phenyl diketone which was isolated as 2-phenyl-3-benzylquinoxaline, m.p. 96–97° (lit. 97–98°,[25] 98–99°[8]). The ultraviolet spectrum of the quinoxaline closely resembles the spectrum of 2-phenyl-3-benzhydrylquinoxaline, absorption peaks occurring at 240 mμ (ϵ_{max} 35,000) and 324 mμ (ϵ_{max} 10,000).

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[25] T. L. Jacobs, THIS JOURNAL, **58**, 2272 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MAINE]

The Synthesis and Reactions of Certain α-Substituted Glycidic Esters

BY HORTON H. MORRIS AND MARGARET L. LUSTH[1]

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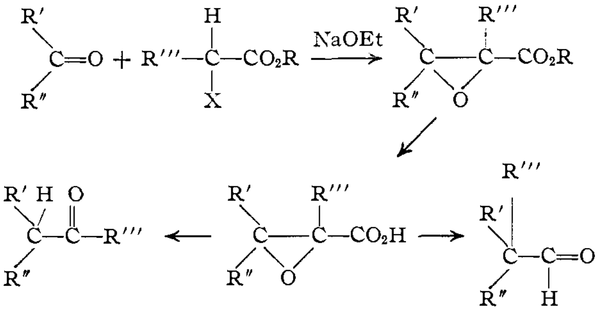
Several α-substituted glycidic esters, ethyl α-*n*-alkyl-α,β-epoxycyclohexylideneacetates, have been prepared. Saponification of these esters and decarboxylation of the resulting glycidic acids gave ketones as primary products, as proved by alternate synthesis, mixed melting points of derivatives and attempted oxidation. Contrary to an earlier report, ethyl α-*n*-decyl-α,β-epoxycyclohexylideneacetic acid decarboxylated to yield 1-cyclohexyl-1-undecanone instead of α-*n*-decylcyclohexanecarboxaldehyde. An important side reaction in the preparation of these glycidic esters was found to be the saponification of a portion of the glycidic ester during the course of the reaction, the resulting acid material accounting for over 40% of the yield in one case.

The condensation of an aldehyde or ketone with an α-halo ester, in the presence of a basic condensing agent, yields an α,β-epoxyester (glycidic ester). The reaction is of interest since it provides a route to aldehydes or ketones of greater complexity than those used in the original condensation.



I II

Darzens has reported[2] that glycidic acids with higher molecular weight α-substituents, in particular *n*-decyl, rearrange on decarboxylation to form tertiary aldehydes of the type II. It has been shown[3a,b] that if the α-substituent is methyl, ethyl, *n*-butyl or *n*-hexyl, a ketone of the type I results. In order to determine at what point between *n*-hexyl and *n*-decyl the rearrangement to aldehyde takes place, an homologous series of glycidic esters (ethyl α-*n*-alkyl-α,β-epoxycyclohexylideneacetates) with α-substituents of methyl through *n*-decyl was prepared from cyclohexanone and α-bromo esters, using sodium ethoxide as the condensing agent. The glycidic esters with α-substituents of *n*-butyl and *n*-hexyl were reported in a previous article[3b] from this Laboratory and are not included here. The esters were saponified and the resulting acids decarboxylated by heating for three or four hours at atmospheric pressure. The decarboxylation products in every case were ketones, as shown by alternate synthesis, mixed melting points of derivatives and oxidation studies. Evidently Darzens was misled by the fact that a small amount of an oxidizable contaminant present in the decarboxylation products gives aldehyde color tests.

In order to prove the structure of the decarboxylation products, a series of cyclohexyl ketones were prepared by the following methods. The ethyl, *n*-propyl and *n*-amyl cyclohexyl ketones were obtained by use of a modified Friedel–Crafts type acylation as adapted from the procedure reported by Nenitzescu and Cioranescu.[4] The *n*-heptyl, *n*-octyl and *n*-decyl cyclohexyl ketones were prepared by means of a condensation of the appropriate di-*n*-alkylcadmium compound and cyclohexanecarboxyl chloride, following a procedure given by Cason.[5] Semicarbazones and 2,4-dinitrophenylhydrazones were prepared from these ketones and mixed melting points determined with the corresponding products obtained from the decarboxylation of the glycidic acids. No depression of the melting point was observed in any case.

