spontaneously or by the evaporation of some of the petroleum ether, the heavy viscous liquid was mainly compound III. A small quantity of II also was isolated from it by taking up the oil in chloroform and diluting with petroleum ether. Removal of the solvents led to product III.

Anal. Calcd. for $C_{12}H_{17}Cl_2NO_2$: Cl, 25.0; N, 4.93. Found: Cl, 24.85; N, 4.52.

Compound III was also prepared by reacting equimolar quantities of I and epichlorohydrin at room temperature in chloroform solution for 2 days.

Anal. Found: Cl, 26.2; N, 4.72.

Compound III was soluble in alcohol, chloroform, and dioxane, but insoluble in petroleum and ethyl ethers. Attempts to vacuum-distill compound III resulted in decomposition. A micro boiling point determination resulted in no definite b.p. up to 165° at 2.5 mm. pressure; and a solid brown resin resulted.

A *hydrochloride* (m.p. 174–175°) was formed when HCl gas was passed into a chloroform solution of III and allowed to cool. The solid was crystallized from chloroform or dioxane.

Anal. Calcd. for $C_{12}H_{23}Cl_2NO_2 \cdot HCl$: ionic Cl, 11.08. Found: ionic Cl, 11.13.

Dehydrochlorination of I. To 0.1 mole of I in dioxane were added 30 g. of commercial sodium orthosilicate paste. After the suspended silicate was stirred, the temperature rose to 40°, and was maintained for 1 hr. at 55–60°. The silicates and chlorides were removed by filtration and the solvent removed under vacuum. The yield of crude epoxide was 12.3 g. (79%) as determined by titration with hydrobromic acid.[10] Over 50% of the yield was lost during vacuum distillation due to polymer formation. The distilled epoxide, b.p. 90° (3.5 mm) was a clear mobile liquid (d_4^{26} 0.9934). The product was water-soluble (pH 8) and polymerized in water on standing to form a soft deformable solid. It self-polymerized on standing at room temperature in a few days to a clear, colorless resin, soluble in acetone.

Anal. Calcd. for *N*-(2,3-epoxypropyl)cyclohexylamine (IV): oxirane oxygen, 10.3; N, 8.92. Found: oxirane oxygen 10.6; N, 8.8.

When HCl was passed into an ether solution of IV, compound II was formed (m.p. 155°). It should be noted that an amine-epoxide such as IV requires two equivalents of HBr in Durbetaki's oxirane method.[10]

Dehydrochlorination of III. When 0.1 mole of III was dehydrochlorinated,[8] an 82% conversion to epoxide based on oxirane oxygen analyses was obtained. Vacuum distillation at 126–128° at 4 mm. resulted in the formation of *N,N*-bis(2,3-epoxypropyl)cyclohexylamine.

Anal. Calcd. for $C_{12}H_{21}NO_2$: oxirane oxygen, 15.1; N, 6.6. Found: oxirane oxygen, 14.9; N, 6.44.

The product was a colorless mobile liquid which yellowed slightly on exposure to air, but did not polymerize on standing. The distilled product (d_4^{24} 1.0403) was largely insoluble in water (pH 7). The polymers formed on distillation were acetone- and methanol-soluble.

Acknowledgment. We thank Messrs. Julian F. Jurgens and Voyce P. Whitley of the Analytical Laboratory (SURDD) for some of the chlorine and nitrogen analyses, and especially do we wish to thank Ruth Benerito of this laboratory for her advice in connection with this manuscript.

NEW ORLEANS, LA.

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[10] A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOYOLA UNIVERSITY]

Studies on 1-Phenylcycloalkyl Derivatives: A New Aldehyde Synthesis

JAMES W. WILT AND BROTHER HERBERT PHILIP, F.S.C.[1]

Received November 11, 1958

The synthesis and properties of some 1-phenylcycloalkyl derivatives in the three-, five- and six-membered ring systems are reported. These materials constitute intermediates in a useful conversion of acids with α-quaternary carbon centers into β-substituted acetaldehyde derivatives.

