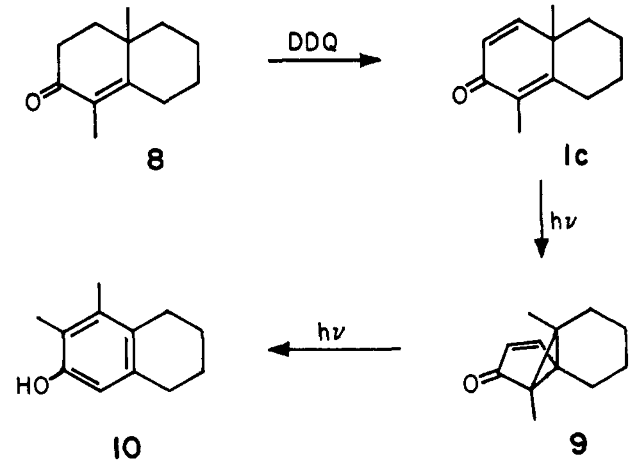

α-methyl substituent as a multiplet at τ 8.32 and the hydroxyl-bearing methyl group as a singlet at 9.08. Hydrogenation over palladium on charcoal gave a dihydro derivative which exhibited the typical cyclopentanone absorption at 5.75 μ.

Also formed in 6–7% yield on irradiation of dienone **1c** was the phenol **10**.[8] This is the expected product from the usual secondary pathway in acidic media involving initial photoisomerization of the dienone to a lumiproduct (**9**) followed by a second light-initiated rearrangement to **10**.[9]

Experimental[10]

1,4a-Dimethyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone (8).—The general procedure of Poos, *et al.*,[11] was employed. To a solution of 39.0 g. (0.348 mole) of 2-methylcyclohexanone in 450 ml. of methanol was added dropwise under an atmosphere of nitrogen 166 ml. (0.356 mole) of 35% methanolic benzyltrimethylammonium hydroxide, followed by 29.9 g. (0.356 mole) of pent-1-en-3-one. The resulting solution was heated under reflux for 2 hr. The solution was then allowed to cool and 270 ml. of 3 *N* hydrochloric acid was added. After an additional 0.5-hr. reflux period, the solution was again cooled and extracted with four 150-ml. portions of ether. The combined ethereal extracts were dried over saturated sodium chloride solution and then anhydrous sodium sulfate and concentrated under reduced pressure on a rotary evaporator. Distillation of the residue gave 25.8 g. (41% yield) of colorless liquid: b.p. 74–78° at 0.4 mm.; λ_{max} 6.05 and 6.24 μ; λ_{max} 246 mμ (ε 16,000); n.m.r. spectrum, τ 8.76 (s,[12a] 3,[12b] CH_3-4a) and 8.20 (s, 3, CH_3-1); 2,4-dinitrophenylhydrazone, red platelets, m.p. 198–199° (lit.[6a] b.p., 99–100° at 1 mm., 2,4-dinitrophenylhydrazone m.p. 198–199°).

1,4a-Dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (1c). A. **Preparation.**—The general procedure of Burn, Kirk, and Petrow[13] was employed. A solution of 10.25 g. (57.5 mmoles) of octalone **8**, 14.32 g. (63 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone, and 25 ml. of glacial acetic acid in 500 ml. of benzene was heated under reflux in an atmosphere of nitrogen for 32 hr. The reaction mixture was cooled to room temperature, filtered, and concentrated under reduced pressure on a rotary evaporator. The resulting amber oil was then filtered through 100 g. of activity II alumina with 1.25 l. of hexane and 4 l. of benzene to give 8.29 g. (82% yield) of a pale yellow oil which crystallized on refrigeration. Repeated low-temperature recrystallization from hexane gave colorless prisms: m.p. 40–40.5°; λ_{max} 6.02, 6.18, and 6.22 μ; λ_{max} 238 mμ (ε 11,000); n.m.r. spectrum, τ 3.24 and 3.78 (2d, 2, J_{AB} = 10 c.p.s., CH-4 and CH-3), 8.06 (s, 3, CH_3-1), and 8.74 (s, 3, CH_3-4a).

