The Reaction of 2-Methoxybutadiene with Enols and Phenols, a Novel Claisen Rearrangement[1a]

L. J. DOLBY,[1b] C. A. ELLIGER,[1c] S. ESFANDIARI, AND K. S. MARSHALL[1d]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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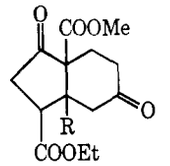
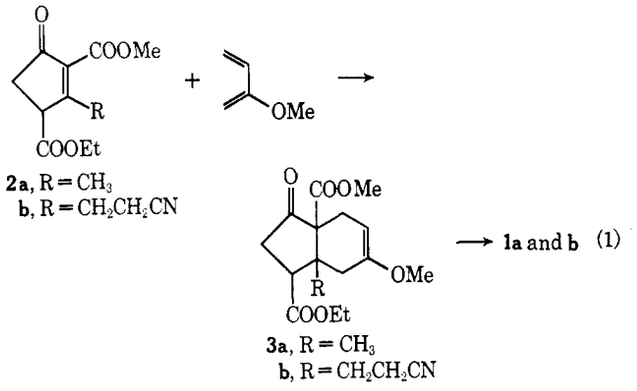
The reaction of 2-methoxybutadiene with highly enolic compounds such as the cyclopentenone **2b** and dimedone gives products **10** and **14**, respectively, in which a four-carbon side chain bearing an enol ether function has been introduced. It is thought that the enolic hydroxyl adds to the diene to produce an allylic enol ether (*e.g.*, **13**). Claisen rearrangement then gives the observed product. Phenols also react with 2-methoxybutadiene to yield rearranged products. However, the products are methoxy chromanes which are formed by closure of the initially formed allyl phenols. These reactions proceed in high yields with the formation of monosubstitution products.

For the preparation of certain multiply substituted perhydroindandiones (*e.g.*, **1a** and **1b**) it was attractive



1a, R = CH_3
b, R = CH_2CH_2CN

to examine the reaction of the highly activated dienophiles **2a** and **2b** with 2-methoxybutadiene. Diels–Alder reaction would be expected to yield the enol ethers **3a** and **3b**,[2] which would give the desired ketones upon hydrolysis (eq 1).

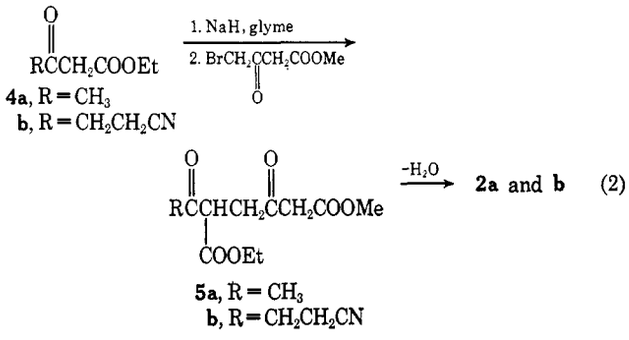


2a, R = CH_3
b, R = CH_2CH_2CN

3a, R = CH_3
b, R = CH_2CH_2CN

→ **1a** and **b** (1)

The required cyclopentenones were prepared in high yields by condensation of the sodium enolates of the β-keto esters **4a** and **4b** with methyl 4-bromoacetoacetate in 1,2-dimethoxyethane (eq 2). The initial reaction is undoubtably formation of the linear diketo diesters **5a** and **5b**, followed by cyclization. The latter step is favored by formation of the sodium enolate of the highly acidic product, and a twofold excess of starting keto ester and sodium hydride was commonly employed. The cyclopentenones prepared in this way are soluble in dilute bicarbonate solution, and they may be conveniently separated from less acidic impurities by extractive work-up. Material obtained by acidification of the bicarbonate extracts is a mixture of



