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Molecular Rearrangements. An Interannular Acylation of Enol Esters

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Several enol esters of 2-benzylcyclohexane-1,3-diones (**5**) were treated with polyphosphoric acid (PPA). The reaction products were the aryl alkyl ketones (**6**). This constitutes a new acylation at aromatic carbon using enol esters as acylating agents, and also a novel molecular rearrangement comprising an interannular migration of the acyl group. The chemical and spectroscopic properties of these compounds, as well as that of other new compounds prepared in the synthetic sequence, are described. When **2b** was treated with cyclohexane-1,3-dione enol acetate in the presence of PPA, **6b** was obtained. Stereochemical considerations suggest the reaction mechanism as intermolecular.

Two of the most well-known organic reactions are the Friedel–Crafts acylation[1] and alkylation and its familiar Fries modification.[2] Acid catalysts are used in both reactions, polyphosphoric acid (PPA) being one that is gaining more adepts.[3] In the Fries rearrangement,[4] treatment of phenol esters with acid catalysts gives rise to 1,3 or 1,5 shifts of the acyl group, producing the *o*- or *p*-acylphenols.

In the present paper we wish to report the results obtained when some enol esters of 2-benzylcyclohexane-1,3-diones are treated with PPA. A rapid, general method for the preparation of enol esters was developed; it consists in the heating of the 1,3-diketone with excess anhydride and a catalytic amount of *p*-toluenesulfonic acid on the steam bath, followed by the high-vacuum distillation of the mixture. This allowed the recovery of the excess anhydride and avoided the hydrolysis of the labile enol esters.

In the cases under study the products obtained from the treatment of the esters with PPA resulted from the migration of the acyl group to the C-4 position of the aromatic ring (Scheme I: **5a** → **6a**, **5b** → **6b**, etc.).

The mentioned sequences appear to be the first reported on acylations of aromatic hydrocarbons by the action of aliphatic enol esters. At the same time they constitute the interesting case of an interannular 1,8 migration of the acyl group. Chemical and spectroscopic evidence of the mentioned structures is given below.

The simplest example of the sequence is the one starting with 2-benzylcyclohexane-1,3-dione (**2a**) which was obtained by the general method of Stetter and Klauke.[5]

A small amount of the 2,2-dibenzyl derivative (**3**) was also obtained in this experiment. It possesses a peculiar nmr spectrum, in which, for example, the C-5 methylene protons are found at a higher field (δ 0.83) than the usual for such protons (δ 2); this must be due to the shielding by the phenyl rings, as a result of the geometry in the molecule.[6]

The enol acetate of **2a** was prepared by its treatment with acetic anhydride and *p*-toluenesulfonic acid. The product **5a** shows in its ir spectrum the characteristic absorption bands for the vinyl ester (1750 cm^{-1}), the α,β-unsaturated carbonyl (1665 and 1645 cm^{-1}), and the monosubstituted benzene (690 cm^{-1}). In its nmr spectrum three singlets are observed at δ 2.06 (3 H), 3.48 (2 H), and 7.15 (5 H), corresponding successively to the acetate, the benzylic methylene, and the aromatic protons; the annular methylene groups exhibit a multiplet centered at δ 2.31 (6 H).

A crystalline product ($C_{15}H_{18}O_3$) could be isolated when this acetate (**5a**) was heated in the presence of PPA, and the reaction mixture was purified by chromatography. The acidic character of this substance, its positive ferric chloride test, and its ir spectrum (which shows bands at 3150 (broad), 1620 and 1630 cm^{-1}) indicated that this product is an isomer of **5a** containing the free enol grouping.