In order further to establish the structure of the decarboxylation product from α-*n*-decyl-α,β-epoxycyclohexylideneacetic acid and to attempt to find an explanation for the fact that the material gave aldehyde color tests, a sample was subjected to oxidation with aqueous permanganate. Less than 15% of the material could be oxidized. Repetition of the oxidation, using acetone as solvent, gave essentially the same results.

There seems to be no doubt that ketones will result on the decarboxylation of α-substituted glycidic acids when the α-substituent is an alkyl group. Glycidic esters, however, have occasionally been reported to rearrange to α-keto esters on heating, and such esters would be expected to yield aldehydes on decarboxylation. Such a rearrangement may have occurred in the case reported by Darzens, and would account for the results he obtained. Preliminary evidence indicates that this is not the case, but the possibility is being checked.

The preparation of the condensing agent in the

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[1] From the thesis submitted by M. L. Lusth in partial fulfillment of the requirements of the degree of Master of Science in Chemistry, June, 1953. Presented before the Division of Organic Chemistry at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953.

[2] G. Darzens, *Compt. rend.*, **195**, 884 (1932).

[3] (a) M. Mousseron and R. Granger, *ibid.*, **218**, 358 (1944); M. Mousseron, *et al.*, *Bull. soc. chim. France*, 598 (1947); (b) N. K. Nelson and H. H. Morris, THIS JOURNAL, **75**, 3337 (1953).

[4] C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69**, 1820 (1936).

[5] J. Cason, THIS JOURNAL, **68**, 2078 (1946).

glycidic ester condensation is a time-consuming task, and therefore the use of finely dispersed sodium (particle size 1–10 μ) in xylene was attempted. The results of this work indicate that sodium dispersions can be used as condensing agent in this reaction only if there is good cooling. The sodium dispersion was used quite successfully, however, to prepare anhydrous sodium ethoxide—the ethoxide often being formed in a finely divided form, which remained in suspension in the xylene and could be poured into the mixture of the other reagents.

From each glycidic ester preparation a certain amount of acid material was recovered. With one exception, the acid materials were found to contain the corresponding glycidic acid, as shown by the fact that they decarboxylated to give the expected ketones in yields comparable to those obtained from the saponification and subsequent decarboxylation of the pure glycidic esters.[6] Although the acid material recovered in the preparation of ethyl *α-n*-heptyl-*α,β*-epoxycyclohexylideneacetate seemed to decarboxylate normally, the decarboxylation product was not a ketone or aldehyde and may have been an unsaturated acid, since it was soluble in base and decolorized bromine in carbon tetrachloride. Yields of the acid material in the various preparations ranged from 20% to as high as 46%, making the over-all yield of condensation product in the neighborhood of 70–80%, although only 40–45% yields of the glycidic esters were obtained. No satisfactory explanation for the formation of the acid material has yet been found, although it is suspected that saponification may be taking place during the washing procedure.

Darzens also reported that *α-n*-decyl-*β,β*-dimethylglycidic acid and *α-n*-decyl-*β*-phenyl-*β*-methylglycidic acid decarboxylated to give tertiary aldehydes. Preliminary work has indicated that ketones are obtained from these acids also.

As expected, the derivatives of the asymmetrical ketones reported here are low-melting—the melting points decreasing with increasing molecular weight of the ketones.

Experimental

Preparation of Intermediates.—The cyclohexanone used was Matheson C.P. grade and was redistilled through a 10 bubbler Clarke–Rahrs fractionation column. The xylene was Will Corporation "Water and Acid Free" xylene. Both the xylene and cyclohexanone were dried over anhydrous sodium sulfate before use. Absolute ethanol was prepared from commercial absolute ethanol by distilling from lump sodium. The sodium dispersion was a 50% by weight dispersion in xylene and was kindly donated for this work by National Distillers Corporation and by E. I. du Pont de Nemours and Company. The particle size of the sodium was stated as being from 1 to 10 μ. The *α*-bromo esters were prepared by the Hell–Volhard–Zelinsky reaction. Technical grade reagents were used and the esters purified by fractionation through a suitable column.