4a, R = CH_3
b, R = CH_2CH_2CN

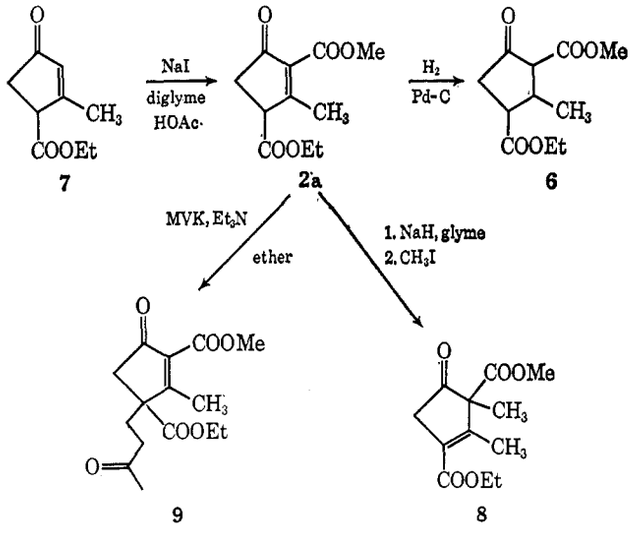
5a, R = CH_3
b, R = CH_2CH_2CN

2a and **b** (2)

keto and enol forms which may be separated by fractional crystallization. The spectral properties (ir and nmr) of the tautomeric forms differ; however, the nmr spectrum in pyridine of keto and enol **2a** as obtained from the extract showed a simple pattern (as opposed to that in $CDCl_3$).

The following transformations (Scheme I) were carried out on **2a**. Catalytic reduction gave the cyclopentanone **6**, clearly showing normal five-membered-

SCHEME I



7 **2a** **6** **9** **8**

ring carbonyl absorption (1765 cm^{-1}) in its ir spectrum. Decarbomethoxylation of **2a** was conveniently carried out by sodium iodide in boiling diglyme–acetic acid to give **7** whose ir (1730, 1720, 1630 cm^{-1}) and nmr spectra (δ 5.92 ppm, 1 H) indicate preservation of the Δ^2-cyclopentenone system. Formation of the anion of **2a** in 1,2-dimethoxyethane followed by treatment with methyl iodide gave **8** in which the position of

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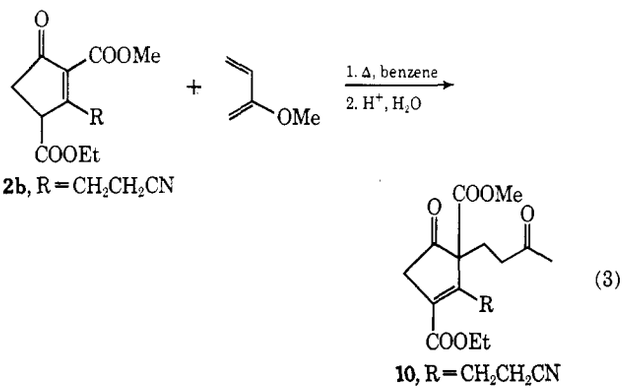
(2) In analogy, the reaction of 2-methoxybutadiene with acrolein gives a single product having the proper orientation [H. L. Holmes, *Org. Reactions*, 4, 64 (1948)].

methylation is shown by the ir spectrum (1755 cm^{-1}, unconjugated five-membered-ring carbonyl). Confirming evidence for the position of unsaturation is provided by the nmr spectrum, which indicates homoallylic coupling between the methyl group attached to C-3 and the two protons of C-5 (J = 2 cps). Reaction of **2a** with methyl vinyl ketone gave **9** which bears the newly introduced side chain at position 4 as shown by ir and nmr (Experimental Section).

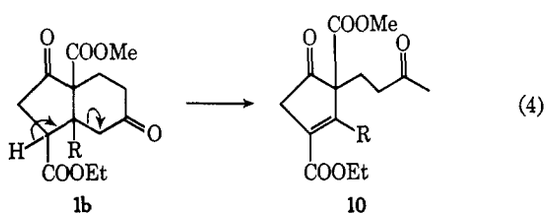
The reaction of cyclopentenones of this type with 2-methoxybutadiene does not lead to the desired perhydroindanones as postulated in eq 1. Treatment of **2b** with 2-methoxybutadiene in refluxing benzene, followed by hydrolysis with dilute hydrochloric acid, gave a substance shown to be **10** (eq 3). The high-



(3)

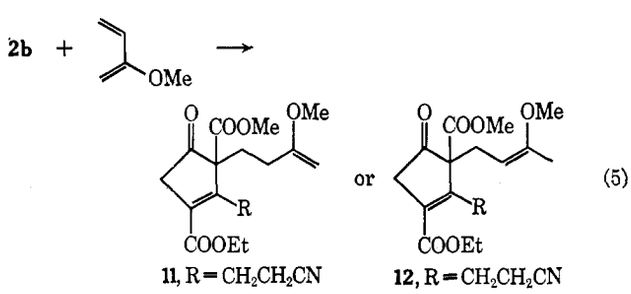
frequency (1770 cm^{-1}) carbonyl absorption of **10** in the ir spectrum points to an unconjugated five-membered-ring carbonyl group, and the nmr spectrum shows the presence of a methyl group adjacent to a carbonyl (δ 2.12 ppm).