B. **Irradiation.**—A solution of 553 mg. of dienone **1c** in 150 ml. of 45% acetic acid was irradiated for 30 min. at 25° using a Hanovia 200-w. high-pressure mercury lamp and the apparatus previously described.[2] The resulting solution was concentrated to dryness on a rotary evaporator under reduced pressure, and the residue was chromatographed on 16.5 g. of silica gel. Elution with 750 ml. of 1:1 benzene–hexane gave 36 mg. (6.5% yield) of **3,4-dimethyl-5,6,7,8-tetrahydro-2-naphthol (10)**, m.p. 108–115°. Recrystallization from hexane gave colorless prisms, m.p. 116–118°, which was unchanged on admixture with an authentic sample of **10**.[8]

Continued elution with 1 l. of 3:1 benzene–hexane, 600 ml. of benzene, 1 l. of 1:19 ether–benzene, and 300 ml. of 1:9 ether–benzene gave 108 mg. of a colorless oil which was shown by gas chromatography to consist of at least five components. Continued elution with 3.3 l. of 1:3 ether–benzene gave 399 mg. (65% yield) of **3,8β-dimethyl-4,5,6,7,8,8aα-hexahydro-8α-hydroxy-2(1H)-azulenone (4c)** as a colorless oil. Further purification by short-path distillation at 131–133° and 0.15 mm. gave a colorless viscous oil which crystallized on standing. Recrystallization from ether–hexane gave colorless needles: m.p. 82.5–83.5° and 100.5–102°; λ_{max} 2.78, 5.92, and 6.14 μ; λ_{max} 242 mμ (ε 14,400); n.m.r. spectrum, τ 8.32 (m, 3, CH_3-3) and 9.08 (s, 3, CH_3-8β).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.85; H, 9.28.

Similarly irradiation of a solution of 269 mg. of dienone **1c** in 120 ml. of 45% acetic acid for 2 hr. with a Hanau NK 6/20 low-pressure mercury lamp gave the phenol **10** and the ketone **4c** in yields of 6 and 70%, respectively.

Treatment of a solution of 56 mg. of the above analytically pure ketone **4c** in 10 ml. of absolute ethanol with 10 mg. of 10% palladium on charcoal in a hydrogen atmosphere resulted in the absorption of 1.1 equiv. of hydrogen and produced a **dihydro derivative**, m.p. 85–90°. Recrystallization from ether–hexane gave long colorless needles: m.p. 90.5–91.5; λ_{max} 2.75 and 5.75 μ.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.42; H, 10.42.

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[8] W. Cocker, *J. Chem. Soc.*, 36 (1946).

[9] It should be noted that santonin is exceptional from other cyclohexadienones in that it does not give a phenolic photoproduct. This anomalous behavior can be ascribed to strain introduced by the *trans*-fused γ-lactone ring in the spiro intermediate normally involved in phenol formation. A more complete discussion is given in ref. 2 and 5a.

[10] Ultraviolet spectra were determined in absolute ethanol with a Cary Model 14 spectrophotometer, and infrared spectra were obtained in 5% methylene chloride solution with a Perkin-Elmer Infracord spectrophotometer. Melting points were determined on a micro hot stage and are calibrated and corrected. Nuclear magnetic resonance spectra were obtained in deuteriochloroform solution with a Varian Model A-60 spectrometer, using tetramethylsilane as an internal standard. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

[11] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[12] (a) Multiplicity (s = singlet, d = doublet, and m = multiplet); (b) integration.