During our investigation of the synthesis and peroxide-induced, liquid-phase decarbonylation of some 1-phenylcycloalkylacetaldehydes[2] we have had occasion to prepare a number of 1-phenylcycloalkyl derivatives, heretofore unreported, which constitute intermediates in a new interesting aldehyde synthesis.

The sequence is illustrated in formulas I–VII. The transformation of the known 1-phenylcycloalkylcarbonitriles (I) into their corresponding acid chlorides III follows established routes.[3] In an effort to construct the aldehyde side chain *via* the acids II by the Rosenmund method, the attempted homologation of these acids by the Arndt-Eistert sequence[4] failed. The formation of the α-methoxy ketones (IV) by the catalyzed interaction of methanol and the diazo ketones derived from III proceeds quite satisfactorily.[5] In these reactions the customary[6] use of excess diazomethane is advisable. Otherwise, subsequent reaction of the diazo ketone with the methanol is immediate, with little or no boron trifluoride

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[1] An Arthur Schmidt Pre-doctoral Fellow, 1957–58.

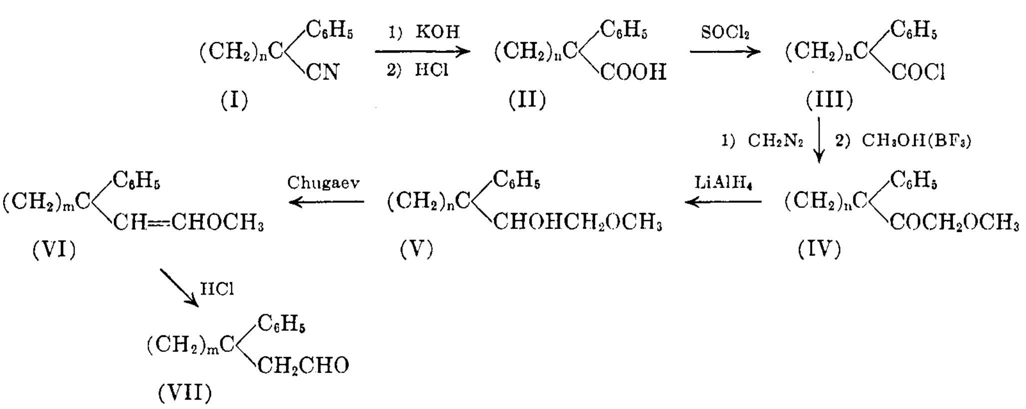
[2] Paper presented at the Fall Chemistry Conference of the *American Chemical Society*, Kansas City, Mo., November 14, 1958.

[3] Among many references to these substances are: (a) F. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934); (b) A. W. Weston, *J. Am. Chem. Soc.*, **68**, 2345 (1946); and (c) R. E. Lyle and G. G. Lyle, *J. Am. Chem. Soc.*, **74**, 4061 (1952).

[4] W. E. Bachmann and W. S. Struve, *Org. Reactions*, 1, 38 (1942).

[5] The method of M. S. Newman and P. F. Beal, III, *J. Am. Chem. Soc.*, **72**, 5161 (1950).

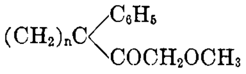
[6] W. J. Hickinbottom, *Reactions of Organic Compounds*, Second Edition, Longmans, Green and Co., London, 1948, p. 259.



n = 2,4,5
m = 2,5

TABLE I

1-Phenylcycloalkyl Methoxymethyl Ketones (IV)



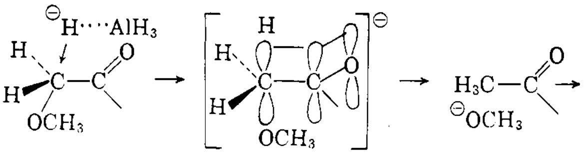
$(CH_2)_nC(C_6H_5)COCH_2OCH_3$

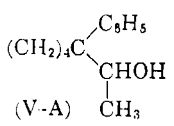
n	Yield (%)	B.P.(°C.)	Mm.	n_D^{20}	d_4^{20}	Analyses[a] Calcd. C	Calcd. H	Found C	Found H
2[b]	88	96– 97	0.8	1.5290	1.103	75.76	7.41	75.56	7.32
4[c]	70	88– 90	0.2	1.5310	1.070	77.03	8.31	76.90	8.13
5[d]	73	122–125	0.4	1.5364	1.078	77.57	8.68	77.48	8.66

