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Diels-Alder Synthesis of 4-Methyl- $\Delta^{4(10)}$ -1-octalone¹

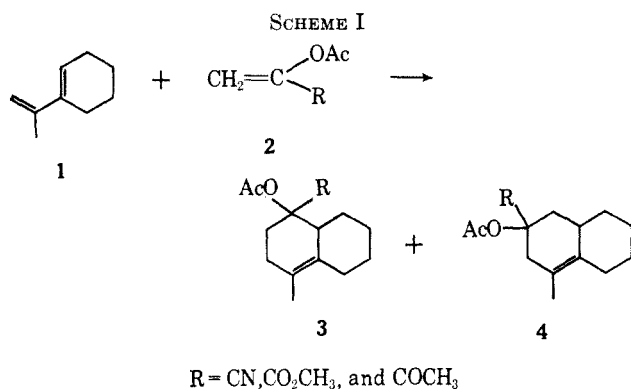
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The Diels-Alder reactions of 1-isopropenylcyclohexene with methyl α -acetoxyacrylate, α -acetoxyvinyl methyl ketone, and α -acetoxyacrylonitrile afforded high yields of adducts, predominantly ($\sim 98\%$) of one orientation. The adducts of methyl α -acetoxyacrylate and α -acetoxyvinyl methyl ketone proved to be useful intermediates for the synthesis of 4-methyl- $\Delta^{4(10)}$ -1-octalone.

This article is a summary of the results of a study of the Diels-Alder reaction of 1-isopropenylcyclohexene with various dienophiles (Scheme I) where the objective



was the selective synthesis of 4-methyl- $\Delta^{4(10)}$ -1-octalone (5) in high yield so that the method could be applied to the preparation of some eudesmane sesquiterpenes. Although the net conversion $1 \rightarrow 5$ is formally described by the Diels-Alder addition of 1 and ketene, an indirect approach was necessary because ketenes do not react as dienophiles.² The dienophiles used and the results they gave are shown in Table I.³ The high orientational selectivities observed parallel those of the closely related reactions of 1-vinylcyclohexene with dienophiles in the acrylic acid series; *e.g.*, with acrylonitrile 1-

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(2) See J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

(3) These dienophiles have rarely been used previously in Diels-Alder reactions and then only with symmetrical dienes. α -Acetoxyacrylonitrile has yielded adducts with cyclopentadiene,⁴ 6,6-dimethylfulvene,⁵ and butadiene.⁶ Esters of α -acetoxyacrylic acid have been added to butadiene,⁷ 2,3-dimethylbutadiene,⁸ 1,4-diphenylbutadiene,⁹ and 1,4-dichlorobutadiene.⁹

(4) P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).

(5) C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960).

(6) J. C. Little, *ibid.*, **87**, 4020 (1965). 1-Isopropenylcyclohexene, unlike butadiene, afforded no 1,2-cycloaddition products.

(7) J. Wolinsky, R. Novak, and R. Vasilieff, *J. Org. Chem.*, **29**, 3596 (1964).

(8) J. Monnin, *Angew. Chem.*, **69**, 762 (1957); *Helv. Chim. Acta*, **41**, 2112 (1958).

(9) E. E. Smissman and M. A. Oxman, *J. Am. Chem. Soc.*, **85**, 2184 (1963).

ciano adducts are favored over 2-cyano adducts by 95 to 5.¹⁰

We chose the simplest unambiguous route to 1, subjecting 1-acetylcyclohexene to the Wittig reaction.¹¹ The product (66%) contained only small amounts of impurities as shown by its behavior on capillary gas-liquid partition chromatography (glpc) (96% one component),¹² nmr spectrum (1:1 ratio of vinyl to methyl hydrogens), ultraviolet spectrum [λ_{\max} 233 m μ (ϵ 19,200)], and subsequent conversion to Diels-Alder adducts in greater than 90% yield.

