII	2.5	39	B.p. 80-84° (50 mm.) $n^{25}\mathrm{D}$ 1.4680	$C_7H_{10}O_2$	C, 66.64 H, 7.99	C, 66.74 H, 8.04	1720 (C=O)[17,20]	298 (60)
XVIa	6	63	M.p. 35–35.5°[b] B.p. 110–112° (0.7 mm.)	$C_{11}H_{10}O_2$	C, 75.84 H, 5.79	C, 75.59 H, 5.93	1760 (C=O)[19,20]	268 (30)
XVIb	2.5	40	B.p. 76–78° (20 mm.) $n^{25}\mathrm{D}$ 1.4471	$C_6H_8O_2$	C, 64.27 H, 7.19	C, 64.03 H, 7.34	1760 (C=O)[17,20]	303 (20)

[a] Lit.[16] b.p. 208-211°, $n\mathrm{D}$ 1.4591. [b] White plates from hexane.

Rearrangement of Isophorone Oxide (Va). Procedure A.—A solution of 10.0 g. (0.065 mole) of the oxide in 200 ml. of benzene was treated with 8 ml. (0.064 mole) of boron trifluoride etherate. The resulting solution was allowed to stand for 5 minutes, diluted with ether, washed with water and dried over magnesium sulfate. After the organic solution had been concentrated, it was distilled through a Holtzmann column under reduced pressure. The yield **of 2,4,4-trimethylcyclopentanone** (VIIa), b.p. 55–60° (20 mm.), $n^{25}\mathrm{D}$ 1.4290 (lit.[22] b.p. 161–165°, $n^{20}\mathrm{D}$ 1.4313), was 2.27 g. (27.7%); the latter fractions from the distillation afforded 3.34 g. (33.4%) of **2-formyl-2,4,4-trimethylcyclopentanone** (VIa), a colorless liquid boiling at 49–50° (2 mm.), $n^{25}\mathrm{D}$ 1.4495. A solution of the pot residue from the distillation in petroleum ether deposited 0.31 g. (3.1%) of **3,5,5-trimethyl-1,2-cyclohexanedione** (VIIIa), m.p. 90–93°. Recrystallization gave the pure diketone as white needles, m.p. 92–93° (lit.[16] 92–93°).

The infrared spectrum[17,18] of 2,4,4-trimethylcyclopentanone (VIIa) has a band at 1740 cm.$^{-1}$ (C=O in a five-membered ring). The ketone formed a semicarbazone, m.p. 161–164°, in 85% yield; the pure semicarbazone separated from aqueous ethanol as white plates, m.p. 171–171.5° (lit.[23] 171–173°). The 2,4-dinitrophenylhydrazone of the ketone crystallized from ethanol as orange plates, m.p. 160–161°, yield 90%. Recrystallization sharpened the melting point of the derivative to 160.5–161° (lit.[22] 160.6–160.9°). The infrared spectrum[18,19] of the dinitrophenylhydrazone has no band attributable to a carbonyl function.

The infrared spectrum[17,18] of 2-formyl-2,4,4-trimethylcyclopentanone (VIa) has bands at 1750 cm.$^{-1}$ (C=O in a five-membered ring), 1725 cm.$^{-1}$ (C=O) and 2720 cm.$^{-1}$ (C—H of an aldehyde); the ultraviolet spectrum has a maximum at 226 mμ (ε 100).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.92; H, 9.94.

The keto aldehyde VIa gives no color with ferric chloride. A solution of 0.1 g. (0.00065 mole) of the product and 3 ml. (0.018 mole) of 6 *N* aqueous sodium hydroxide in 10 ml. of ethanol was boiled for 30 minutes, diluted with an equal volume of water and extracted with ether. Concentration of the ether followed by treatment of the residue with 2,4-dinitrophenylhydrazine produced the 2,4-dinitrophenylhydrazone of 2,4,4-trimethylcyclopentanone, m.p. 159.5–161°, yield 0.18 g. (90%). A mixed melting point determination established the identity of the product with the sample previously described.

The infrared spectrum[17,18] of 3,5,5-trimethyl-1,2-cyclohexanedione exhibits bands at 1680 cm.$^{-1}$ (conjugated C=O) 1655 cm.$^{-1}$ (conjugated C=C) and 3500 cm.$^{-1}$ (O—H); the ultraviolet spectrum has a maximum at 274 mμ (ε

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(11) G. F. Woods and I. W. Tucker, THIS JOURNAL, **70**, 2174 (1948).

(12) F. C. Whitmore and G. W. Pedlow, Jr., *ibid.*, **63**, 758 (1941).