Since it did not prove practicable to use the sodium dispersion as condensing agent for the reaction, the dispersion was used to prepare sodium ethoxide and was very satisfactory for this purpose, since it eliminated the time-consuming and somewhat dangerous method previously reported.[3b] The condensing agent, sodium ethoxide, was prepared by dropping the stoichiometric amount of absolute ethanol into a vigorously stirred sodium–xylene dispersion. A dry nitrogen atmosphere was maintained throughout the reaction. The product was usually a *dispersion* of sodium ethoxide in xylene and could be added from the flask to the mixture of cyclohexanone and *α*-bromo ester by means of a suitable addition tube or a separatory funnel having a wide bore stopcock.

Preparation of Glycidic Esters.—To a mixture of one mole of the *α*-bromo ester and 1.5 moles (147 g.) of cyclohexanone in a 2-liter, 3-necked flask partially immersed in an ice–salt-bath, and equipped with a Trubore (Ace Glass, Inc.) stirrer fitted with a Hirschfelder type blade, a reflux condenser equipped with nitrogen gas inlet and outlet, is added 1.5 moles of freshly prepared sodium ethoxide dispersed in xylene, by means of a suitable addition tube or separatory funnel. The condensing agent should be added at such a rate that the mixture does not heat up. Throughout the addition the mixture is vigorously stirred. The addition, subsequent stirring, and steam-bath treatment should take place in an atmosphere of dry nitrogen. When the addition is complete, the mixture is stirred for three hours, and allowed to stand under nitrogen for 18 hours. The mixture is then heated on a steam-bath for one hour, with stirring, during which time the mixture usually changes from a dark yellow to a pale yellow or white color. The cooled mixture is then treated with 100–150 ml. of 5% acetic acid solution, the water layer separated, and 500 ml. of ether added to the xylene layer. The ether–xylene solution is washed with two 100-ml. portions of saturated sodium bicarbonate solution, two 100-ml. portions of water, 100 ml. of saturated sodium chloride solution, and dried over anhydrous sodium sulfate for several hours. The ether is then removed on the steam-bath, the xylene removed by flask distillation at reduced pressure and the crude ester fractionated at reduced pressure. A 40–45% yield of glycidic ester is obtained. The sodium bicarbonate, water and sodium chloride washes are combined with the original water layer, which is then poured slowly and with constant stirring into a slurry of concentrated hydrochloric acid and ice. The mixture is immediately extracted with ether and the ether solution washed with water, after which it is dried over anhydrous sodium sulfate. The ether is removed on the steam-bath leaving the highly viscous, crude glycidic acid behind. The acids are probably solids, but are very difficult to crystallize. The crude acid is subjected to the decarboxylation procedure described later.

Saponification of the Esters.—A sample of the ester is added to 1.5 times the equivalent amount of sodium hydroxide dissolved in diethylene glycol. A small amount of water may be added to effect the solution of the sodium hydroxide in the glycol. The mixture is refluxed for one hour or until a homogeneous mixture is obtained. The cooled mixture is then poured into a slurry of concentrated hydrochloric acid and ice and the mixture immediately extracted three times with ether. The ether layer is separated and washed twice with water and once with a saturated sodium chloride solution, after which it is dried over anhydrous sodium sulfate. The ether is removed by means of a steam-bath, leaving a 90–95% yield of crude acid.

Decarboxylation of the Glycidic Acids.—The decarboxylation of the glycidic acids was effected by heating the crude acids at atmospheric pressure, under a fractionating column at such a temperature that they bubbled vigorously, but did not distil. Evidence of decarboxylation was obtained by testing the evolved gas with lime water. After three hours, or after bubbling ceased, the decarboxylated product was distilled at reduced pressure. A 40–60% yield (based on glycidic ester) of ketone was obtained.

The results of some preliminary work on the use of sodium dispersion as condensing agent in the glycidic ester condensation indicate that the sodium dispersion is satisfactory only when there is good cooling. Of four attempted preparations of ethyl *α-n*-butyl-*α,β*-epoxycyclohexylideneacetate, using a sodium–xylene dispersion as condensing agent, only

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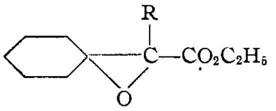
[6] W. S. Johnson, *et al.*, THIS JOURNAL, **75**, 4995 (1953), in an excellent study of the glycidic ester condensation, published after this paper was written, have shown that the method of saponifying the glycidic esters used in this work often gives cyclohexenylglycolic acids as a product. The formation of such acids is entirely possible in the present work and might account for the results reported concerning the acid material recovered in the preparation of ethyl *α-n*-heptyl-*α,β*-epoxycyclohexylideneacetate. We have assumed, for purposes of yield calculation, that the acid materials were entirely glycidic acid (our basis for this is mentioned), but the presence of appreciable amounts of the cyclohexenylglycolic acids is certainly not prohibited in view of the relatively low yields of ketone obtained from the decarboxylation of the glycidic acids.