α -Acetoxyacrylonitrile was prepared by dehydrohalogenation of the cyanohydrin acetate of chloroacetaldehyde,¹³ methyl α -acetoxyacrylate, and α -acetoxyvinyl methyl ketone by enol acetylation of methyl pyruvate and biacetyl, respectively, the latter in poor yield (12%) by a modification of the reported procedure.¹⁴

The orientation ratios (3:4) in the Diels-Alder reactions were determined by converting each adduct mixture to a mixture of the two possible α,β -unsaturated ketones (6, 4-methyl- Δ^9 -1-octalone, and 7, 4-methyl- Δ^3 -2-octalone) using the reagents shown in Scheme II (which shows the transformations only for compounds derived from the predominant orientation of addition).¹⁵ Analysis by glpc of the various α,β -unsaturated ketone mixtures showed that they contained 97.5–98.5% 6 and 1.5–2.5% 7. Each conjugate pair of analyses was taken to represent the extent of formation of the two orientation adducts in the corresponding Diels-Alder reaction (see Table I). Although this method of analysis established that effectively only one orientation of addition occurred in the Diels-Alder reactions of 2 (R = CN, CO₂CH₃, and COCH₃), glpc

(10) I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *Zh. Obshch. Khim.*, **25**, 88 (1955).

(11) Previously reported preparations of 1 almost certainly yielded mixtures of isomers. See H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940); D. Nightingale, E. C. Milberger, and A. Tomisch, *J. Org. Chem.*, **13**, 357 (1948); V. R. Skvarchenko, L. Weeng-lien, and R. Ya. Levina, *J. Gen. Chem. USSR*, **30**, 2117 (1960). Cf. H. E. Eschinazi and H. Pines, *J. Org. Chem.*, **20**, 1666 (1955).

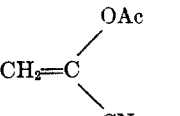
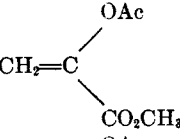
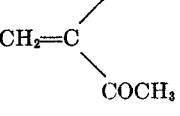
(12) All ratios and percentages quoted for glpc data are direct area comparisons of the observed peaks.

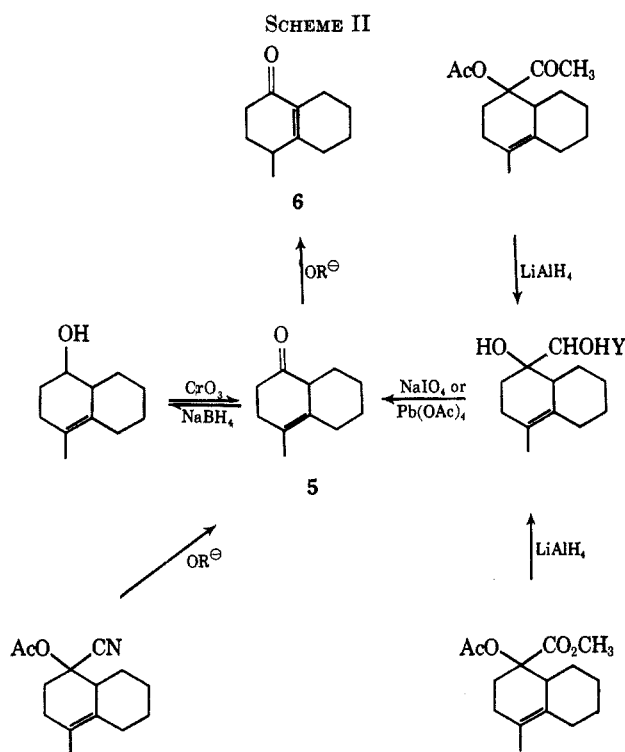
(13) R. M. Nowak, *J. Org. Chem.*, **28**, 1182 (1963).

(14) H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(15) Ketones 6 and 7 were prepared and characterized via the Diels-Alder reaction of 1 with vinyl acetate, where the two orientation adducts were found to have formed in roughly equal amounts.

TABLE I
 RESULTS GIVEN BY DIENOPHILES

Dienophile (equiv)	Conditions	% Diels-Alder adduct		Orientation 3:4	% yield of 5 based on unrecovered diene
		Based on total diene	Based on unrecovered diene		
 (1.1)	3 days, 120°	81	84	97.5:2.5	48
 (1.0)	24 hr, 120°	92	94	98:2	76
 (1.0)	24 hr, 80°	85	93	98.5:1.5	72



and nmr spectra of the adducts showed the presence of two components in ratios of 1:1, 3:1, and 4:1, respectively; these components must be the two epimers of the predominant orientation. In one case a single crystalline epimer was obtained, but in no cases were experiments undertaken to relate the stereochemistry of the individual epimers to their relative abundance.