(13) E. W. Warnoff and W. S. Johnson, *ibid.*, **75**, 494 (1953).

(14) A. L. Wilds and co-workers, *ibid.*, **69**, 1985 (1947).

(15) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1127 (1952).

(16) W. Treibs, *Ber.*, **66**, 1483 (1933).

(17) Determined in carbon tetrachloride solution.

(18) Determined with a Perkin–Elmer double beam infrared recording spectrophotometer, model 21, fitted with a sodium chloride prism.

(19) Determined in chloroform solution.

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

(21) Determined as a pure liquid.

(22) S. F. Birch and E. A. Johnson, *J. Chem. Soc.*, 1493 (1951).

(23) A. N. Dey and R. P. Linstead, *ibid.*, 1063 (1935).

9,400). A solution of 2.0 g. (0.013 mole) of isophorone oxide (Va) and 10 ml. of 6 *N* aqueous sodium hydroxide in 40 ml. of ethanol was boiled for 2 minutes, acidified with dilute hydrochloric acid, and extracted with ether. After the extract had been washed with water, dried and concentrated, the residual oil was taken up in petroleum ether. The crude 3,5,5-trimethyl-1,2-cyclohexanedione, m.p. 88–92°, yield 0.05 g. (2.5%), which separated was recrystallized.[24] The pure α-diketone, m.p. 92–92.5°, was shown to be identical with the sample isolated from the acid-catalyzed isomerization of isophorone oxide by a mixed melting point determination and by comparison of the infrared and ultraviolet spectra of the two samples.

Procedure B.—A 10.0-g. (0.065 mole) sample of the oxide was treated with 5 ml. (0.04 mole) of boron trifluoride etherate and 200 ml. of benzene as described previously. The crude mixture of rearrangement products was dissolved in a solution of 15 ml. (0.09 mole) of 6 *N* aqueous sodium hydroxide in 60 ml. of ethanol. After the resulting solution had been boiled under reflux for 30 minutes an equal volume of water was added and the mixture was extracted with ether. The ethereal extract was dried, concentrated and distilled under reduced pressure to give 5.7 g. (70%) of 2,4,4-trimethylcyclopentanone (VIIa), b.p. 71–73° (30 mm.), $n^{25}D$ 1.4290. Acidification of the aqueous phase from the reaction mixture followed by appropriate manipulations afforded 0.3 g. (3%) of 3,5,5-trimethyl-1,2-cyclohexanedione (VIIIa), m.p. 92–93°. In a similar experiment the yield of the ketone VIIa, isolated as its 2,4-dinitrophenylhydrazone m.p. 160–161°, was 75%; the yield of the α-diketone VIIIa was 3.5%. When a 10-g. (0.065 mole) sample of the oxide was treated with 10 ml. (0.08 mole) of boron trifluoride etherate as described the yields of the ketone VIIa and the α-diketone VIIIa were 55 and 3.3%, respectively.

Rearrangement of 2,3-Epoxy-3-phenylcyclohexanone (Vb).—A solution of 2.3 g. (0.012 mole) of the oxide and 1 ml. (0.008 mole) of boron trifluoride etherate in 75 ml. of benzene was allowed to stand for 5 minutes. The resulting mixture was worked up as described previously. A solution of the crude product and 13.6 g. (0.1 mole) of sodium acetate trihydrate in 50 ml. of ethanol was boiled under reflux for 45 minutes, diluted with water and extracted with ether. The extract was dried over magnesium sulfate and concentrated. Distillation of the residue afforded 1.30 g. (68%) of **2-phenylcyclopentanone (VIIb)**, b.p. 84–86° (0.3 mm.), which solidified on standing, m.p. 37–38°. Recrystallization from hexane gave the pure ketone as white plates melting at 38–38.5° (lit.[25] b.p. 114–124° (2 mm.), m.p. 38°). No acidic product could be isolated from the reaction mixture.

The infrared spectrum[17,18] of the ketone VIIb has a band at 1742 cm.$^{-1}$ (C=O in a five-membered ring); the ultraviolet spectrum exhibits maxima at 253 mμ (ϵ 173), 259 mμ (ϵ 210) and 264 mμ (ϵ 173). The semicarbazone of the product separated from ethanol as white needles, m.p. 213–213.5° dec. (lit.[26] 213–214° dec.), yield 90%. The 2,4-dinitrophenylhydrazone separated as light orange needles, m.p. 140–145°, yield 95%; recrystallization from hexane raised the melting point to 145–146° (lit.[25] 146°). The infrared spectrum[18,19] of the 2,4-dinitrophenylhydrazone has no band attributable to a carbonyl function.