TABLE I

ETHYL α-n-ALKYL-α,β-EPOXYCYCLOHEXYLIDENEACETATES

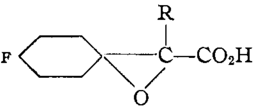


R-	Yield, %	B.p., °C.	Mm.	n^{20}_D	d^t_4	t, °C.	MR Found	MR Calcd.	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.	Yield acid material from reacn., %
CH_3[a]	54.9	91	4	1.4589	1.0362	20	52.29	52.94	66.73	66.64	8.93	9.15	..
					1.0540	0			66.54		9.09		
C_2H_5	25.5	99–100	3.5	1.4612	1.0177	20	57.18	57.59	69.05	67.89	9.22	9.50	28
									69.09		9.32		
n-C_3H_7	46.5	110	4	1.4610	1.0060	20	61.64	62.28	69.10	68.99	9.19	9.81	35
									69.48		9.42		
n-C_5H_{11}	45.2	140	4	1.4601	0.9838	20	70.83	71.54	71.12	70.82	10.42	10.30	20
					.9760	30			70.81		10.55		
n-C_7H_{15}	45.7	170	7	1.4636	.9717	20	80.14	80.83	72.23	72.30	10.63	10.71	(49 g.)[d]
					.9855	0			72.44		10.23		
n-C_8H_{17}	19[b]	164	3.5	1.4638	.9638	20	84.84	85.42	73.78	72.93	10.96	10.88	46
					.9788	0			74.07		10.65		
n-$C_{10}H_{21}$[c]	45	185	4	1.4657	.9518	20	94.37	94.72	74.02	74.02	10.94	11.19	36
					.9667	0			74.21		10.73		

[a] Previously reported, refs. 7 and 8. [b] See discussion under Experimental. [c] Previously reported (ref. 2) b.p. 173–176° (5 mm.), $n^{20}D$ 1.4652, d^0_0 0.994. [d] Not the glycidic acid. See under Experimental.

TABLE II

n-ALKYL CYCLOHEXYL KETONES OBTAINED FROM THE DECARBOXYLATION OF



R-	Yield, %	B.p., °C.	Mm.	$n^{20}D$	d^t_4	t, °C.	MR Found	MR Calcd.	M.p., °C. 2,4-dinitrophenylhydrazone	Nitrogen, % 2,4-Dinitrophenylhydrazone Found	Nitrogen, % 2,4-Dinitrophenylhydrazone Calcd.
C_2H_5[a]	44.6	65	5	1.4542	0.913	20	41.60	41.78	151		
					.928	0					
C_3H_7[b]	46.8	79	6	1.4531	.903	20	46.17	46.41	114		
					.915	0					
C_5H_{11}[c]	37	100	3	1.4569	.894	20	55.52	55.67	71.5	14.93	15.45
					.906	0				14.85	
C_7H_{15}[d]	45	127	5	1.4552	.884	20	64.59	64.94	60	14.30	
					.899	0				13.96	14.35
C_8H_{17}[d]	38	142	6	1.4585	.888	20	69.06	69.57	46	13.88	13.85
					.901	0				14.13	
C_9H_{19}[e]	25	158	6	1.4551	.892	20	72.53	74.20	61.5	13.52	13.40
					.907	0				13.59	
$C_{10}H_{21}$[d]	36	166	6	1.4580	.878	20	78.46	78.83	47.5	13.09	12.95
										12.70	

[a] Previously reported (ref. 9); b.p. 88.89° (19 mm.), $n^{20}D$ 1.4530, d^{20}_4 0.9105; semicarbazone m.p. 152°, reported 150–152°. [b] Previously reported (ref. 10); b.p. 92° (9 mm.), $n^{19}D$ 1.4515, d^{19}_4 0.901; semicarbazone m.p. 155°, reported 155°. [c] Previously reported (ref. 4); b.p. 122–125 (11 mm.), $n^{20}D$ 1.4584, d^{20}_4 0.8938; no derivatives. [d] Constants determined on product from dialkyl preparation. [e] See discussion under Experimental. Composition not proved.

the run at 0 to −10° proved successful—the ester being obtained in 25% yield.