Preparation of the desired β,γ -unsaturated ketone 5 was then examined. This was simply accomplished from 3 (R = CO₂CH₃, COCH₃) by reduction of the adducts with lithium aluminium hydride and cleavage of the resulting diols with either sodium periodate or lead tetraacetate (which both gave the same yield of product). Under these mild reaction conditions the amounts of α,β -unsaturated ketone formed by isomerization were negligible except in one run with lead tetraacetate when 5% isomerization was observed. Direct obtention of 5 from 3 (R = CN) by saponification could not be effected as it was isomerized to 6 faster

than it was formed in the alkaline medium. The desired transformation was therefore circuitously effected. Treatment of 3 (R = CN) with sodium borohydride in ethanol gave a mixture of secondary alcohols, the nmr spectrum of which showed the position of the double bond to be unchanged, *i.e.*, reduction of 5 was faster than isomerization under these conditions. Regeneration of 5 could then be effected by oxidation with chromic acid. However, the transformation was not ideal because the yield in the oxidation step was low (60–70%) and some isomerization was unavoidable, even with incomplete conversion, so that the β,γ -unsaturated ketone had to be separated from unreacted alcohol and α,β -unsaturated ketone by preparative glpc or fractional distillation.

Experimental Section

Physical Data.—Melting points were taken in capillary tubes in a Thomas-Hoover melting point apparatus and are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on a Beckman IR-8 spectrometer, liquids as films and solids as solutions in carbon tetrachloride. Ultraviolet spectra of solutions, in 95% ethanol, were recorded on a Cary spectrometer, Model 11MS. Nmr spectra of solutions in carbon tetrachloride containing tetramethylsilane were recorded on a Varian A-60 spectrometer. Mass spectra were recorded on a Consolidated CEC 103 spectrometer operated at 70 ev with samples introduced *via* a heated glass inlet system maintained at 200°. Glpc data were obtained using 5 ft \times 1/4 in. and 5 ft \times 3/8 in. columns of 5 and 10% Carbowax 20M on Teflon 6 and Chromosorb P (60–80 mesh), respectively, in conjunction with an Aerograph A-90-P2 (thermal conductivity) and Disc chart integrator, and with a 150-ft Ucon Polar capillary column in conjunction with a Perkin-Elmer F-11 (flame ionization) and Disc chart integrator.

α -Acetoxyacrylonitrile was prepared according to the procedure of Nowak:¹³ λ_{\max} 4.46, 5.65, 6.10 μ ; nmr chemical shifts at τ 4.28 and 4.34 (2 H, AB, J = 2.7 cps) and 7.80 (3 H).

Methyl α -acetoxyacrylate was prepared according to the procedure of Wolinsky:⁷ λ_{\max} 5.65, 5.75 μ ; nmr chemical shifts at τ 4.09 and 4.65 (2 H, AX, J = 1.5 cps), 6.24 (3 H), and 7.83 (3 H).

α -Acetoxyvinyl methyl ketone was prepared by a modification of the published procedure.¹⁴ A mixture of 44 g (0.5 mole) of freshly distilled biacetyl, 93 g (0.93 mole) of distilled isopropenyl acetate, and 25 g of *p*-toluenesulfonic acid was refluxed and the acetone formed was continuously removed at a head temperature of 57° by distillation through an 18-in. Vigreux column. After 4.5 hr, when the amount of distillate was 35 g, 100 ml of distilled decalin was added to the reaction mixture and the total mixture

was distilled as fast as possible at reduced pressure through a short head. The distillate was redistilled at 90 mm, affording 32 g, bp 27–75° (starting materials); 23 g, bp 77–97°, which separated into two layers, the top 3.4 g of decalin, the bottom largely acetic anhydride; and 42 g, bp 101–118°, which separated into two layers, the bottom 12.9 g, largely the desired product. This material was redistilled, affording 8 g (12%): bp 71–72° (7 mm); λ_{\max} 5.69, 5.90, 6.10 μ ; nmr chemical shifts at τ 4.20 and 4.57 (2 H, AX, $J = 2$ cps), 7.78 (3 H), and 7.88 (3 H).