[a] All combustion analyses by Galbraith Laboratories, Knoxville, Tenn. [b] 2,4-Dinitrophenylhydrazone, m.p. 178–179°. *Anal.* Calcd. for $C_{18}H_{18}N_4O_5$: N, 15.12. Found: N, 14.85. [c] 2,4-Dinitrophenylhydrazone, m.p. 145.5–146.5°. *Anal.* Calcd. for $C_{20}H_{22}N_4O_5$: N, 14.10. Found: N, 14.06. [d] 2,4-Dinitrophenylhydrazone m.p. 169.5–170.5°. *Anal.* Calcd. for $C_{21}H_{24}N_4O_5$: N, 13.59. Found: N, 13.60.

catalysis needed, and the α-methoxy ketone product is less pure.[7] The properties of these α-methoxy ketones are given in Table I.

The reduction of the α-methoxy ketones IV to the corresponding alcohols V by means of lithium aluminum hydride proceeds acceptably in the cyclopropyl and cyclohexyl compounds. The attempted reduction of IV (n = 4) in the normal fashion, however, leads to much recovered ketone. When longer reaction times are employed, an apparent reductive displacement of the methoxyl function occurs and a mixture of V (n = 4) with the *methyl* carbinol (V-A) results. Reduction of α-methoxy ketones to the corresponding alcohols with lithium aluminum hydride appears to be unreported previously. There are, therefore, no precedents for reductive displacement of the methoxyl function in such reactions.[8] The reactivity of these substances to such reductive displacement may be rationalized in that the transition state for such a process would be stabilized through the interaction of the developing *p*-orbital of the carbon atom undergoing attack with the pi-orbital of the adjacent carbonyl group, as shown in the following:





(V-A)

$(CH_2)_4C(C_6H_5)CHOHCH_3$

Analogous mechanisms have been proposed for the great reactivity of α-halo ketones in nucleophilic displacement reactions.[9] Various attempts to separate this mixture of alcohols failed and no analytical sample of V (n = 4) was obtained. For this reason, the investigation of the substituted cyclopentyl compound was not carried further in any detail (see Experimental Part). The properties of the alcohols V are given in Table II. The

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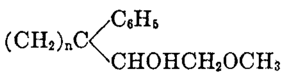
(7) We have observed spectrophotometrically and by the Beilstein test that these products have a minor contaminant containing chlorine, presumably the α-chloro ketone. Such a substance may be methanolyzed subsequently to the slight extent sufficient for proton catalysis of the methanol-diazo ketone reaction.

(8) Similar displacements have been observed in the reduction of α-alkoxy acids and α-halo ketones with lithium aluminum hydride. See N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, 1956, p. 644 and pp. 904–7.

(9) See the discussion of E. L. Eliel with several references in *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, pp. 103–6.

TABLE II

(1-PHENYLCYCLOALKYL)METHOXYMETHYLCARBINOLS (V)



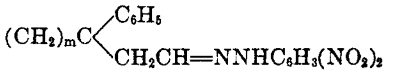
$$(CH_2)_nC\begin{matrix}\diagup C_6H_5\\ \diagdown CHOHCH_2OCH_3\end{matrix}$$

n	Yield (%)	B.P.(°C)	Mm.	n_D^{20}	d_4^{20}	Analyses Calcd. C	H	Found C	H
2	93	94- 96	1.0	1.5330	1.082	74.96	8.39	74.83	8.42
4	87[a]	95- 96	0.5	1.5329	1.066	...	..	...	..
5	64	119-121	0.3	1.5431	1.070	76.88	9.47	76.99	9.62

[a] Crude.

