All of the dihydropyrans **1–5** have fair stability. In contrast, hexafluoroacetone and cyclopentadiene react at room temperature or below to form an adduct as evidenced by the F^{19} n.m.r. pattern of the resulting liquid and the formation of a dibromide. Attempted distillation of the product, however, results in reversal of the reaction with the regeneration of the reactants.

Experimental

6,6-Bis(chlorodifluoromethyl)-5,6-dihydro-3,4-dimethyl-2H-pyran (2).—A mixture of 1,3-dichlorotetrafluoroacetone (10 g., 0.05 mole) and 2,3-dimethylbutadiene (4.1 g., 0.05 mole) was sealed in a Carius tube and heated for 10 hr. at 200°. The recovered product was distilled to give 10.6 g. (76%) of colorless adduct, b.p. 101–102° (22 mm.), $n^{25}\mathrm{D}$ 1.4362.

The above reaction was repeated at lower temperature by adding 7.3 g. (0.089 mole) of dimethylbutadiene to 30.3 g. (0.15 mole) of 1,3-dichlorotetrafluoroacetone dissolved in 15 ml. of ethyl acetate. The solution was stirred at room temperature for 16–18 hr. and then heated to 80° for 15 min. The solution was cooled and concentrated on a rotary evaporator at 25° (1 mm.). The residual colorless oil (16.5 g.) was distilled to give 13.6 g. (55%) of colorless oil, b.p. 83° (5 mm.), $n^{25}\mathrm{D}$ 1.4358. The product was identical with that of the above reaction as shown by a comparison of the infrared spectra.[6]

6,6-Bis(trifluoromethyl)-5,6-dihydro-4-methyl-2H-pyran (5).—A mixture of 85% hexafluoroacetone (26.4 g., 0.135 mole) and isoprene (8.8 g., 0.13 mole) was sealed in a Carius tube. The reaction mixture was heated overnight (16 hr.) on a steam bath. The tube was chilled and opened, and the liquid product was distilled. There was obtained 25.3 g. (83%) of colorless liquid, b.p. 133–140°. Most of the product distilled at 137°, $n^{25}\mathrm{D}$ 1.3646.

The last fraction (4.6 g.) collected was separated on a 12 ft. × 0.75 in. column of 20% diglyceride of ω-trifluorohexanoic acid on Chromosorb at a column temperature of 100° and a helium flow rate of 860 ml./min. The major compound (**5**, 64.3%) eluted at 30.1 min. and the minor (**6**, 33.8%) at 35.8 min.

Anal. Calcd. for $C_8H_8F_6O$: C, 41.0; H, 3.4; F, 48.7. Found for **5**: C, 41.5; H, 3.7; F, 48.5. Found for **6**: C, 41.5; H, 3.7; F, 49.1.

Reaction of Hexafluoroacetone and Cyclopentadiene.[7]—Hexafluoroacetone, 26 ml. (at −78°, 0.25 mole), and 14.5 g. (0.25 mole) of cyclopentadiene were mixed at −78° and allowed to warm to room temperature. The F^{19} n.m.r. spectrum showed two quadruplets. The melting point of the adduct was about 19°, but the product was unstable to distillation. A portion of the product was brominated for further identification. A solution of 4.5 g. (0.025 mole) of bromine in 10 ml. of methylene chloride was added dropwise to a solution of 5.65 g. (0.025 mole) of the adduct in 15 ml. of methylene chloride. The reaction mixture was cooled by means of an ice bath. When most of the bromine color had faded, the solution was evaporated to dryness under nitrogen, and the residue was recrystallized from carbon tetrachloride to give 5.0 g. of colorless prisms, m.p. 75–76°.

Anal. Calcd. for $C_8H_6Br_2F_6O$: C, 24.48; H, 1.55; F, 29.07. Found: C, 24.55; H, 1.70; F, 28.45.

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[6] This experiment was performed by Dr. F. D. Marsh.

[7] This experiment was performed by Dr. W. J. Middleton.

Synthesis of α-Diketones from Ethyl Alkylideneacetoacetates

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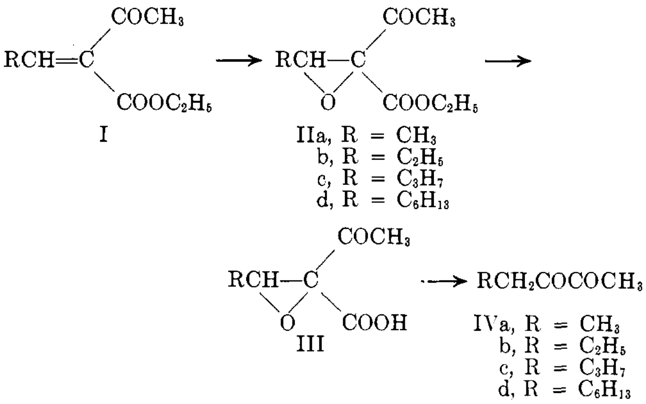
Epoxidation and subsequent decarboxylation of ethyl alkylidenecyanoacetates have been shown to provide a convenient route for the preparation of α-keto amides,[1] and many α-keto acids[2] have also been prepared from diethyl alkylidenemalonates by modification of the method. In order to examine further the synthetical applications of the epoxidation and decarboxylation reactions, several ethyl alkylideneacetoacetates have now been used.