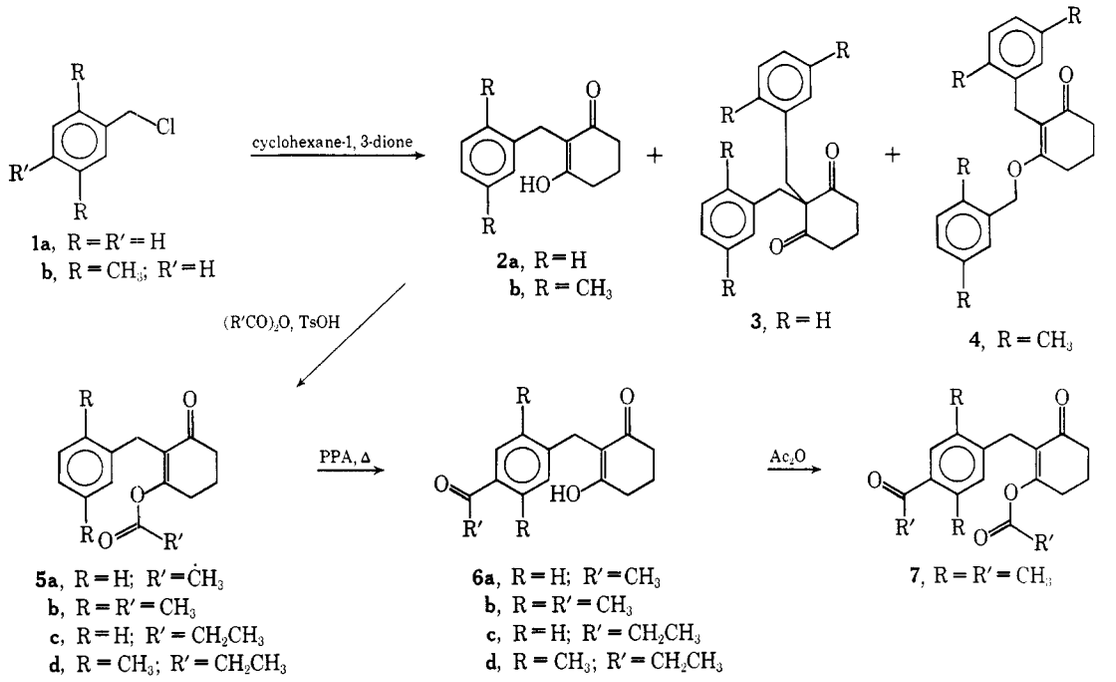
The fact that the acetyl group had migrated to the aromatic ring in this compound was deduced from its ir spectrum which exhibits a strong peak at 1670 cm^{-1} (Ar–CO) and lacks the band in the 700-cm^{-1} region. This group was assigned to C-4 position in the aromatic ring, based on the nmr spectrum which has a singlet at δ 2.54 (3 H) (due to the CH_3COAr) and two doublets at 7.33 (2 H, J = 8 cps) and 7.72 (2 H, J = 8 cps) (due to the aromatic protons); the shape and position of the doublets are in full agreement with the ABA′B′ aromatic system of a *p*-alkylacetophenone.[7] The other bands in the nmr spectrum, those due to the methylene protons of this compound (**6a**), appear as a quintet at δ 1.96 (2 H, J = 5.5 cps) (C-5), a triplet at 2.45 (4 H, J = 5.5 cps) (C-4 and C-6), and a singlet at 3.70 (benzylic methylene).

The propionic enol ester (**5c**) of the 2-benzylcyclohexane-1,3-dione was also prepared; all of these spectra are also in accord with its structure.

Transposition of the propionyl group by heating the ester with PPA gave the 2-(4-propionylbenzyl)cyclohexane-1,3-dione. Its spectroscopic behavior is very similar to that of the acetylbenzyl derivative (**6a**) and fully supports the proposed structure (**6c**).

(1) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 282.
(2) Reference 1, p 292.
(3) F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).
(4) P. de Mayo, "Molecular Rearrangements," Vol. I, Interscience Publishers, New York, N. Y., 1967, p 318.
(5) H. Stetter and E. Klauke, *Chem. Ber.*, **85**, 1065 (1952).
(6) E. Cortés and F. Walls, *Bol. Inst. Quim. Univ. Nacl. Auton. Mex.*, **17**, 165 (1965); H. A. P. de Jongh and H. Wynberg, *Tetrahedron*, **21**, 515 (1965).
(7) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "Varian High Resolution NMR Spectra Catalog," No. 188, Varian Associates, Palo Alto, Calif.; D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 121.