Rearrangement of 2,3-Epoxycyclohexanone (Vc).—A solution of 0.20 g. (0.0018 mole) of the oxide and 0.2 ml. (0.0016 mole) of boron trifluoride ether in 20 ml. of benzene was allowed to stand for 3 minutes. The reaction mixture was worked up as described in procedure B for the rearrangement of isophorone oxide. The ether extract of the alkaline solution was treated with a solution of 2,4-dinitrophenylhydrazine and hydrochloric acid in boiling ethanol. The mixture of dinitrophenylhydrazones obtained was separated by fractional crystallization from ethanol and from an ethanol–ethyl acetate mixture to give 0.12 g. (24.5%) of the 2,4-dinitrophenylhydrazone of cyclopentanone, m.p. 143–144° (lit.[27] 144–145°) and 0.20 g. (23.3%) of the **bis-2,4-dinitrophenylhydrazone of 1,2-cyclohexanedione**, m.p. 220–224° dec. Recrystallization from an ethanol–ethyl acetate mixture raised the melting point of the bis-2,4-dinitrophenylhydrazone to 227–228° dec. (lit.[28] 227–228° dec.). Acidification of the aqueous solution from the reaction mixture followed by extraction with ether and treatment of the extract with 2,4-dinitrophenylhydrazine afforded an additional 0.28 g. (32.7%) of the 1,2-cyclohexanedione derivative (total yield 0.48 g. or 56%). Each of the derivatives was identified both by a mixed melting-point determination with an authentic sample and by comparison of the infrared spectra of the two samples.

A solution of 0.10 g. (0.0009 mole) of the oxide in 25 ml. of benzene was saturated with gaseous boron trifluoride and the resulting solution was allowed to stand for 5 minutes. The products, isolated as in the previous case, were the 2,4-dinitrophenylhydrazone of cyclopentanone, yield 0.05 g. (20%), and the bis-2,4-dinitrophenylhydrazone of 1,2-cyclohexanedione, yield 0.22 g. (51%).

Rearrangement of 2,3-Epoxy-2-methylcyclohexanone (XIII).—A solution of 0.50 g. (0.004 mole) of the epoxy ketone in 20 ml. of benzene was saturated with gaseous boron trifluoride and the resulting mixture was allowed to stand for 30 minutes. The reaction mixture was diluted with ether, washed with a saturated, aqueous solution of sodium chloride and then extracted with 5% aqueous sodium hydroxide. Attempts to isolate a crystalline product or a 2,4-dinitrophenylhydrazone from the material remaining in the ether solution were unsuccessful. The alkaline extract was acidified and extracted with ether. The ethereal extract was shaken with a saturated, aqueous solution of cupric acetate, concentrated and diluted with pentane. The crude copper salt which separated was recrystallized from an ether–pentane mixture to give 0.18 g. (29%) of the **copper salt of 2-acetylcyclopentanone** as gray-green needles, m.p. 237–238° dec. (lit.[29] 240° dec.). No other acidic product could be isolated. The reaction of a solution of 2,3-epoxy-2-methylcyclopentanone in benzene with one equivalent of boron trifluoride etherate produced the same copper salt in 15% yield.

The infrared spectrum[20,30] of the copper salt has a broad band in the 6 μ region with its center at 1590 cm.$^{-1}$. The copper salt was shown to be identical with an authentic sample[29] both by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

Rearrangement of 2,3-Epoxy-3-phenylcyclopentanone (XVIa).—A solution of 0.2 g. (0.001 mole) of the epoxide and 0.1 ml. (0.0008 mole) of boron trifluoride etherate in 15 ml. of benzene was allowed to stand for 5 minutes and then worked up in the usual manner. The crude product, m.p. 188–191°, was recrystallized from benzene to give 0.17 g. (85%) of the enol form of **3-phenyl-1,2-cyclopentanedione** as colorless plates melting at 191–191.5°. The diketone gave a dark green color with alcoholic ferric chloride. The infrared spectrum[20,30] of the enolic diketone exhibits bands at 3300 cm.$^{-1}$ (associated O—H), 1680 cm.$^{-1}$ (conjugated C=O)[31] and 1635 cm.$^{-1}$ (conjugated C=C). The ultraviolet spectrum of the product has maxima at 226 mμ (ϵ 7,500), 233 mμ (ϵ 6,900) and 307 mμ (ϵ 24,600).

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79; mol. wt., 174. Found: C, 75.74; H, 6.03; mol. wt., 183 (Rast).