The starting materials, ethyl alkylideneacetoacetates (I),[3] were readily obtained by condensation of aldehydes with ethyl acetoacetate.

Payne[4] examined the reaction of 3-butylideneacetylacetone with hydrogen peroxide to produce the epoxy-type compound, and observed that the reaction gave not the expected epoxy diketone, but 2-methyl-3-hexenoic acid. Tishchenko, *et al.*,[5] prepared some epoxy ketones by the action of hydrogen peroxide on α,β-unsaturated ketones. They also showed that by heating the epoxy ketones with dilute sulfuric acid, rearrangement occurred to give the corresponding α-diketones.

In the present paper, the epoxidation of ethyl alkylideneacetoacetates (I) with hydrogen peroxide was most readily achieved when sodium tungstate was a catalyst. The epoxy esters (II) were readily hydrolyzed in an aqueous sodium hydroxide solution at low temperatures to epoxy acids (III) which were characterized by conversion into the corresponding α-diketones (IV). All these α-diketones showed maximal absorption at or near 1710 cm.⁻¹. The continued presence of the ketonic groups was further shown by preparing dioximes from two of them by reaction with hydroxylamine.



As a model reaction sequence 2,3-heptanedione was first prepared by the series of reactions (I–IV). This α-diketone had already been made by Cuvigny, *et al.*,[6] who used a different route. Epoxidation of ethyl *n*-butylideneacetoacetate was achieved at 70–80° by using 30% hydrogen peroxide and sodium tungstate. Ethyl 2-acetyl-2,3-epoxycaproate (IIc) was isolated by distillation in 65% yield. The conversion of the epoxy ester to the epoxy acid salt was effected by aqueous alkaline hydrolysis. 2-Acetyl-2,3-epoxycaproic acid produced by acidification of an aqueous solution of the salt was stable in hot water, but, when the substance

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[1] M. Igarashi and H. Midorikawa, *J. Org. Chem.*, **28**, 3088 (1963).

[2] M. Igarashi and H. Midorikawa, *ibid.*, **29**, 2080 (1964).

[3] K. Knoevenagel, *Ber.*, **31**, 730 (1898).

[4] G. B. Payne, *J. Org. Chem.*, **24**, 1830 (1959).

[5] (a) I. G. Tishchenko, A. A. Akhrem, and I. N. Nazarov, *Zh. Obshch. Khim.*, **29**, 809 (1959); (b) I. G. Tishchenko, *Zhidkofaznoe Okislenie Nepredel'n Organ. Soedin.*, *Sb.*, **73**, 123 (1961); (c) I. G. Tishchenko, O. N. Bubel, and I. P. Zyat'kov, *Zh. Obshch. Khim.*, **33**, 2613 (1963).

[6] T. Cuvigny and H. Hormant, *Compt. rend.*, **237**, 815 (1953).

TABLE I

EPOXIDATION OF ETHYL ALKYLIDENEACETOACETATES

Ethyl alkylideneaceto-acetate	Epoxy compd.	B.p., °C. (mm.)	Yield, %	Formula	Calcd., %		Found, %	
					C	H	C	H
Ethylidene[a]	IIa	123–125 (23)	47	$C_8H_{12}O_4$	55.80	7.03	55.14	6.93
Propylidene	IIb	127–130 (20)	60	$C_9H_{14}O_4$	58.05	7.58	57.69	7.36
Butylidene[b]	IIc	140–143 (20)	65	$C_{10}H_{16}O_4$	59.98	8.05	59.58	8.04
n-Heptylidene[c]	IId	151–152 (6)	70	$C_{13}H_{22}O_4$	64.44	9.15	64.46	9.00

[a] See ref. 3. [b] A. C. Cope and C. M. Hofmann, *J. Am. Chem. Soc.*, **63**, 3456 (1941). [c] J. M. L. Stephen, I. M. Tonkin, and J. Walker, *J. Chem. Soc.*, 1034 (1947).