SCHEME I



1a, R = R' = H
b, R = CH3; R' = H

2a, R = H
b, R = CH3

3, R = H

4, R = CH3

5a, R = H; R' = CH3
b, R = R' = CH3
c, R = H; R' = CH2CH3
d, R = CH3; R' = CH2CH3

6a, R = H; R' = CH3
b, R = R' = CH3
c, R = H; R' = CH2CH3
d, R = CH3; R' = CH2CH3

7, R = R' = CH3

In this transposition experiment (from **5c**) as in the former one (from **5a**) no other product was obtained on treatment with PPA, but the yields were very low and a large amount of substrate was recovered (in the form of **2a** and not of the esters **5c** or **5a**, probably because of the hydrolytic conditions of the isolation procedure).

Based on the consideration that this acylation is an electrophilic substitution on the aromatic ring and so electron-donor groups must facilitate it, another series was found which gives much better yields. The series starts with the 2-(2,5-dimethylbenzyl)cyclohexane-1,3-dione (**2b**). It was prepared through the condensation of 2,5-dimethylbenzyl chloride (**1b**) with cyclohexane-1,3-dione.

A small amount of the 2,O-dibenzyl derivative **4** was produced in the reaction. The structure of this compound was easily deduced from the examination of its nmr spectrum; it resembles that of the monobenzyl derivative **2b** (see Table I) and indeed **4** may be transformed into **2b** by heating with diluted acid, as corresponds to the behavior of an enol ether.

The enol acetate of **2b** (**5b**) was prepared by the usual method. The strong, characteristic, enol-ester band appears in its ir spectrum at 1750 cm^{-1}. Its nmr spectrum exhibits in the aromatic region (δ 6.96) a signal with the familiar shape of the 1,2,4-trisubstituted benzene.

When **5b** was treated with PPA it was rearranged in a quantitative manner to **6b**, which has an acid character and gives a positive ferric chloride test.

The ir spectrum for **6b** confirms the proposed structure showing bands for its enolic 1,3-diketone at 3150 (broad), 1710 and 1600 cm^{-1}, for the aryl ketone at 1665 cm^{-1}, and for the 1,2,4,5-tetrasubstituted benzene at 870 cm^{-1}. In its nmr spectrum the aromatic methyl, acetyl, and benzylic methylene protons appear as singlets, respectively, at δ 2.33, 2.42, 2.53, and 3.56; the annular methylene protons are shown as a complex signal centered at δ 2.28. The peaks corresponding to the aromatic protons are seen as two well-separated singlets at δ 6.87 and 7.47, as is expected for two isolated protons in different electronic environments. This evidence permits an assignment of the 4 position in the aromatic ring to the migrated acyl group. The compound **6b** gives an enol acetate (**7**) and a 2,4-dinitrophenylhydrazone.

In a similar way the enol propionate of **2b** (**5d**) was obtained. It underwent the aforementioned rearrangement to give the 4-acetyl derivative **6d** whose structure was derived from its chemical and spectroscopic properties. Its nmr, for example, is very similar to that of the 4-acetyl derivative **6b** (see Table I).

The examination of models permits one to see that in the conformations of **5** the acyl carbon atom lies near the C-2 aromatic carbon and not as near the C-3 or C-4 positions. If the reaction mechanism were intramolecular, the C-2 acyl derivatives should have been obtained. The fact that we obtained only the C-4 acyl compounds led us to think that the mechanism here is intermolecular. A further experiment was carried out in connection with this; the nonacetylated compound **2b** was treated with cyclohexane-1,3-dione enol acetate in the presence of PPA, giving a good yield of **6b**; this result also suggests the mechanism of the reaction as being intermolecular, although it does not exclude the possibility of the production of **6b** intramolecularly through an initial ester-exchange reaction before the final acylation.