3-Phenylcyclopentanone (XIX).—A solution of 2.0 g. (0.0126 mole) of 3-phenyl-2-cyclopentenone in 25 ml. of

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[24] Treibs (ref. 16) has reported that the reaction of isophorone oxide (Va) with methanolic alkali yields a mixture of the enolized form of the α-diketone VIIIa and its methyl ether. The nature of the oil which remained after our separation of the crystalline diketone VIIIa is being investigated currently.

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[26] R. T. Arnold, J. S. Buckley, Jr., and R. M. Dodson, THIS JOURNAL, **72**, 3153 (1950).

[27] J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

[28] F. Ramirez and A. F. Kirby, *ibid.*, **74**, 4331 (1952).

[29] R. M. Manyik, F. C. Frostick, Jr., J. J. Sanderson and C. R. Hauser, *ibid.*, **75**, 5030 (1953).

[30] Determined as a suspension in a potassium bromide pellet.

[31] Both this ketone and 3-phenyl-2-cyclopentenone have bands in the 6μ region, attributable to a conjugated carbonyl group in a five-membered ring, which are found at abnormally long wave lengths. We have observed a similar result with 3,4-diphenyl-4-hydroxy-2-cyclopentenone. However, if the 3-phenyl-2-cyclopentenone system has an additional substituent in the 2-position, the location of the carbonyl band is normal (*i.e.*, 1700–1710 cm.$^{-1}$). For example, this band is found at 1700 cm.$^{-1}$ in the spectrum[17,20] of 2-methyl-3-phenyl-2-cyclopentenone. Similar results have been observed when the substituent at the 2-position is an aryl group [see N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, THIS JOURNAL, **75**, 2283 (1953); P. Yates and G. H. Stout, *ibid.*, **76**, 5110 (1954)].

ethanol was hydrogenated over a 10% palladium-on-charcoal catalyst, 314 ml. (0.0126 mole) of hydrogen being absorbed. The yield of 3-phenylcyclopentanone, b.p. 110–111° (1 mm.), $n^{25}D$ 1.4533 (lit.[32] b.p. 90–95° (0.05 mm.)), was 1.85 g. (91.5%). The 2,4-dinitrophenylhydrazone of the ketone, m.p. 154–154.5° (lit.[32] 154–155°) was obtained in 99% yield. The infrared spectrum of the ketone[19,20] has a band at 1760 cm.$^{-1}$ (C═O in a five-membered ring).

3-Phenyl-1,2-cyclopentanedione (XVIIa).—A solution of 1.0 g. (0.00625 mole) of 3-phenylcyclopentanone, 0.69 g. (0.00625 mole) of selenium dioxide and 2 drops of acetic acid in a mixture of 10 ml. of water and 30 ml. of dioxane was boiled under reflux for 3 hours. The selenium which was separated by filtration amounted to 0.42 g. (85%). The filtrate was concentrated and the residue dissolved in a hot benzene–hexane mixture. The crude solid which separated from the cold solution afforded 0.20 g. (18%) of 3-phenyl-1,2-cyclohexanedione, m.p. 189–191°, after recrystallization from benzene. An additional recrystallization sharpened the melting point to 190–191°. The product was shown to be identical with the sample obtained from 2,3-epoxy-3-phenylcyclopentanone both by a mixed melting point determination and by comparison of the infrared and ultraviolet spectra of the two samples.

Rearrangement of 2,3-Epoxy-3-methylcyclopentanone (XVIb).—A solution of 0.5 g. (0.0045 mole) of the epoxy ketone and 0.5 ml. (0.004 mole) of boron trifluoride etherate in 30 ml. of benzene was allowed to stand for 2 minutes and then worked up in the usual manner. The product, the **enol form of 3-methyl-1,2-cyclopentanedione**, crystallized from hexane as white needles, m.p. 99–100° (lit.[33] 100°), yield 0.40 g. (80%). The bis-2,4-dinitrophenylhydrazone of the diketone separated as red plates, m.p. 220–230° dec., yield 99%. Recrystallization from an ethanol–ethyl acetate mixture raised the melting point of the derivative to 237–238° dec. (lit.[33] 238°). The enolic diketone gave a violet color with alcoholic ferric chloride. The infrared spectrum[20,30] of the enolized diketone has bands at 3350 cm.$^{-1}$ (associated O—H), 1695 cm.$^{-1}$ (conjugated C═O in a five-membered ring) and 1635 cm.$^{-1}$ (conjugated C═C); the ultraviolet spectrum has a maximum at 259 mμ (ε 9,000).