Although the formation of **10** might be considered to proceed *via* **1b** in a reverse Michael reaction (eq 4),



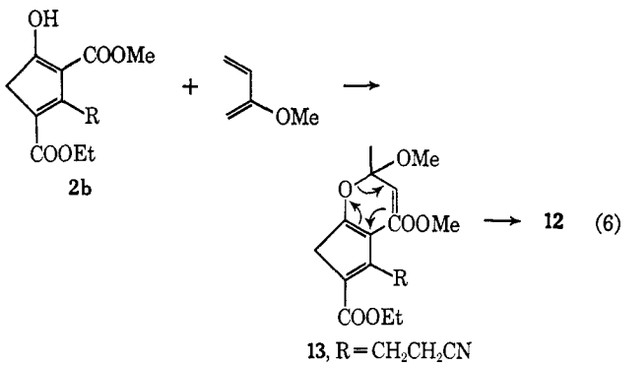
(4)

such a reversal is not precedented for the mild acidic conditions employed during hydrolysis.[3] It appeared far more likely that one of the two possible enol ethers **11** or **12** was formed directly by reaction of **2b** with 2-methoxybutadiene (eq 5), and that subsequent hydrol-



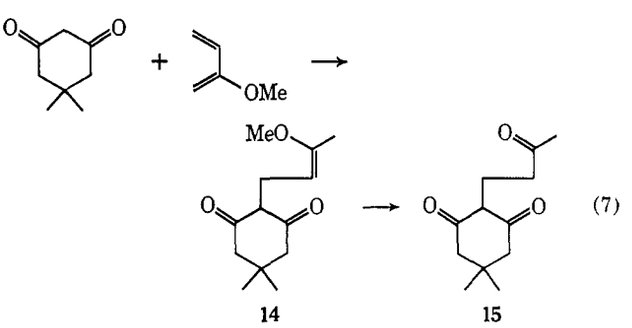
(5)

ysis gave **10**. Since it is difficult to explain addition of **2b** to the diene at position 4 (addition of ROH, *e.g.*, takes place at position 2[4]), the possibility was considered that the enol form of **2b** adds normally *at the enol oxygen* to give **13**, and that subsequent Claisen rearrangement leads to **12** (eq 6).



(6)

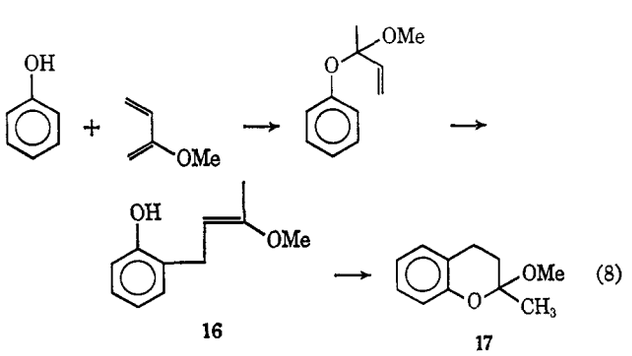
A test of this suggestion lies in the reaction of 2-methoxybutadiene with other highly enolic substances. To this end, dimedone was permitted to react with the diene in refluxing benzene to give an excellent yield of the enol ether **14** (eq 7) which was identified by ir and



(7)

nmr spectra and by hydrolysis to the triketone **15**. The reaction of dimedone with methyl vinyl ketone gives **15** along with disubstituted material;[5] however, the diene pathway leads to the formation of essentially pure monoadduct.

Phenols also react with 2-methoxybutadiene to yield rearranged products. In the case of phenol it was found that polymerization of the diene took place in the absence of base. However, the addition of a trace of triethylamine inhibited polymerization; and the desired reaction was effected at a temperature of 150° to give the chromane **17**. This material is presumably formed by closure of the initial rearrangement product, **16** (eq 8). The reaction of *o*-cresol with 2-



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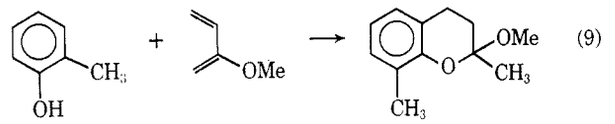
(3) E. D. Bergman, D. Ginsberg, and R. Pappo, *Org. Reactions*, **10**, 187 (1959).