TABLE III

1-PHENYLCYCLOALKYLACETALDEHYDE (VII) 2,4-DINITROPHENYLHYDRAZONES



$$(CH_2)_mC\begin{matrix}\diagup C_6H_5\\ \diagdown CH_2CH{=}NNHC_6H_3(NO_2)_2\end{matrix}$$

m	Yield (%)	M.P.(°C.)	Analyses Calcd. N	Found N
2[a]	51	115.5-116.5	16.46	16.41
5[b,c]	90	163-164	14.65	14.53

[a] Yield from crude enol ether. [b] Enol ether, b.p. 105-107° at 0.5 mm., n_D^{20} 1.5409, d_4^{20} 0.960. *Anal.* Calcd. for $C_{15}H_{20}O$: C, 83.26; H, 9.34. Found: C, 83.30; H, 9.11. [c] Aldehyde, obtained by a route soon to be reported, b.p. 112-113° at 0.5 mm., n_D^{20} 1.5395, d_4^{20} 1.080. *Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: C, 82.95; H, 9.09. Oxidizes readily in air to 1-phenylcyclohexylacetic acid (85%), m.p. 85-86°. *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.36; H, 8.31. G. F. Woods, *et al.*, *J. Am. Chem. Soc.*, **74**, 5126 (1952), report m.p. 85-86°.

formal dehydration step proceeding from the methoxycarbinols V to the vinyl (enol) ethers VI was achieved at length by the Chugaev method.[10] Because of the pinacolyl character of the carbinols, acid-catalyzed dehydration was not attempted since it was considered likely to involve phenyl group migration and to result in a mixture of rearranged unsaturated ethers. Similarly, conversion of the carbinols to halides in normal fashion (e. g., using the phosphorus halides), followed by dehydrohalogenation of the β-halo ethers[11] was also avoided because retropinacol rearrangements seemed probable in the halide-producing step. The new method for such reactions due to Sommer[12] was not successful. The transformation of the carbinols to *p*-toluenesulfonate derivatives was moderately successful, but detosylation or conversion to halides by nucleophilic displacement reactions failed under a variety of conditions. Pyrolysis of the V-acetates on glass helices at 500-525°, according to the technique of Bailey,[13] led to extensive charring with little acetic acid elimination, although enol ether is detectable in the pyrolysate. Relevant to this point is the fact that the methoxyl function does not activate adjacent methylene hydrogens (indeed it may *de*activate them) to elimination in acetate pyrolyses.[14] While the Chugaev method was carried through in a detailed manner only in the cyclohexyl (n = 5) substance the elimination succeeds in both the ring compounds used, as evidenced by the good yield of appropriate aldehyde 2,4-dinitrophenylhydrazone directly from the crude enol ether VI (see Table III). The Chugaev dehydrations on α-methoxycarbinols appear to be the first such reported and constitute a novel entry to substituted acetaldehydes when the elimination is prevented in the other direction by a quaternary carbon site. The acid-catalyzed hydrolysis of the enol ethers VI is inordinately slow, most likely for steric reasons.[15] Nonetheless, slow conversion to the aldehydes VII is shown by the development of the 5.8-5.9μ band (C=O stretch) in the infrared spectrum of the hydrolysis products. This production of carbonyl substances from the enol ethers incidentally affords evidence that the reactions in this sequence take place without rearrangement, as does the identity of the aldehyde 2,4-dinitrophenylhydrazone (VII, m = 5) produced *via* this route with that obtained in another way.[16] The value of the sequence reported here would be greater if a practical route for the regeneration of these aldehydes from their 2,4-dinitrophenylhydrazones were available. The technique given in the literature[17] for analogous ketone regeneration fails

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(10) D. J. Cram, ref. 9, pp. 305-9.

(11) (a) W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, **53**, 1533 (1931); (b) W. H. Puterbaugh and M. S. Newman, *J. Am. Chem. Soc.*, **79**, 3469 (1957).

(12) L. H. Sommer, H. D. Blankman, and P. C. Miller, *J. Am. Chem. Soc.*, **76**, 803 (1954).

(13) W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

(14) W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 648 (1956).

(15) Essentially instantaneous hydrolysis of enol ethers under acidic conditions is usually observed. *Cf.* ref. 11(a). The use of the "rule of six" of M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950), although not directly applicable to these compounds, does indicate such structures to be hindered about the enol ether double bond.