[13] D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

Diels–Alder Reactions of Acyclic Fluoro Ketones

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Contribution No. 975 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware

Received May 11, 1964

The use of carbonyl compounds as dienophiles in the Diels–Alder reaction is limited. Formaldehyde adds to 2-methyl-1,3-pentadiene at 185° but not to butadiene.[1] At 150°, chloral participates in the diene reaction, but here again no adduct forms with butadiene.[2] However, the exceptionally reactive hexafluorocyclobutanone and butadiene combine to give a normal Diels–Alder adduct below 0°.[3]

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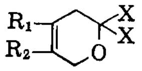
[1] T. L. Gresham and T. R. Steadman, *J. Am. Chem. Soc.*, **71**, 737 (1949).

[2] W. J. Dale and A. J. Sisti, *ibid.*, **76**, 81 (1954).

[3] D. C. England, *ibid.*, **83**, 2205 (1961).

TABLE I

DIELS–ALDER ADDUCTS OF ACYCLIC FLUORO KETONES



							Calcd., %			Found, %		
Compd.	R_1	R_2	X	Yield, %	B.p., °C. (mm.)	n^{25}_D	C	H	F	C	H	F
1	CH_3	CH_3	CF_3	92	92–93 (110)	1.3755	43.5	4.1	45.9	43.8	4.3	46.2
2	CH_3	CH_3	CF_2Cl	76	101–102 (22)	1.4362	38.5	3.6	27.0	38.8	3.9	27.0
3	CH_3	CH_3	C_2F_5[a]	95	71–72 (19)	1.3622	37.9	2.9	54.6	38.3	3.0	54.9
4	H	H	CF_2Cl	87.5	79–79.5 (21)	1.4271	33.2	2.4	30.0	33.8	2.6	29.3
5	CH_3[b]	H	CF_3	83	137 (760)	1.3646	41.0	3.5	48.7	41.1	3.4	48.5

[a] Decafluoro-3-pentanone was prepared by the method of D. W. Wiley, U. S. Patent 3,091,643 (1963). [b] This product contains a small per cent of an isomer as discussed in the text.

Although both hexafluorocyclobutanone[3] and acyclic fluoro ketones[4] react with nucleophilic olefins, there has been no report of the participation of the latter in the Diels-Alder synthesis.

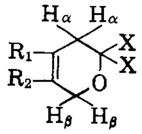
Acyclic fluoro ketones have now been found to be good dienophiles as shown by the addition of hexafluoroacetone, decafluoro-3-pentanone and 1,3-dichlorotetrafluoroacetone to butadiene, isoprene, and 2,3-dimethylbutadiene.[5] The 1,4-dihydropyrans listed in Table I have been prepared. Most of these syntheses were carried out at 100–200° without a solvent. The reactions are clean, and the yields are exceptionally good. High temperatures are probably required only because the fluoro ketone and diene are immiscible as liquids. In support of this hypothesis is the observation that 2,3-dimethylbutadiene and 1,3-dichlorotetrafluoroacetone react at room temperature in ethyl acetate solution.

According to the literature,[2] chloral and 2-methyl-1,3-butadiene give a single isomer, the structure of which was assigned on the basis of analogy with the earlier work on formaldehyde. The reaction product of hexafluoroacetone and 2-methyl-1,3-butadiene was thought to be homogeneous as evidenced by the elemental analysis, boiling point, and refractive index of successive fractions. However, analysis by gas chromatography showed that these fractions contained a minor component, the amount of which increased as the distillation progressed. Approximately 15% of the total product consisted of this impurity. The mixture was easily separated by gas chromatography, and analysis of both the major and minor substituents showed them to be 1:1 adducts of hexafluoroacetone and the diene.