1-Isopropenylcyclohexene.—In a 5-l., three-necked, round-bottom flask fitted with a stirrer, condenser, and thermometer, were placed 1.1 l. of dimethyl sulfoxide (freshly distilled from calcium hydride) and 93 g of 52% dispersion of sodium hydride in oil (2.0 moles). The suspension was heated gradually under nitrogen until the evolution of hydrogen ceased, taking 3 hr to reach 70°. The resulting solution of sodium methyl sulfinylcarbanion was stirred at room temperature overnight.¹⁶

In a 12-l., three-necked, round-bottom flask fitted with a stirrer, condenser, and thermometer, were placed 714 g (2.0 moles) of triphenylmethylphosphonium bromide¹⁷ in 2 l. of freshly distilled dimethyl sulfoxide. The mixture was stirred until the solid dissolved completely. The previously prepared solution of methylsulfinyl carbanion was then added, with stirring, by pumping it over under nitrogen pressure, and a further 250 ml of dimethyl sulfoxide was used to rinse the flask and complete the transfer. The temperature of the reaction mixture reached 40° after the addition was complete. The mixture was stirred for an additional hour at room temperature and then 236 g (1.90 moles) of 1-acetylcyclohexene¹⁸ (99% pure by glpc) was added dropwise over 45 min. The total mixture was stirred for a further 5 hr and then 9 l. of water was added. The solution was divided into three portions, each of which was extracted with three 1200-ml portions of ether. The combined ether extracts were divided into two portions and each was washed with three 1000-ml portions of saturated sodium chloride solution and then dried over magnesium sulfate. The solutions were filtered and solvent was evaporated. The resulting slush was stirred several times with portions of pentane to extract the product from triphenylphosphine oxide. The pentane solutions were combined and evaporated and the residue was distilled through a spinning-band column at reduced pressure, yielding 129 g, bp 50–61° (11 mm), of desired product and 42 g, bp 67–69° (11 mm), of starting ketone. The first fraction was distilled more carefully through a spinning-band column, yielding 11 g of forerun, bp 41–49° (7 mm), and then the main fraction of 102 g, bp 49–50° (7 mm), which was 96% one component according to capillary glpc at 75°: $\lambda_{\max}^{\text{EtOH}}$ 233 μ (ϵ 19,200); nmr chemical shifts (CCl_4) at τ 4.15 (1 H), 5.1 (1H), 5.2 (1 H), 8.15 (3 H), and two groups of 4 H each centered at τ 7.85 and 8.35.

Anal. Calcd for C_9H_{14} : C, 88.45; H, 11.55. Found: C, 88.82; H, 11.36.

Diels-Alder Reaction of 1-Isopropenylcyclohexene. A. Vinyl Acetate.—A mixture of 5.08 g (42 mmoles) of 1-isopropenylcyclohexene, 5.02 g (58 mmoles) of freshly distilled vinyl acetate, and 200 mg of hydroquinone was heated in a sealed-glass tube for 3 days at 190°. Distillation of the product afforded 5.3 g of a viscous liquid, bp 93–135° (0.2 mm), showing, on glpc at 200°, two poorly separated peaks at 9–10 min (49%) in a ratio of 40:60 and one peak at 17 min (49%).

A solution of 2.23 g of this viscous liquid in 25 ml of ether was added, with stirring, over 15 min to a solution of 1.08 g of lithium aluminum hydride in 40 ml of ether. The mixture was stirred for a further 2 hr and then worked up, yielding, on distillation, 1.91 g of viscous liquid, bp 93–103° (0.2 mm), which showed, on glpc at 180°, two poorly separated peaks at 19–21 min (40%) and one peak at 31 min (60%).