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[32] F. Winternitz, M. Mousseron and G. Rouzier, *Bull. soc. chim. France*, 190 (1953).

[33] T. Enkvist, B. Alfredsson, M. Merikallio, P. Pääkkönen and O. Järvelä, *Acta Chem. Scand.*, **8**, 51 (1954); *C. A.*, **48**, 6690 (1954).

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Further Evidence for the Existence of Three Different Free Hydroxyl Groups in Acetone-soluble Cellulose Acetate

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The free hydroxyl groups of an acetone-soluble cellulose acetate were replaced by tosyloxy groups which were in turn replaced by pyrrolidino groups. In the course of the second reaction, the acetyl groups were removed. Hydrolysis of the resulting pyrrolidinopolysaccharide yielded, in addition to D-glucose, three nitrogen-containing hexoses. Determination of the position of the pyrrolidino group in each hexose led to the conclusion that the free hydroxyl groups in acetone-soluble cellulose acetate are distributed among the 2-, 3- and the 6-positions of the anhydroglucose unit.

A considerable amount of effort has been spent on the investigation of the positions occupied by the free hydroxyl groups of acetone-soluble cellulose acetate.[2] Gardner and Purves studied the kinetics of the tosylation of a cellulose acetate containing 0.56 free hydroxyl group per anhydroglucose unit. Interpretation of the rate curve resulted in the assignment of 0.197 free hydroxyl group to the 6-position, 0.139 to the 3-position and 0.223 to the 2-position. Malm, Tanghe and Laird[3] have shown that the distribution of free hydroxyl groups is influenced by the amount of water present in the bath during hydrolysis of the cellulose acetate.

We believed that a substitution of the free hydroxyl groups with an amine, followed by hydrolysis and identification of fragments, would be of considerable value in studying this problem. An acetone-soluble cellulose acetate[4] containing 0.73 free hydroxyl group per anhydroglucose unit was allowed to react with *p*-toluenesulfonyl (tosyl) chloride in pyridine. This tosylated cellulose acetate was then treated with pyrrolidine by refluxing for 30 hr. A quantitative and stoichiometric replacement of tosyl groups by pyrrolidino groups took place. At the same time acetyl groups were completely replaced by hydroxyl groups. It may be assumed that the pyrrolidino groups occupy the positions originally occupied by the free hydroxyl groups of the cellulose acetate. It is to be expected that the replacement of tosyl groups by pyrrolidino groups would result in inversion of the carbon atom. As far as we know there is no previous report in the literature of a quantitative and stoichiometric replacement of tosyl groups by amino groups in cellulose derivatives.[5]

This pyrrolidinopolysaccharide was then hydrolyzed with hydrochloric acid. The resulting mixture of sugars was separated on a column of Dowex-50 using a technique described by Gardell.[6] When the column was developed with 0.3 *N* hydrochloric acid, D-glucose came through immediately (zone 1). This was followed by three well-defined zones (zones 2, 3 and 4). We did not succeed in crystallizing the three amino sugars, but analysis of the

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[1] Abstracted from the 1955 Thesis of S. G. Sunderwirth, du Pont teaching fellow 1954–1955.

[2] I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind. Japan*, **37**, Supplementary Binding, 604 (1934); F. B. Cramer and C. B. Purves, THIS JOURNAL, **61**, 3458 (1939); T. S. Gardner and C. B. Purves, *ibid.*, **64**, 1539 (1942); C. J. Malm, L. J. Tanghe and C. B. Laird, *ibid.*, **70**, 2740 (1948).

[3] C. J. Malm, L. J. Tanghe and C. B. Laird, THIS JOURNAL, **72**, 2674 (1950).

[4] The cellulose acetate used was supplied by Eastman Kodak Co., Rochester, N. Y. Repeated analysis in our laboratory gave consistent results from 37.9–38.00% acetyl, corresponding to 0.73 free hydroxyl group per anhydroglucose unit.

[5] P. Karrer and W. Wehrli, *Helv. Chim. Acta*, **9**, 591 (1926); I. Sakurada, *J. Soc. Chem. Ind., Japan*, **32**, 11 B (1929); K. Hess and N. Ljubitsch, *Ann.*, **507**, 68 (1933); Ssokolowa, *Chem. Zentr.*, **108**, II, 319 (1937); T. S. Gardner, *J. Polymer Sci.*, **1**, 121 (1946); J. F. Haskins, U. S. Patent 2,136,299 (Nov. 8, 1939); A. H. Weinstein, Ph.D. thesis, The Ohio State University, 1950.

[6] Sven Gardell, *Acta Chem. Scand.*, **7**, 207 (1951)