(16) J. W. Wilt and H. Philip (Hogan), F. S. C., *J. Org. Chem.*, **24**, 441 (1959).

(17) J. Demaecker and R. H. Martin, *Nature*, **173**, 266 (1954).

here. Nevertheless, the synthesis does allow the construction of an acetaldehyde grouping from a "homologous" acid of lower carbon content.

EXPERIMENTAL

All melting points and boiling points are uncorrected. The former were determined on a Fisher-Johns block. Infrared spectra were obtained on a Perkin-Elmer Model 21 Infrared Spectrophotometer using sodium chloride optics. Since several preparations of most of the reported compounds were carried out, only representative procedures are described below. Individual preparations varied in slight detail in some cases.

1-Phenylcycloalkylcarbonitriles (I). The three nitriles were prepared by the method of Weston:[3b] *1-phenylcyclopropylcarbonitrile* (63%, b.p. 80° at 1 mm.); *1-phenylcyclopentylcarbonitrile* (45%, b.p. 127° at 3.5 mm.); *1-phenylcyclohexylcarbonitrile* (49%, b.p. 144–146° at 3.5 mm.).

1-Phenylcycloalkanecarboxylic acids (II). The three acids were obtained in nearly quantitative yield by the hydrolysis of the above nitriles with potassium hydroxide in diethylene glycol (190°, 3–4 days), followed by acidification:[3c] *1-phenylcyclopropanecarboxylic acid*, m.p. 87.5–88° (literature[3b] m.p. 86–87°); *1-phenylcyclopentanecarboxylic acid*, m.p. 155–156° (literature[3a] m.p. 158–159°); *1-phenylcyclohexanecarboxylic acid*, m.p. 121–122° (literature[3b] m.p. 121°).

1-Phenylcycloalkanecarboxylic acid chlorides (III). Treatment of the acids (II) with fresh thionyl chloride in the usual fashion gave the acid chlorides as follows: *1-phenylcyclopropanecarboxylic acid chloride* (93%, b.p. 96–97° at 0.8 mm.); *1-phenylcyclopentanecarboxylic acid chloride* (91%, b.p. 73–74° at 0.3 mm.); *1-phenylcyclohexanecarboxylic acid chloride* (85%, b.p. 126–127° at 2 mm.). While III ($N = 2,5$) are known compounds,[3b] III ($n = 4$) appears to be new. Because these materials decomposed readily on standing no analysis was attempted on III ($n = 4$).

1-Phenylcycloalkyl methoxymethyl ketones (IV). Into a cold (0–2°) solution of diazomethane (0.25–0.30 mole) in ether (250 ml.), prepared in the usual manner from nitrosomethylurea, was added dropwise with stirring a solution of the appropriate acid chloride (0.10 mole) in an equal volume of ether. The mixture was stirred in the cold until the evolution of nitrogen subsided (6–8 hr.). The yellow solution was washed with sodium bicarbonate solution (5%), dried over sodium sulfate and the ether removed. The crude diazo ketone was used directly in the next step.

Methanol (200 ml.) was added to the diazo ketone in one portion. Occasionally, if the diazo ketone had traces of acidic impurities present, nitrogen evolution occurred at this point. The purity and yield of the product in such instances suffered somewhat. Ordinarily, however, there was little reaction of the methanol with the diazo ketone on mixing. Boron trifluoride etherate (1.5 ml.) was next added and the mixture allowed to stand with stirring at room temperature overnight. Nitrogen evolution was normally 90–100% of theory. Excess methanol was removed by distillation and the crude methoxy ketone collected by a simple Claisen head vacuum distillation. The crude ketones were of excellent grade and were used subsequently as such, though the analytical samples were heart cuts of a column distillation. The materials exhibited normal $C=O$ bands (5.75–5.85 μ) and $O-CH_3$ bands (6.86–6.90 μ) in their infrared spectra. The properties of the methoxy ketones are given in Table I, together with their readily prepared 2,4-dinitrophenylhydrazone derivatives.