To a solution of 1.79 g of this viscous liquid in 200 ml of acetone (distilled from potassium permanganate), cooled in ice-water, was added, with stirring, 2.2 ml of Jones reagent.¹⁹ After 5 min the mixture was worked up, affording 1.56 g of crude product after evaporation of solvent, λ_{\max} 5.82 μ . The crude product was dissolved in 15 ml of methanol, 3 drops of 10% potassium hydroxide was added, and the solution was boiled for 5 min

under nitrogen. Work-up yielded, after distillation, 1.26 g of a liquid, bp 70–100° (0.2 mm), which was filtered through 33 g, of alumina: 705 mg was eluted with hexane, 366 mg with ether, and 194 mg with methanol. Material eluted with hexane was subjected to preparative glpc and an analytical sample was thereby obtained: nmr chemical shifts (CCl_4) at τ 4.65 (1 H), 8.41 (3 H), and 9.16 (3 H); from the mass spectrum, mol wt 244.

Anal. Calcd for $\text{C}_{18}\text{H}_{28}$: C, 88.45; H, 11.53. Found: C, 88.03; H, 11.59.

Material eluted with ether was shown, on glpc at 180°, to consist of two components with retention times of 19 min (43%) and 28 min (57%). The two were separated by preparative glpc and analytical samples of 6 and 7 were thereby obtained. Material corresponding to the peak at 19 min showed λ_{\max} 6.02 μ ; $\lambda_{\max}^{\text{EtOH}}$ 247 μ (ϵ 12,700); nmr chemical shifts (CCl_4) at τ 8.82 (3 H, doublet, $J = 7$ cps) with no vinyl hydrogens observable; from the mass spectrum, mol wt 164.

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: C, 80.22; H, 9.80.

Material corresponding to the peak at 28 min showed λ_{\max} 6.0 μ ; $\lambda_{\max}^{\text{EtOH}}$ 238 μ (ϵ 11,900); nmr chemical shifts (CCl_4) at τ 4.30 (1 H) and 8.10 (3 H); from the mass spectrum, mol wt 164.

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: C, 80.06; H, 9.76.

B. Methyl α -Acetoxyacrylate.—A mixture of 11.02 g (90.3 mmoles) of freshly distilled 1-isopropenylcyclohexene and 13.03 g (90.5 mmoles) of freshly distilled methyl α -acetoxyacrylate, containing 0.4 g of *t*-butylcatechol, was heated with stirring under nitrogen at 120°. The course of the reaction was monitored by infrared spectroscopy, the original sharp bands at 5.65 and 5.75 μ being replaced by two poorly separated ones at 5.70 and 5.75 μ . After 24 hr, distillation afforded 1.0 g, bp 31–33° (0.2 mm), of a mixture of diene and dienophile in a 25:75 ratio according to nmr data, and then 22.19 g (94% based on unrecovered diene), bp 107–124°, mainly 120–124° (0.2 mm), of a light yellow viscous oil which slowly solidified (λ_{\max} 5.70 and 5.75 μ) showing, on glpc at 180°, only two poorly separated peaks at 12–15 min in a 1:3 ratio, and nmr chemical shifts (CCl_4) at τ 6.35 (3 H), 8.36 (3 H), and 8.0 (3 H), the last consisting of two sharp singlets in a 75:25 ratio, separated by 1.5 cps. This material afforded excellent analytical data corresponding to $\text{C}_{15}\text{H}_{22}\text{O}_4$.

C. α -Acetoxyvinyl methyl ketone similarly yielded an adduct in 93% yield, based on unrecovered diene, bp 114–127° (0.4 mm), λ_{\max} 5.76 and 5.82 μ , showing, on glpc at 180°, one peak at 9 min (2%) and two poorly separated peaks at 15–18 min (95%) in a 1:4 ratio, and nmr chemical shifts (CCl_4) at τ 7.97 (3 H), 8.00 (3 H), and 8.35 (3 H). This material afforded excellent analytical data corresponding to $\text{C}_{15}\text{H}_{22}\text{O}_3$. It solidified on standing and yielded white plates, mp 99–100°, after two crystallizations from pentane.

Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$: C, 71.97; H, 8.86. Found: C, 71.96; H, 9.00.