Ethyl α-Methyl-α,β-epoxycyclohexylideneacetate.—The name listed in the heading is the name generally applied to this type of ester. For indexing purposes, however, the compound may be named ethyl 2-methyl-1-oxaspiro[2.5]-octane-2-carboxylate. In like manner the general name of the esters prepared in this series is ethyl 2-alkyl-1-oxaspiro[2.5]octane-2-carboxylate.

The preparation of the methyl α-substituted glycidic ester has been reported previously,[7,8] but since no constants other than the boiling point were reported, the product from several preparations of this ester were combined and refractionated through a Todd precise fractionating assembly to give a sample of colorless, viscous liquid whose constants and analysis are reported in Table I.

The saponification and subsequent decarboxylation of ethyl α-methyl-α,β-epoxycyclohexylideneacetate has been reported to yield methyl cyclohexyl ketone.[7,8]

Ethyl α-Ethyl-α,β-epoxycyclohexylideneacetate.—A 25.5% yield of this compound was obtained from 293 g. (1.49 moles) of ethyl α-bromobutyrate, 221 g. (2.25 moles) of cyclohexanone and 153 g. (2.25 moles) of sodium ethoxide, using the procedure described previously. Fractionation through the Todd assembly gave a sample of colorless, viscous liquid having the constants and analysis shown in Table I. The reaction appeared to go smoothly, but the yield and analysis leave much to be desired. The product obtained, however, was undoubtedly the glycidic ester, for the acid obtained by saponification decarboxylated smoothly to give the expected 1-cyclohexyl-1-propanone. The preparation of this ester has been attempted twice before in this Laboratory. A 7% yield of a rather impure product was obtained using sodium ethoxide as condensing agent and ether as solvent—the product gave a positive test for halogen and also a poor analysis. A 3% yield was obtained when sodium amide was used as the condensing agent. Appar-

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(7) G. Darzens, *Compt. rend.*, **144**, 1123 (1907).

(8) W. A. Yarnall and E. S. Wallis, *J. Org. Chem.*, **4**, 270 (1939).

ently some complicating factor has caused the low yields and poor analyses obtained in the preparation of this ester.

1-Cyclohexyl-1-propanone.—Twenty-five grams (0.12 mole) of ethyl α-ethyl-α,β-epoxycyclohexylideneacetate was saponified, then decarboxylated, and finally distilled to give a 44.6% yield of 1-cyclohexyl-1-propanone. Fractionation through a 10" Vigreux column gave a sample of colorless pleasant-smelling liquid with the constants given in Table II and which formed a 2,4-dinitrophenylhydrazone and a semicarbazone. Mixed melting points of the 2,4-dinitrophenylhydrazone and semicarbazone with the corresponding derivatives prepared from an authentic sample of the ketone showed no depression. The authentic sample of 1-cyclohexyl-1-propanone was prepared by a modified Friedel–Crafts type acylation previously mentioned,[4] following a procedure which has been described in detail in an earlier report from this Laboratory.[3b] This ketone has been reported by Meerwein.[9]

Acid Material from the Ethyl α-Ethyl-α,β-epoxycyclohexylideneacetate Preparation.—Acidification of the wash waters from the preparation of the glycidic ester gave 77 g. of a crude acid. This material was distilled rapidly without previous decarboxylation, and yielded a lower boiling fraction which gave a 2,4-dinitrophenylhydrazone and a semicarbazone and which was shown by melting points and mixed melting points of its derivatives to be 1-cyclohexyl-1-propanone. A second cut, which proved to be soluble in dilute sodium hydroxide solution, may have been undecarboxylated glycidic acid. If it is assumed that all the product discussed here is glycidic acid, the 77 g. of acid represents a 28% yield and makes the total yield of condensation product in the neighborhood of 50% (see, however, footnote 6).