(4) R. O. Norris, J. J. Verbanc, and G. F. Hennion, *J. Amer. Chem. Soc.*, **60**, 1159 (1938).

(5) I. N. Nazarov and S. I. Zav'yalov, *Zh. Obshch. Khim.*, **23**, 1703 (1953); *Chem. Abstr.*, **48**, 13667 (1954).

methoxybutadiene takes place less readily. Addition of triethylamine to this reaction mixture is not necessary or desirable as the base exerts a very pronounced inhibitory effect. In the absence of base at 160° chromane **18** is formed in good yield after 21 hr (eq 9).



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In conclusion it may be pointed out that these reactions of 2-methoxybutadiene provide a method for introduction of the elements of methyl vinyl ketone to enols and phenols that differ greatly in reactivity and specificity from the reactions of the unsaturated ketone. The formation of monoadduct **14** in the dimedone reaction is especially attractive in that monomethyl vinyl ketone condensation products are less easily obtained in good yields.

Experimental Section

Methyl 4-Bromoacetoacetate.—Bromination of methyl acetoacetate in carbon tetrachloride solution in a manner analogous to that of Burger and Ullyot[6] gave methyl 4-bromoacetoacetate in 64% yield: bp 78–86° (2 mm); ir $\nu_{max}^{CCl_4}$ 1740, 1720 cm^{-1}; nmr (CCl_4) δ 3.67 (s, 2 H), 3.74 (s, 3 H), 4.05 (s, 2 H).

4-Carbethoxy-2-carbomethoxy-3-methyl-Δ^2-cyclopentenone (2a).—In a 1-l. flask equipped with reflux condenser, addition funnel, and magnetic stirrer were placed 700 ml of 1,2-dimethoxyethane and 23.0 g (1.00 g-atom) of sodium metal. The flask was cooled to 0°, and 130 g (1.00 mol) of ethyl acetoacetate was added with stirring over 0.5 hr. The mixture was then permitted to come to about 50° as the last of the sodium dissolved. The cooling bath was replaced, and 98.0 g (0.500 mol) of methyl 4-bromoacetate was added in one portion. After stirring for 2.5 hr, the reaction mixture was concentrated by removal of most of the solvent under reduced pressure. Water, *ca.* 1.5 l., was then added until a homogeneous mixture was obtained, and the material was then washed with three 300-ml portions of ether. Acidification of the aqueous solution followed by extraction with two 300-ml portions of ether afforded 66.4 g of crude substance after drying over magnesium sulfate and removal of solvent. Distillation gave 54.5 g (0.241 mol, 48%) of product as a semisolid mixture of keto and enol forms: bp 140–150° (0.5 mm).

Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.36; H, 6.34.

Pure enol form of **2a** was obtained by crystallization of the distillate from ether: melting point variable and ill defined; ir $\nu_{max}^{CHCl_3}$ 3200 (very broad), 1720, 1680, 1600, 1550 cm^{-1}; nmr ($CDCl_3$) δ 1.30 (t, J = 7 cps, 3 H), 2.15 (t, J = 2.5 cps, 3 H), 3.40 (q, J = 2.5 cps, 2 H), 3.87 (s, 3 H), 4.23 (q, J = 7 cps, 2 H), 11.34 (broad singlet, 1 H); uv λ_{max}^{EtOH} 350, 300, 226 mμ (ϵ_{max} 1650, 2200, 9330); $\lambda_{max}^{EtOH-NaOH}$ 353, 298 mμ (ϵ_{max} 11,700, 13,300).

Nearly pure keto form of **2a** was obtained as an oil by distillation of the residues left from crystallization of the enol: ir $\nu_{max}^{CHCl_3}$ 1720 (broad), 1640 cm^{-1}; nmr (CCl_4) δ 1.28 (t, J = 7 cps, 3 H), 2.33 (s, 3 H), 2.58 (d, J = 5 cps, 2 H), 3.77 (s, 3 H) on top of *ca.* 3.74 (poorly defined triplet, 1 H), 4.17 (q, J = 7 cps, 2 H).