(1-Phenylcycloalkyl)methoxymethylcarbinols (V). A solution of the appropriate methoxy ketone (IV) (0.25 mole) in dry ether (50–75 ml.) was added dropwise with stirring into a suspension of lithium aluminum hydride (2.66 g., 0.07 mole) in dry ether (100–150 ml.) held at 0°. Stirring was continued for an hour, followed by reflux for another 1–2 hr. Isolation of the carbinol was achieved in the customary manner using dilute hydrochloric acid (5%) in the work-up. The properties of the carbinols are given in Table II. The alcohols (V) showed a broad $-O-H$ band (2.8–2.9 μ) and retained the methoxyl band in their infrared spectra. V ($n = 4$), as usually prepared, had a $C=O$ (5.75 μ) peak present from unreduced ketone. Generally, however, the methoxy ketones could be entirely reduced in 3-hour reduction times. While the products V ($n = 2,5$) were blank in the C-methyl region (7.23–7.26 μ), V ($n = 4$) invariably showed a *moderately strong C-methyl peak* (7.24 μ) in addition to the aforementioned peaks. The appearance of this C-methyl absorption peak was evidence for the reductive displacement of the methoxyl function (see text of paper). The mixture of V ($n = 4$) with the C-methyl contaminant (assumed to be V-A) proved tenacious. Fractional distillation on available columns failed to separate the components. Various reduction times, periods of reflux, etc., gave mixtures of varying methylcarbinol contamination (C-methyl absorption intensity), but no method was found to remove V-A or to prevent its formation. Combustion analyses indicated 30–40% methylcarbinol (assuming a binary mixture). No derivatives of any of the alcohols (V) were obtained. Attempts to prepare various urethans, benzoates, and sulfonates gave oils. In the case of V ($n = 2$), rapid decomposition of the derivatives into dark tar was noticed.

1-Phenylcycloalkylacetaldehyde enol methyl ethers (VI). The S-methyl xanthate esters of the carbinols (V) were obtained by the method of Alexander and Mudrak,[18] with the excellent modification of using phenyllithium to obtain the alkoxide salt developed by Weinstock and Bordwell.[19] The xanthate esters were obtained as deep yellow-orange oils. Solidification of the xanthates did not occur. To establish the conditions for these eliminations, the pyrolysis of the cyclohexyl substance was investigated more thoroughly than the others. A typical pyrolysis is described. The crude S-methyl xanthate obtained from V ($n = 5$) (30 g., 0.127 mole) was heated at 190–195° (Wood's metal bath temperature) for 4.5 hr. vented into concentrated sodium hydroxide solution. Distillation under reduced pressure gave the crude enol ether (VI, $m = 5$) (17.5 g., 64%, b.p. 95–135° at 1 mm.). This material was taken up in ether, washed repeatedly with dilute (5%) sodium hydroxide, water, and then dried. The ether was removed from the dried extract and the enol ether distilled under vacuum. Its properties are given in Table III. The enol ethers (VI) so obtained were colorless to pale yellow oils with a faint odor. A strong $C=C$ peak at 6.05 μ with no trace of carbonyl absorption (5.7–5.9 μ) characterized their infrared spectra. 2,4-Dinitrophenylhydrazone derivatives of their respective aldehydes (VII) were readily obtained in good yield upon treatment with the reagent in phosphoric acid-ethanol.[20] The yields and properties of these latter substances are given in Table III.

Attempted hydrolyses of the enol ethers (VI) *to the aldehydes* (VII). The rates of these hydrolyses were followed by the gradual diminution of the $C=C$ peak of VI (6.05 μ) and the concomitant appearance of the $C=O$ peak of the aldehydes (5.8–5.9 μ) as the time of reflux was lengthened. The hydrolyses were quite slow, considering the usually rapid hydrolysis of such ethers in acid.[11a] Thus, a mixture of VI ($m = 5$) (11.3 g., 0.052 mole), concentrated hydrochloric acid (1.8 ml.), water (12 ml.) and ethanol (95%, 25 ml.) was refluxed with stirring for 1 hr. The mixture was then poured over ice and extracted with ether. The extracts were

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(18) E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

(19) J. Weinstock and F. G. Bordwell, *J. Am. Chem. Soc.*, **77**, 6706 (1955).