On the basis of polar effects in the diene and ketone, one would predict the major product of this reaction to be 6,6-bis(trifluoromethyl)-5,6-dihydro-4-methyl-2H-pyran (**5**, $R_1 = CH_3$; $R_2 = H$). A logical assumption is that the minor isomer **6** results from inverse addition and therefore has the methyl group at position 3 rather than 4. The proton resonance spectrum of **6** suggests that this is not the case. An examination of Table II shows the similarities in the proton spectra of the adducts **1**–**5**. For example, single peaks are observed for each pair of methylene protons. The spectrum of **6** also indicates two pairs of methylene hydrogens, but these peaks are triplets, each with a splitting of 5.5 c.p.s. Inspection of molecular models shows that that there is no difference in the spatial relationship of the two methylene groups that is caused by reversing the positions of the carbon and oxygen atoms derived from the carbonyl group. There is no obvious reason why these two methylene groups should appear as triplets if the minor isomer were that derived from an inverse addition.

TABLE II

N.M.R. SPECTRA OF DIELS–ALDER ADDUCTS OF FLUORO KETONES[a]



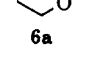
	Chemical shift (τ)				
Compd.	CH_3	CH_3	H_α	H_β	Vinyl H
1	8.42	8.26	7.61	5.88	
2	8.37	8.25	7.50	5.75	
3	8.50	8.22	7.40	5.80	
4			7.35	5.53	4.03[b]
5		8.21	7.65	5.68	4.42
6		8.08	7.61[c]	5.88[c]	4.50

[a] The spectra were determined neat on a Varian A60 instrument with tetramethylsilane as an internal standard. [b] This is actually two peaks with a very small separation. [c] Triplets with $J = 5.5$ c.p.s.

Furthermore, there are three dimethyl derivatives listed in Table II, and each adduct has the methyl group resonances in narrowly defined regions, one around τ 8.4 and the other at 8.2. The monomethyl derivative **5** has its methyl resonance at τ 8.21 and it follows reasonably that an isomer of **5** with the position of the methyl group reversed should exhibit a peak at higher field strength, around τ 8.4–8.5. Instead, the methyl group resonance of **6** is found at τ 8.08.

This leaves unanswered the question of the structure of **6**. There are no distinguishing features in the infrared spectrum which is rather similar to that of **5** except in the long wavelength region. The double bond stretching frequency which appears at 5.95 μ in each isomer is actually stronger in **6** than in **5**.

A double bond isomer such as **6a** would account for the observed proton resonance pattern, but this in itself is insufficient as a structure proof.



6a

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(4) H. R. Davis, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 25M.

(5) Dr. J. F. Harris, Jr., of these laboratories first noted the formation of a Diels-Alder adduct from 1,3-dichlorotetrafluoroacetone and butadiene under the influence of chemically activating energy, *i.e.*, when irradiated with ultraviolet light at room temperature: J. F. Harris, Jr., U. S. Patent 3,136,786 (June 9, 1964).

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.), $n^{25}\text{D}$ 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.), $n^{25}\text{D}$ 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°, $n^{25}\text{D}$ 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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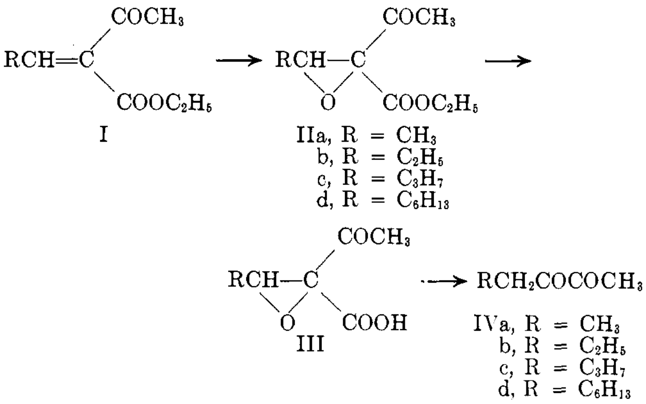
Epoxidation and subsequent decarboxylation of ethyl alkylidenecyanoacetates have been shown to provide a convenient route for the preparation of α-keto amides,[1] and many α-keto acids[2] have also been prepared from diethyl alkylidenemalonates by modification of the method. In order to examine further 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. Hormánt, *Compt. rend.*, **237**, 815 (1953).