D. α -Acetoxyacrylonitrile similarly yielded an adduct in 84% yield, based on unrecovered diene, bp 132–133° (1 mm), λ_{\max} 5.72 μ , showing, on glpc at 210°, one peak at 11 min (1.6%) and two poorly separated peaks at 28–30 min (97.4%), and nmr chemical shifts (CCl_4) at τ 7.9 (3 H) and 8.3 (3 H), the latter consisting of two sharp singlets in a 55:45 ratio, separated by 1.5 cps. Distillation of 141 g of crude product through an 18-in. Vigreux column afforded first 21 g, bp 70–101° (0.2 mm), which was enriched in material corresponding to the glpc peak at 11 min and then 129 g, bp 100–125° (0.2 mm), which contained a negligible amount of this material and which afforded excellent analytical data corresponding to $\text{C}_{14}\text{H}_{19}\text{NO}_2$. The enriched impurity in the first fraction was separated by preparative glpc and shown to be the same $\text{C}_{15}\text{H}_{23}$ hydrocarbon as that obtained in the vinyl acetate experiment.

4-Methyl- $\Delta^{4(10)}$ -1-octalone. A. From 3 (R = CO_2CH_3 and COCH_3).—Exemplary procedures for R = CO_2CH_3 are given.

(i) A solution of 1.08 g (4.00 mmoles) of adduct in 15 ml of ether was added dropwise, with stirring under nitrogen, over 10 min to a solution of 0.608 g (16 mmoles) of lithium aluminum hydride in 10 ml of ether, cooled in ice-water. The mixture was stirred for a further 90 min and then quenched with saturated magnesium sulfate solution, followed by magnesium sulfate powder. The solution was filtered, the solid was extracted several times with ether, and the various ether solutions were combined. Evaporation of solvent yielded 0.782 g of a light yellow oil showing no carbonyl absorption. To a stirred solution of this oil in

(16) M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963); E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(17) G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960).

(18) J. H. Saunders, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 22.

(19) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lenin, *J. Chem. Soc.*, 258 (1953).

5 ml of alcohol was added, under nitrogen, a solution of 0.951 g (4.4 mmoles) of sodium metaperiodate in 5 ml of water. The resulting milky solution was stirred at room temperature for 1 hr and then diluted with water and extracted with several portions of ether. The combined ether solutions were washed with sodium thiosulfate solution and saturated sodium chloride solution. After drying and evaporation of solvent, distillation yielded 0.546 g (82%) of a colorless liquid, bp 59° (0.2 mm), with the infrared and nmr spectral characteristics of **5**, showing on capillary glpc at 80° one major peak at 39 min (99%) and no peak corresponding to **6**. (ii) In another run 0.602 g (2.36 mmoles) of adduct yielded 0.428 g of diol after reduction with lithium aluminum hydride. To this diol in 5 ml of acetic acid (distilled from chromic oxide) was added, with stirring under nitrogen, a suspension of 2.08 g (4.7 mmoles) of lead tetraacetate in 10 ml of acetic acid. The resulting solution was stirred at room temperature for 30 min and a few drops of glycerol were added to destroy the excess oxidant. Water was added and the mixture was extracted with several portions of pentane. The combined pentane solutions were washed with water, sodium bicarbonate solution, and water. After drying and evaporation of the solvent, distillation yielded 0.303 g (82%) of a colorless liquid with the infrared and nmr spectral characteristics of **5**, showing, on capillary glpc at 80°, one major peak at 33 min (99%) and no peak corresponding to **6**.

B. From 3 (R = CN).—A solution of 5.66 g of adduct in 80 ml of alcohol was added, with stirring under nitrogen, to a solution of 10.58 g of sodium borohydride in 150 ml of alcohol. After standing overnight the mixture was worked up, affording, after distillation, 3.59 g (90%) of a viscous liquid, bp 83–84° (0.5 mm), which solidified on cooling: mp 60–66°; nmr chemical shifts (CCl₄) at τ 6.1–6.4 (1 H), 7.2–7.6 (1 H), and 8.42 (3 H).