Ethyl α-*n*-Propyl-α,β-epoxycyclohexylideneacetate.—A 46.5% yield of ethyl α-*n*-propyl-α,β-epoxycyclohexylideneacetate was obtained from 209 g. (1 mole) of ethyl α-bromovalerate, 147 g. (1.5 moles) of cyclohexanone and 102 g. (1.5 moles) of sodium ethoxide. Fractionation through the Todd assembly gave a colorless, viscous liquid having the indicated constants and analysis (Table I).

1-Cyclohexyl-1-butanone.—Forty-four grams (0.19 mole) of ethyl α-*n*-propyl-α,β-epoxycyclohexylideneacetate were successively saponified, decarboxylated, and distilled to give a 46.8% yield (based on glycidic ester) of 1-cyclohexyl-1-butanone. Fractionation gave a sample of colorless liquid with the constants shown in Table II. The material formed a 2,4-dinitrophenylhydrazone and a semicarbazone. In order to prove the structure of the decarboxylation product, an authentic sample of the ketone was prepared by the modified Friedel–Crafts acylation previously mentioned. Melting points of the 2,4-dinitrophenylhydrazone and the semicarbazone agreed with those obtained from the decarboxylation product. Mixed melting points showed no depression. The compound has been reported by Douris.[10]

Acid Material from the Ethyl α-*n*-Propyl-α,β-epoxycyclohexylideneacetate Preparation.—Seventy grams of acid material, representing a 35% yield, if the material is assumed to be glycidic acid, was obtained by acidifying the wash waters from the original condensation. Rapid distillation, without previous decarboxylation, gave a cut which was shown to be 1-cyclohexyl-1-butanone by the preparation of a 2,4-dinitrophenylhydrazone and a semicarbazone and the determination of mixed melting points with the corresponding derivatives prepared from an authentic sample of the ketone. The remaining material was soluble in sodium hydroxide, and was probably undecarboxylated glycidic acid (see, however, footnote 6).

Ethyl α-*n*-Amyl-α,β-epoxycyclohexylideneacetate.—A 45.2% yield of ethyl α-*n*-amyl-α,β-epoxycyclohexylideneacetate was obtained from 239 g. (1 mole) of ethyl α-bromoheptanoate, 147 g. (1.5 moles) of cyclohexanone and 102 g. (1.5 moles) of sodium ethoxide. Fractionation through the Todd column gave a sample with the indicated constants and analysis.

1-Cyclohexyl-1-hexanone.—A 37% yield of 1-cyclohexyl-1-hexanone was obtained from the saponification, decarboxylation and subsequent fractionation of 50 g. of ethyl α-*n*-amyl-α,β-epoxycyclohexylideneacetate. Refractionation through a semimicro fractionation assembly equipped with a 5" Vigreux column and a head with stopcock to control the reflux ratio gave a sample of colorless liquid with the constants and analysis shown in Table II.

An authentic sample of 1-cyclohexyl-1-hexanone was prepared by the Friedel–Crafts type acylation mentioned previously and formed a semicarbazone and a 2,4-dinitrophenylhydrazone. Mixed melting points with the similar derivatives prepared from the decarboxylation product of the glycidic acid showed no depression.

Nenitzescu[4] has reported constants for 1-cyclohexyl-1-hexanone but no derivatives.

Acid Material from the Ethyl α-*n*-Amyl-α,β-epoxycyclohexylideneacetate Preparation.—Acidification of the wash waters in the preparation of the above-mentioned ester gave 46 g. of acid material. This material was heated at atmospheric pressure until evidence of decarboxylation had ceased and was then distilled at reduced pressure. There was obtained 25 g. of a product which was shown to be 1-cyclohexyl-1-hexanone by formation of a 2,4-dinitrophenylhydrazone and the determination of a mixed melting point with the corresponding derivative prepared from an authentic sample of the ketone. This represents a 68% yield of ketone, assuming the acid layer to be the corresponding glycidic acid. The total yield of condensation product was therefore about 77% of which 20% came from the acid layer.

Ethyl α-*n*-Heptyl-α,β-epoxycyclohexylideneacetate.—This compound was obtained in 45.7% yield from 265 g. (1 mole) of ethyl α-bromononanoate, 147 g. (1.5 moles) of cyclohexanone and 102 g. (1.5 moles) of sodium ethoxide. Fractionation through a 12" glass helices packed column with an electrically heated jacket and equipped with a fractionating head gave a sample of colorless viscous liquid having the indicated constants.