(20) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

washed until neutral with dilute base and water, dried, and freed of ether. Distillation of the residual oil gave a series of fractions (8.1 g., b.p. 85–110° at 0.4 mm.), all of which showed both $C=C$ and $C=O$ bands in the infrared. Other hydrolyses involved reaction times as long as 12 hr. with Girard-T reagent work-up. While such measures decreased the enol ether content of VII, analytically pure samples of the aldehydes were not obtained. *1-Phenylcyclohexylacetaldehyde* (VII, $m = 5$) has been obtained pure, however, *via* another route[16] and its infrared spectrum was comparable to that of the aldehyde prepared in this work, with slight contamination by the enol ether evident.

CHICAGO 26, ILL.

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Catalytic Hydrogenation of 9,10-Epoxyoctadecanol and 9,10-Epoxyoctadecyl Acetate

SARA P. FORE AND W. G. BICKFORD

Received October 13, 1958

cis-9,10-Epoxyoctadecanol and *cis*-9,10-epoxyoctadecyl acetate have been hydrogenated in ethanolic solution employing palladium-carbon catalyst. Examination of the reaction products established the fact that nearly equal proportions of the 9- and 10-hydroxy isomers were formed in both cases. These results are in marked contrast to the preferential formation of methyl 10-hydroxyoctadecanoate encountered previously during the catalytic reduction of methyl 9,10-epoxyoctadecanoate. The difference in results obtained with the two esters is attributed to the relative position of the oxirane center with respect to the acyl and alkoxyl oxygen atoms of the ester.

Investigations conducted in this laboratory[2] and elsewhere[3,4] into the catalytic hydrogenation of the 9,10-epoxyoctadecaonates have shown that the reaction products consist principally of one positional isomer. Reduction of methyl *cis*-9,10-epoxyoctadecanoate, for instance, results in the formation of methyl 10-hydroxyoctadecanoate with little or no attendant formation of the 9-isomer.

The results obtained in our previous investigation suggested that the reaction proceeded by an ionic mechanism involving the preferential attack of a hydride ion on the ninth carbon-oxygen bond of an oxonium ion intermediate.[5] The specificity of the reaction was attributed to the influence exerted at both the oxirane center and the catalyst surface by the electrophilic —COO— group.

To obtain further information regarding the nature of this reaction we have now investigated the catalytic reduction of both *cis*-9,10-epoxyoctadecanol and *cis*-9,10-epoxyoctadecyl acetate. These epoxides were hydrogenated in ethanolic solution employing a palladium-carbon catalyst. The exact positions of the secondary alcohol groups thus formed were established by the following series of reactions: the diols obtained upon hydrolysis of the acetate, as well as those derived from the free alcohol, were oxidized to the corresponding keto acids; the oximes prepared from the keto acids were transformed by means of the Beckmann rearrangement; hydrolysis of the resultant amides and separation of the hydrolysis products were effected by the procedure of Bharucha and Gunstone[6]; the mixed dicarboxylic acid fraction was separated into its components by application of elution chromatography employing a modification[7] of the method of Higuchi *et al.*[8]

Application of the above described series of reactions to either *cis*-9,10-epoxyoctadecanol or *cis*-9,10-epoxyoctadecyl acetate resulted in the formation of azelaic and sebacic acids only, which were found to be present in nearly equimolar proportions. It may be concluded, therefore, that catalytic hydrogenation of either epoxide leads to the formation of equivalent amounts of the 9- and 10-hydroxy isomers. Apparently the acyl oxygen of the acetate exerted no greater directive influence on the course of the reaction than did the hydroxyl oxygen of the alcohol. These results are in marked contrast to those obtained by the catalytic hydrogenation of methyl *cis*-9,10-epoxyoctadecanoate and *cis*-9,10-epoxyoctadecanoic acid in which cases the 10-isomer was produced prefer-

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) C. H. Mack and W. G. Bickford, *J. Org. Chem.*, **18**, 686 (1953).

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(4) J. Ross, A. I. Gebhart, and J. F. Gerecht, *J. Am. Chem. Soc.*, **71**, 282 (1949).

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