A mixture of keto and enol forms showing sets of overlapping bands in the nmr spectrum (in $CDCl_3$) was dissolved in pyridine. The nmr spectrum in this basic solvent became greatly simplified corresponding to one form: in C_5H_5N δ 1.20 (t, J = 7 cps, 3 H), 2.41 (s, 3 H), *ca.* 2.8 (multiplet, 2 H), 3.80 (s, 3 H) and 4.20 (q, J = 7 cps, 2 H) superimposed on multiplet (1 H) centered at *ca.* 3.9 ppm.

4-Carbethoxy-2-carbomethoxy-3-methylcyclopentanone (6).—In 50 ml of ethyl acetate was dissolved 2.26 g (10.0 mmol) of **2a**, and 0.1 g of 10% Pd–C was added. Hydrogenation was carried out at atmospheric pressure until gas uptake ceased. Filtration of the resulting mixture followed by removal of solvent and evaporative distillation at 70° (0.005 mm) gave 1.81 g (7.9 mmol, 79%) of reduction product: ir $\nu_{max}^{CCl_4}$ 1765, 1730 cm^{-1}; nmr (CCl_4) δ 1.17 and 1.34 (t and d superimposed, J = 7 cps, 6 H), 2.3–3.4 (complex, 5 H), 3.72 (s, 3 H), 4.16 (q, J = 7 cps, 2 H).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 57.80; H, 7.29.

4-Carbethoxy-3-methyl-Δ^2-cyclopentenone (7).—In a 250-ml flask equipped with stirrer and reflux condenser were placed 100 ml of diglyme, 10 ml of acetic acid, 60 g (400 mmol) of sodium iodide, and 25.5 g (113 mmol) of **2a**. The mixture was refluxed until gas evolution ceased (*ca.* 15 min) and then was cooled to room temperature. The mixture was added to 250 ml of water and was extracted with one 200-ml and two 100-ml portions of ether. The combined ethereal extracts were washed with one 100-ml portion of water followed by two 100-ml portions of 5% sodium bicarbonate solution. After drying over magnesium sulfate the solution of product was concentrated under reduced pressure and distilled under vacuum to give 8.81 g (52.5 mmol, 46.5%) of substance: bp 70–75° (*ca.* 0.5 mm); ir $\nu_{max}^{CCl_4}$ 1730, 1720, 1630 cm^{-1}; nmr (CCl_4) δ 1.28 (t, J = 7 cps, 3 H), 2.13 (s, 3 H), 2.51 (d, J = 5 cps, 2 H), *ca.* 3.7 (complex, 1 H), 4.23 (q, J = 7 cps, 2 H), 5.92 (complex, 1 H); uv λ_{max}^{EtOH} 272, 221 mμ (ϵ_{max} 561, 8740).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.15; H, 7.17.

The 2,4-dinitrophenylhydrazone was prepared in the usual way: mp 135–137° (EtOAc).

4-Carbethoxy-2-carbomethoxy-2,3-dimethyl-Δ^3-cyclopentenone (8).—In a 50-ml flask equipped with a stirrer, addition funnel, and drying tube were placed 48 mg (2.0 mmol) of oil-free sodium hydride and 20 ml of 1,2-dimethoxyethane. To the resulting suspension was added with stirring 452 mg (2.00 mmol) of **2a** in 5 ml of 1,2-dimethoxyethane. When hydrogen evolution had ceased methyl iodide (1.0 g, 6.8 mmol) was added, and the mixture was allowed to stir 23 hr at room temperature. The solvent was removed, and the residue was taken up in 40 ml of ether. Extraction with two 15-ml portions of 2% sodium hydroxide solution removed unchanged starting material, and the ethereal solution was then dried over magnesium sulfate. Evaporation of solvent gave 230 mg (0.96 mmol, 48%) of product: ir $\nu_{max}^{CCl_4}$ 1755, 1730, 1710, 1640 cm^{-1}; nmr (CCl_4) δ 1.1–1.5 (s and t, J = 7 cps, 6 H), 2.12 (t, J = 2.0 cps, 3 H), 3.18 (q, J = 2.0 cps, 2 H), 3.70 (s, 3 H), 4.22 (q, J = 7 cps, 2 H); uv λ_{max}^{EtOH} 226, 212 (sh) mμ (ϵ_{max} 8860, 8150).

Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.29; H, 6.67.