1-Cyclohexyl-1-octanone.—Successive saponification, decarboxylation and distillation of 28 g. of ethyl α-*n*-heptyl-α,β-epoxycyclohexylideneacetate gave a 45% yield of 1-cyclohexyl-1-octanone. The material was not pure, however, since successive cuts obtained by fractionation through the 12" packed column mentioned above did not show constant refractive index. Because of the small amount of material, no further attempt at purification was made, and constants were determined on a sample of the ketone prepared by an alternate method and are listed in Table II. Derivatives were obtained from the decarboxylation product, however, and were used to prove its structure. The material formed the indicated semicarbazone and 2,4-dinitrophenylhydrazone. The derivatives showed no depression of the melting point when mixed with the similar derivatives obtained from an authentic sample of the ketone.

An authentic sample of 1-cyclohexyl-1-octanone was obtained by the dialkylcadmium ketone synthesis. The detailed procedure used has been given in an earlier report.[3b] A sample of colorless liquid was obtained by fractionation through the 12" packed column mentioned earlier and was used to determine the constants given in Table II.

Acid Material from the Ethyl α-*n*-Heptyl-α,β-epoxycyclohexylideneacetate Preparation.—The 49 g. of material recovered from the wash waters from the glycidic ester preparation was heated at atmospheric pressure for three hours. On distillation, 22 g. of material boiling from 128–138° at 4 mm. was obtained. In contrast to the other acid layers, however, this material was not the expected ketone, but seemed to be an unsaturated acid, since the cut was soluble in dilute base, decolorized bromine in carbon tetrachloride, and would not yield ketone derivatives. The material was not further investigated (see footnote 6 for possible explanation).

Ethyl α-*n*-Octyl-α,β-epoxycyclohexylideneacetate.—A 19% yield of this compound was obtained from 279 g. of ethyl α-bromocaprate, 147 g. (1.5 moles) of cyclohexanone and 102 g. (1.5 moles) of sodium ethoxide. During the preparation, the nitrogen supply gave out and this fact is reflected in the low yield obtained. The ester had been prepared several times previously, in connection with another problem, in yields of about 45%. Fractionation through the Todd column gave a sample with the reported constants. The analysis is poor and a preparation of this ester under more favorable conditions is indicated.

1-Cyclohexyl-1-nonanone.—A 38% yield of 1-cyclohexyl-1-nonanone was obtained from the saponification, decarboxylation and subsequent distillation of 20 g. of ethyl α-*n*-octyl-α,β-epoxycyclohexylideneacetate. Because of the small amount of material and because of the doubtful composition

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(9) H. Meerwein, *Ann.*, **419**, 167 (1919).

(10) R. Douris, *Compt. rend.*, **157**, 57 (1913).

of the ester, the product was identified through its derivatives and the constants determined on a sample prepared by alternate synthesis. The product gave a semicarbazone and a 2,4-dinitrophenylhydrazone.

An authentic sample of this ketone was prepared by means of the dialkylcadmium synthesis mentioned earlier and the product obtained gave the constants reported in Table II after fractionation through a 12″ packed column. The 2,4-dinitrophenylhydrazone from the decarboxylation product showed no depression of melting point when mixed with the corresponding derivative from the dialkylcadmium synthesis product. The two derivatives from the acid layer (discussed later) were mixed with the corresponding derivatives from the dialkylcadmium synthesis product and no depression of melting points was observed.

Acid Material from the Ethyl α-*n*-Octyl-α,β-epoxycyclohexylideneacetate Preparation.—A large amount of acid material, 137 g., was obtained from the preparation of the above mentioned ester. Assuming the material to be glycidic acid, this represents a 46% yield which, together with the yield of ester, made the total yield of condensation product 65%. Decarboxylation and distillation of the acid material gave 86 g. of crude ketone. A semicarbazone and a 2,4-dinitrophenylhydrazone were obtained from this cut and neither showed a melting point depression when mixed with the corresponding derivatives obtained from the alternately prepared ketone.