TABLE II

PREPARATION OF α-DIKETONES FROM EPOXY ESTERS (II)

α-Diketone	B.p., °C.	Yield, %	Formula	Calcd., %		Found, %	
				C	H	C	H
IVa[a]	112–113[b]	41	$C_5H_8O_2$	59.98	8.05	59.70	7.98
IVb	127–128[c]	62	$C_6H_{10}O_2$	63.13	8.83	62.77	8.75
IVc[d]	150–151[e]	52	$C_7H_{12}O_2$	65.59	9.44	64.99	9.62
IVd	104–107[f] (20 mm.)	53	$C_{10}H_{18}O_2$	70.54	10.66	69.83	10.16

[a] Dioxime m.p. 172°, lit. m.p. 172–173° [I. M. Heilbron, E. R. H. Jones, P. Smith, and B. C. L. Weedon, *J. Chem. Soc.*, 54 (1946)]. *Anal.* Calcd. for $C_5H_{10}N_2O_2$: C, 46.14; H, 7.75; N, 21.53. Found: C, 46.31; H, 7.70; N, 21.67. [b] Lit.[a] b.p. 110–112°. [c] Lit.[a] b.p. 128–130°. [d] Dioxime m.p. 173°, lit. m.p. 173° [H. J. Cavell and S. Sugden, *J. Chem. Soc.*, 621 (1935)]. *Anal.* Calcd. for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 53.04; H, 8.73; N, 17.80. [e] Lit.[6] b.p. 46° (13 mm.). [f] Lit[5c] b.p. 66–68° (2 mm.).

was kept at 180–200° in an oil bath, decarboxylation took place and the product was the expected α-diketone. The yield of 2,3-heptanedione (IVc), b.p. 150–151°, was 52% based on IIc. The epoxy acid also gave a considerable amount of viscous oil distilling at 170–175° (6 mm.) with slight decomposition as a by-product of decarboxylation. The substance was reflected in the analytical figure but no further details were investigated.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.86; H, 8.93.

The compounds and yields obtained by this method are summarized in Tables I and II.

Experimental

General Procedure. Epoxidation.—To ethyl alkylideneacetoacetate (0.01 mole) in ethanol (15 ml.) were added 30% hydrogen peroxide (15 ml.) and sodium tungstate dihydrate (0.7 g.). The mixture was kept for 1 hr. at 70–80° on a water bath. After removal of ethanol, the oily layer was separated from the aqueous layer. The aqueous layer was shaken with ether. The ethereal extract was combined with the oil and then dried over anhydrous sodium sulfate. After removal of ether, the residue was distilled under reduced pressure to give epoxy ester (II).

Hydrolysis.—A mixture of the epoxy ester (II) and a 1 *N* sodium hydroxide (mole equiv.) solution was allowed to saponify overnight at low temperatures (10–15°). The alkaline solution was shaken with ether and then acidified with dilute hydrochloric acid. The aqueous solution was extracted with ether. The ethereal solution was dried for several hours over anhydrous sodium sulfate. Removal of the solvent left the impure epoxy acid (III) as a viscous oil which decomposed on attempted distillation. The yields of crude epoxy acids were 75–80%. The acids were used without further purification for the following reaction.

Decarboxylation—The epoxy acid (III) was placed in a Claisen flask and heated at atmospheric pressure in an oil bath at 180–200° until the decarboxylation had ceased. The product was distilled directly from the reaction flask. Redistillation gave α-diketone (IV) as a yellow oil.

Ethyl Propylideneacetoacetate.—The titled compound was prepared by Knoevenagel's[3] method from propionaldehyde and ethyl acetoacetate. The yield was 65%, b.p. 116–118° (20 mm.).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.30; H, 8.01.

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Fluoro Ketones. II. Reaction of Amides with Fluoroacetones[1]

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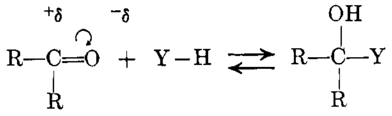
The fluoroacetones are highly reactive compounds which have been shown to undergo a number of interesting reactions. Moreover, their commercial availability[2] makes them even more attractive for chemical synthesis. The facility of the fluoro ketones to react



$$\overset{+\delta}{\mathrm{C}}(\mathrm{R})(\mathrm{R})\!=\!\overset{-\delta}{\mathrm{O}} + \mathrm{Y{-}H} \rightleftharpoons \mathrm{R{-}C(OH)(R){-}Y} \tag{1}$$

with nucleophilic agents can be attributed to the strong electropositive nature of the carbonyl carbon. A comparison of the reactivity of a series of fluoroacetones illustrates the powerful I effect of the α-fluorine atoms, *i.e.*, the greater the number of α-fluorine atoms, the greater the electrophilicity of the ketone. This effect is also manifested in the position of the equilibrium of eq. 1. In contrast to acetone, the position of equilibrium for hexafluoroacetone lies far to the right. We have observed the reversibility of this reaction in our

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(1) For paper I of this series, see B. Farah and S. Horensky, *J. Org. Chem.*, **28**, 2494 (1963).

(2) General Chemical Division, Allied Chemical Corp., Morris Township, N. J.