4-Carbethoxy-2-carbomethoxy-4-(3-ketobutyl)-3-methyl-Δ^2-cyclopentenone (9).—To a solution of 4.52 g (20.0 mmol) of **2a** in 50 ml of ether was added 1.60 g (23 mmol) of methyl vinyl ketone and 0.2 ml of triethylamine. After standing at room temperature for 5 min the reaction mixture was extracted with two 50-ml portions of 5% sodium bicarbonate solution to remove unreacted starting cyclopentenone. The ethereal solution was dried over magnesium sulfate and concentrated under reduced pressure. The residue was evaporatively distilled at 120° (5 μ) to give 4.71 g (15.9 mmol, 80%) of product: ir $\nu_{max}^{CCl_4}$ 1730 (broad), 1630 cm^{-1}; nmr ($CDCl_3$) δ 1.26 (t, J = 7 cps, 3 H), 4.20 (q, J = 7 cps, 2 H), singlets at 2.17, 2.30 and 3.83 (3 H each), and a complex pattern between 2.2 and 3.2 (6 H); uv λ_{max}^{EtOH} 294, 236, 225 mμ (ϵ_{max} 662, 8680, 8290).

Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.70; H, 6.62.

β-Cyanopropionyl Chloride.—To a solution of thionyl chloride (143 ml, 2.0 mol) in 500 ml of ether maintained below 20° was added 121 g (1.00 mol) of anhydrous sodium β-cyanopropionate[7] over about 15 min. The mixture was then allowed to stir at about 30° for an additional 0.5 hr. Celite, 10 g, was added, and the suspension of solids was removed by filtration through a 7-cm sintered funnel (coarse grade) upon which had been prepared a bed of Celite, 20 g. The filtrate was concentrated to 200 ml by rotary evaporator, and the residual thionyl chloride was then removed at oil-pump pressure. Distillation of the residue gave 100.0 g (0.85 mol, 85%) of light yellow oil: bp 78–80° (0.5 mm); ir $\nu_{max}^{CCl_4}$ 2260, 1795 cm^{-1}; nmr (CCl_4) δ *ca.* 2.6 and 3.2, complex multiplets of equal intensity (A_2B_2).

(6) A. Burger and G. E. Ullyot, *J. Org. Chem.*, **12**, 346 (1947).

(7) T. L. Gresham, *J. Amer. Chem. Soc.*, **74**, 1323 (1952). Anhydrous material was obtained by drying the monohydrate under vacuum at 100°.

The product decomposed slowly upon standing even at −10° and was used without further treatment.

Ethyl δ-Cyano-β-ketovalerate (4b).—In a 1000-ml flask equipped with stirrer, addition funnel, and drying tube were placed 400 ml of 1,2-dimethoxyethane and 26.2 g (1.09 mol) of oil-free sodium hydride. The suspension was cooled to about −20°, and 102.2 g (0.544 mol) of ethyl *t*-butyl malonate[8] was added over 15 min. To the stirred, cooled solution was then added over 30 min 70.5 g (0.600 mol) of β-cyanopropionyl chloride. Precipitation of a solid was noticeable after a few minutes. After 1 hr the cooling bath was removed, and the mixture was allowed to stir and additional 16 hr. An ice-cold solution of 50 ml of concentrated HCl in 250 ml of water was added to the reaction mixture with stirring. The resulting material was transferred to a separatory funnel, and two layers separated upon standing. The bottom layer was removed and discarded, whereas the upper was concentrated under reduced pressure. This residue was taken up in 250 ml of ether which was then washed with three 300-ml portions of 5% sodium bicarbonate solution and dried over magnesium sulfate. After removal of solvent the crude substance was pyrolyzed under aspirator pressure (150–170°) to give a distillate consisting mainly of ethyl *t*-butyl malonate and the desired product. Fractionation of the material through a 70-cm Podbielniak spiral column gave 45.7 g (0.270 mol, 49.6%) of ethyl δ-cyano-β-ketovalerate: bp 128–138° (*ca.* 1 mm); ir $\nu_{max}^{CCl_4}$ 3300 (very broad), 2250, 1740, 1725, 1650 cm^{-1}; nmr (CCl_4) δ 1.28 (t, J = 7 cps, 3 H), *ca.* 2.6 and 2.8 (A_2B_2, 4 H), 3.48 (s, 2 H), 4.17 (q, J = 7 cps. 2 H).