Ethyl α-*n*-Nonyl-α,β-epoxycyclohexylideneacetate.—Work on the α-*n*-nonyl substituted glycidic ester was hampered by the small quantity of starting material available. We therefore wish to report only that the glycidic ester obtained was saponified and the acid decarboxylated to yield a crude product which formed the 2,4-dinitrophenylhydrazone reported in Table II. The acid material obtained from the original condensation was decarboxylated, and then fractionated to yield a sample having the constants given in Table II and which formed a 2,4-dinitrophenylhydrazone and a semicarbazone. The structure of the decarboxylation product has not been proved conclusively, but in view of the results obtained with the next higher and next lower members of the series, it seems safe to assume that the decarboxylation product was 1-cyclohexyl-1-decanone.

Ethyl α-*n*-Decyl-α,β-epoxycyclohexylideneacetate.—A 45% yield of this product was obtained from 307 g. (1 mole) of ethyl α-bromolaurate, 147 g. (1.5 moles) of cyclohexanone and 102 g. (1.5 moles) of sodium ethoxide. The material began to decompose when an attempt was made to distil it on the Todd column. Using the 12″ packed column, a sample with the constants listed in Table I was obtained. The compound has been reported by Darzens.[2]

1-Cyclohexyl-1-undecanone.—Darzens had reported that the saponification and decarboxylation of this ester gave the tertiary aldehyde, α-*n*-decylcyclohexanecarboxaldehyde. We obtained, however, a 36% yield of 1-cyclohexyl-1-undecanone upon the saponification, decarboxylation and distillation of 32 g. of ethyl α-*n*-decyl-α,β-epoxycyclohexylideneacetate. The product readily reduced Tollens solution, and decolorized 1% permanganate solution, facts which may have misled Darzens. On subjecting this material to oxidation with aqueous potassium permanganate, however, according to the method of Shriner and Fuson,[11] less than 15% of the material could be oxidized. The same results were obtained when a second sample was dissolved in acetone and subjected to the oxidation. The material that did oxidize was not identified, although the acid so formed appeared to melt around 0°. The unoxidized portion from the oxidation procedure above gave a 2,4-dinitrophenylhydrazone melting at 48.5°, which agrees with the melting point of the similar derivative from the authentic 1-cyclohexyl-1-undecanone.

The ketone has the constants shown in Table II and formed a semicarbazone and a 2,4-dinitrophenylhydrazone.

An authentic sample of 1-cyclohexyl-1-undecanone was prepared by the dialkylcadmium ketone synthesis. The sample did not decolorize 1% permanganate and reduced Tollens reagent only very slightly. This would seem to indicate that the decarboxylation product discussed above may have had a trace of an aldehyde as contaminant. The authentic sample gave a semicarbazone melting at 108° after three recrystallizations from 50% ethanol and a 2,4-dinitrophenylhydrazone melting at 49° after three recrystallizations from ethanol. Mixed melting points of the 2,4-dinitrophenylhydrazone derivative from the decarboxylation product and from the dialkylcadmium synthesis melted at 47.5–48°. The semicarbazones showed no depression when mixed. Darzens[2] reported a boiling point of 166–170° (15 mm.) and a semicarbazone melting at 98.5° for the decarboxylation product that he obtained.

Acid Material from the Ethyl α-*n*-Decyl-α,β-epoxycyclohexylideneacetate Preparation.—A 44% yield of 1-cyclohexyl-1-undecanone was obtained from the decarboxylation of 117 g. of acid material obtained by acidifying the wash waters from the preparation of ethyl α-*n*-decyl-α,β-epoxycyclohexylideneacetate. Assuming the acid material to be only glycidic acid, the 117 g. represented a 36% yield, making the total yield of condensation product 81%. The decarboxylated material gave a 2,4-dinitrophenylhydrazone which melted at 47.5° after three recrystallizations and which, as mentioned before, gave a mixed melting point of 48° when mixed with the corresponding derivative obtained from an authentic sample of 1-cyclohexyl-1-undecanone.

Any sample taken for analysis and the determination of constants, unless otherwise noted, was the middle cut of at least three successive cuts having essentially constant refractive index. Atomic refractivity values were taken from those given by Vogel.[12] Derivatives were recrystallized three times from 95% ethanol (the 2,4-dinitrophenylhydrazones) or from 50% ethanol (the semicarbazones). Melting points are uncorrected.

Analyses were made by the Oakwold Laboratories, Alexandria, Va.

Samples of the glycidic esters reported here have been submitted to S. P. Sadtler Research Laboratories, 1517 Vine St., Philadelphia 3, Pa., for the determination of their infrared spectra.

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