To a solution of 9.69 g (58.3 mmoles) of alcohol, obtained as above, in 1300 ml of acetone (distilled from potassium permanganate), cooled in ice-water, was added dropwise over 5 min, with stirring under nitrogen, 18 ml of Jones reagent (144 mequiv). The mixture was then diluted with 400 ml of water and enough sodium bisulfite solution was added to destroy the excess oxidant. Work-up yielded, after distillation, 7.26 g which showed, for the combined fractions, on glpc at 160°, three peaks at 10 min (75%), 13 min (15%), and 20 min (9%), corresponding to **5**,

starting material, and **6**, respectively. The three fractions collected from the distillation were (a) 2.85 g, bp to 85° (0.2 mm), showing peaks at 10 min (90%) and 13 min (10%); (b) 2.62 g, bp 85–87° (0.2 mm), showing peaks at 10 min (82%), 13 min (15%), and 20 min (3%); and (c) 1.79 g, bp 87–140° (0.2 mm), showing peaks at 10 min (40%), 13 min (24%), and 20 min (32%).

Material corresponding to the peak at 10 min was collected by preparative glpc and an analytical sample of **5** was thereby obtained: λ_{\max} 5.82 μ ; $\lambda_{\max}^{\text{EtOH}}$ 237 m μ (ϵ 270); nmr chemical shift at τ 8.29 (3 H).

Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.31; H, 10.00.

Upon addition of sodium hydroxide solution to a solution of **5** in alcohol in an ultraviolet cell, the absorption of **6**, λ_{\max} 247 m μ (ϵ 11,900), was rapidly established.

Orientation Ratios.—A solution of 212 mg of crude **5**, obtained as described from crude adduct **3** (R = CO₂CH₃), in 3 ml of methanol containing 2 drops of 10% potassium hydroxide solution, was boiled under nitrogen for 5 min. The solution was cooled, diluted with saturated sodium chloride solution, and extracted with several portions of ether. The combined ether solutions were washed with saturated sodium chloride solution and dried. Evaporation of solvent and short-path distillation of the residue at 0.4 mm from an oil bath at 85–90° afforded 195 mg (92% recovery) of a colorless liquid with the ultraviolet and nmr spectral characteristics of **6**, and showing, on capillary glpc at 80°, peaks at 61 min (98%) and 87 min (2%) corresponding to those for **6** and **7**, respectively. Material corresponding to each glpc peak was collected and identified by a comparison of spectral data with those from authentic **6** and **7**.¹⁵

Samples of crude **5** from the other Diels–Alder adducts were similarly isomerized and analyzed with the results shown in Table I.

A synthetic mixture of 19.7 mg of **6** and 18.7 mg of **7**, showing two peaks on glpc of 57.7 and 42.3%, was subjected to the isomerization procedure and subsequent work-up. Before distillation, 31.2 mg (82% recovery) of a slightly yellow oil was obtained showing two peaks on glpc of 57.6 and 42.4%. After distillation, 28.4 mg (74% recovery) of a colorless liquid was obtained showing two peaks on glpc of 57.5 and 42.5%.

Acylation. I. The Mechanisms of Enol Ester and 1,3-Diketone Formation in the Reaction of Ketone–Enol Systems with Acyl Halides

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Acylation of ketone–sodium amide systems with acid chlorides gave mixtures of enol esters and 1,3-diketones, with the ratio of products formed being dependent on reaction conditions. 1,3-Diketones were obtained in good yields by acylation of the ketones–base system with enol benzoates. Several enol benzoates were also shown to rearrange, in the presence of sodium amide (and absence of ketone), to give 1,3-diketones.

The acylation of ketones having an α -hydrogen atom with acid chlorides or acid anhydrides has been reported as a convenient preparation route to many 1,3-diketones.^{1–3} With acid chlorides, the condensation is usually effected by means of a basic reagent such as sodium amide; with acid anhydrides, a Lewis acid such as boron trifluoride is generally used. O-Acyl derivatives are formed in these reactions, but the conditions can be controlled so that favorable yields of 1,3-

diketones can be obtained. In contrast to this it has been reported^{4,5} that enolates from various unsymmetrical ketones and triphenylmethylpotassium react with acid anhydrides (and presumably acid chlorides) to give primarily O-acylated products. The isomeric 1,3-diketones were not detected in these experiments, even in trace amounts.

The specificity of the latter reaction system to give only esters together with reported synthesis of 1,3-diketones from, for example, the sodium amide–aliphatic ketone–acid halide reaction suggests that the formation of products is more complex than the simple,

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