Anal. Calcd for $C_8H_{11}NO_3$: C, 56.80; H, 6.55; N, 8.28. Found: C, 57.06; H, 6.60; N, 7.82.

4-Carbethoxy-2-carbomethoxy-3-(2-cyanoethyl)-Δ²-cyclopentenone (2b).—In a 1000-ml flask equipped with stirrer, addition funnel, and drying tube were placed 6.48 g (240 mmol) of oil-free sodium hydride and 500 ml of 1,2-dimethoxyethane. The suspension was cooled to −10°, and 45.6 g (270 mmol) of ethyl δ-cyano-β-ketovalerate was added with stirring over 15 min. To the resulting light brown solution was added 26.3 g (135 mmol) of methyl 4-bromoacetoacetate over about 5 min. The cooling bath was removed, and the mixture was allowed to come to room temperature during which time precipitation of solid took place. After 2 hr, the solvent was removed by rotary evaporator, and the residue was taken up in 500 ml of water. The aqueous mixture was washed with three 150-ml portions of methylene chloride, then acidified to pH 2, and extracted three times with 150-ml volumes of methylene chloride. After drying over magnesium sulfate and removal of solvent, the residual semisolid substance was crystallized from ether to give 24.23 g (93 mmol, 68%) of the enol form of **2b**: ir $\nu_{max}^{CCl_4}$ 3200 (very broad), 2250, 1730, 1700, 1665, 1550; nmr ($CDCl_3$) δ 1.32 (t, J = 7 cps, 3 H), 2.62 (broadened triplet, J = 7 cps, 2 H), a broad singlet at 3.48 partly superimposed on a broadened triplet (J = 7 cps) centered at 3.40 (4 H over-all), 3.92 (s, 3 H), 4.24 (q, J = 7 cps, 2 H), 11.25 (broad singlet, 1 H); uv λ_{max}^{EtOH} 353 (broad sh), 302, 268 mμ (ϵ_{max} 15,000, 15,300).

No satisfactory elemental analysis for this compound could be obtained; however, the mass spectrum exhibited a parent peak at *m/e* 265 with the base peak at 233 (corresponding to loss of MeOH) having respective relative intensities of 51:100.

4-Carbethoxy-2-carbomethoxy-3-(2-cyanoethyl)-2-(3-ketobutyl)-Δ³-cyclopentenone (10).—In a 100-ml flask equipped with reflux condenser and provision for nitrogen atmosphere were placed 6.88 g (25.9 mmol) of **2b**, 3.63 g (43.2 mmol) of 2-methoxybutadiene, 50 ml of dry benzene, and 75 mg of 2,6-di-*t*-butylhydroquinone. Air was excluded from the flask, and the mixture was refluxed for 19 hr. The benzene solution was cooled and extracted with 30 ml of 5% sodium bicarbonate solution to remove unreacted starting material and then dried over magnesium sulfate. Evaporation of solvent under reduced pressure gave 9.49 g of crude enol ether which was dissolved in 50 ml of dioxane. Concentrated hydrochloric acid, 1 ml, was added, and the mixture was warmed to *ca.* 80° for 5 min. The dioxane solution was concentrated on the rotary evaporator, and the residue was taken up in 100 ml of ether. The ethereal solution was washed with 50 ml of 5% sodium bicarbonate solution and then dried over magnesium sulfate. Evaporation yielded a viscous oil which was evaporatively distilled at 130° (5 μ) to give 6.12 g of product (18.3 mmol, 71%) which solidified upon standing: mp 98–100° (benzene–isooctane); ir $\nu_{max}^{CHCl_3}$ 2250, 1770, 1730 (sh), 1715, 1630 cm^{-1}; nmr ($CDCl_3$) δ 1.37 (t, J = 7 cps, 3 H), 2.12 (s, 3 H), 2.25–3.45 (complex, 10 H), 3.75 (s, 3 H), 4.33 (q, J = 7 cps, 2 H); uv λ_{max}^{EtOH} 285, 225 mμ (ϵ_{max} 625, 7800).

Anal. Calcd for $C_{17}H_{21}NO_6$: C, 60.89; H, 6.31; N, 4.18. Found: C, 60.91; H, 6.13; N, 4.23.

5,5-Dimethyl-2-(3-methoxy-2-butenyl)cyclohexane-1,3-dione (14).—In a 50-ml flask equipped with stirrer and condenser were placed 25 ml of benzene, 7.00 g (50 mmol) of 5,5-dimethylcyclohexane-1,3-dione, and 4.62 g (55.0 mmol) of 2-methoxybutadiene. The mixture was refluxed for 16.5 hr, and the solvent was then removed under reduced pressure. Evaporative distillation of the crude substance through a short-path apparatus at 80° (5 μ) gave 10.23 g (45.7 mmol, 91.5%) of pure product which solidified upon standing: mp 55–58° (hexane); ir $\nu_{max}^{CCl_4}$ 3010, 2990, 2920, 2850, 1630 (broad), 1380, 1082, 1060 cm^{-1}; nmr (CCl_4) δ 1.05 (s, 6 H), 1.45 (s, 3 H), 1.7–2.3 (complex, 8 H), 3.26 (s, 3 H).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.23; H, 9.13.

A small amount of **14** was hydrolyzed by shaking a dilute ethereal solution with 3 *N* HCl to give 5,5-dimethyl-2-(3-ketobutyl)cyclohexane-1,3-dione: mp 101–102° (lit.[5] mp 100–101°).

2-Methoxy-2-methylchromane (17).—In a 20 × 600 mm thick-walled Pyrex tube were placed 9.40 g (100 mmol) of phenol, 50 ml of dry benzene, 0.1 g of 2,5-di-*t*-butylhydroquinone, and 0.15 ml of triethylamine followed by 9.24 g (110 mmol) of 2-methoxybutadiene. The contents of the tube were degassed in the usual way, and the tube was sealed under vacuum. After heating at 150° for 11.5 hr, the tube was opened, and most of the benzene was removed on the rotary evaporator. The crude product was taken up in 150 ml of ether and washed with two 50-ml portions of 5% sodium hydroxide solution. The organic phase was dried over potassium carbonate and evaporated to give a light yellow oil which was distilled through a 70-cm Podbielniak spiral column under reduced pressure to yield 14.62 g (82 mmol, 82%) of 2-methoxy-2-methylchromane: bp 108–112° (14 mm); ir (CCl_4) shows no hydroxyl or carbonyl absorptions; nmr (CCl_4) δ 1.47 (s, 3 H), 1.6–3.1 (complex, 4 H), 3.20 (s, 3 H), 6.4–7.2 (complex, 4 H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.01; H, 8.17.

2,8-Dimethyl-2-methoxychromane (18).—In a 20 × 250 mm thick-walled Pyrex tube were placed 2.70 g (25.0 mmol) of *o*-cresol, 2.31 g (27.5 mmol) of 2-methoxybutadiene, and 10 ml of dry benzene. The contents of the tube were degassed in the usual way, and the tube was sealed under vacuum. After heating at 160° for 21 hr, the tube was opened, and its contents were taken up in 60 ml of ether. This solution was washed with two 30-ml portions of 5% sodium hydroxide solution. The combined aqueous basic solutions were washed once with 30 ml of ether and then acidified to give upon extraction 0.54 g (5 mmol, 20%) of crude recovered *o*-cresol. Removal of solvent from the dried neutral fraction followed by distillation under reduced pressure gave 3.64 g (19.0 mmol, 76%) of 2,8-dimethyl-2-methoxychromane: bp 78–85° (*ca.* 1 mm); ir (CCl_4) shows no hydroxyl or carbonyl absorptions; nmr (CCl_4) δ 1.47 (s, 3 H), 1.6–2.1 (complex, 2 H), 2.16 (s, 3 H), 2.2–3.1 (complex, 2 H), 3.18 (s, 3 H), 6.5–7.0 (complex, 3 H).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.66; H, 8.34.

Registry No.—2-Methoxybutadiene, 3588-30-5; keto **2a**, 17790-69-1; enol **2a**, 17790-70-4; enol **2b**, 17790-71-5; **4b**, 17790-72-6; **6**, 17790,-73-7; **7**, 17790-74-8; **7** 2,4-dinitrophenylhydrazone, 17790-75-9; **8**, 17790-83-9; **9**, 17790-76-0; **10**, 17790-77-1; **14**, 17790-78-2; **17**, 17790-79-3; **18**, 17790-80-6; methyl 4-bromoacetoacetate, 17790-81-7; β-cyanopropionyl chloride, 17790-82-8.

(8) R. E. Strube, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 417.