Further studies on mechanistic aspects of the reaction are in progress.

Experimental Section

Melting points are uncorrected. Ir spectra were run in chloroform solution on a Beckman IR-8 spectrophotometer. Uv spectra were determined in ethanol solution on a Unicam SP-800 spectrophotometer. Nmr (Table I) and mass spectra were determined, respectively, on a Varian A-60A spectrometer and on a double-focusing Hitachi-Perkin-Elmer RMU-6D spectrometer. The microanalyses were performed by Dr. Franz Pascher, Bonn, Germany, and by Schwarzkopf Microanalytical Labs, Woodside,

TABLE I
NMR SPECTRA OF BENZYLCYCLOHEXANEDIONE DERIVATIVES[a]

Compd	δ, ppm					
	CH_3–Ar	Cyclic CH_2	R'COO	R'CO–Ar	Benzyl CH_2	H–Ar
2a[b]		2.04 (qn, 2, *J* 6), 2.42 (t, 4, *J* 6)			3.60 (s, 2)	7.18 (s, 5)
2b	2.30 (s, 6)	2.23 (m, 6)			3.64 (s, 2)	6.93 (m, 3)
3		0.83 (qn, 2, *J* 6), 1.87 (t, 4, *J* 6)			3.25 (s, 4)	7.15 (m, 10)
4	2.18 (s, 6), 2.24 (s, 6)	2.15 (m, 6)			3.61 (s, 2), 5.02 (s, 2)	7.00 (m, 6)
5a		2.31 (m, 6)	2.06 (s, 3)		3.48 (s, 2)	7.15 (s, 5)
5b	2.24 (s, 6)	2.34 (m, 6)	1.98 (s, 3)		3.52 (s, 2)	6.96 (m, 3)
5c		2.26 (m, 6)	1.12 (t, 3, *J* 7), 2.41 (q, 2, *J* 7)		3.53 (s, 2)	7.18 (s, 5)
5d	2.23 (s, 6)	2.31 (m, 6)	1.99 (t, 3, *J* 7), 2.17 (q, 2, *J* 7)		3.43 (s, 2)	6.48 (m, 3)
6a		1.93 (qn, 2, *J* 6), 2.45 (t, 4, *J* 6)		2.54 (s, 3)	3.70 (s, 2)	7.33 (d, 2, *J* 8), 7.72 (d, 2, *J* 8)
6b	2.33 (s, 3), 2.42 (s, 3)	2.28 (m, 6)		2.53 (s, 3)	3.56 (s, 2)	6.87 (s, 1), 7.47 (s, 1)
6c		1.97 (qn, 2, *J* 6), 2.50 (t, 4, *J* 6)		1.23 (t, 3, *J* 7), 2.98 (q, 2, *J* 7)	3.75 (s, 2)	7.34 (d, 2, *J* 8), 7.87 (d, 2, *J* 8)
6d[b]	2.33 (s, 3), 2.36 (s, 3)	2.25 (m, 6)		1.10 (t, 3, *J* 7), 2.90 (q, 2, *J* 7)	3.57 (s, 2)	6.93 (s, 1), 7.50 (s, 1)
7	2.34 (s, 3), 2.48 (s, 3)	2.42 (m, 6)	2.17 (s, 3)	2.56 (s, 3)	3.57 (s, 2)	6.90 (s, 1), 7.52 (s, 1)

[a] TMS was the internal standard. Coupling constants (*J*) are given in Hz; s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet; chloroform solutions were used unless otherwise specified. The signal of the hydroxylic proton suffers variation in its form and position and sometimes is lost in the noise. [b] In acetone solution.

N. Y. Aluminum oxide standarized Merck (Brockmann grade I–II), was used for chromatographic columns.

2-Benzylcyclohexane-1,3-dione (2a) and 2,2-Dibenzylcyclohexane-1,3-dione (3).—Using the method of Stetter and Klauke,[5] and starting with 11.5 g of cyclohexane-1,3-dione, 14 g of **2a** (mp 185°) was obtained; ir, 3200 broad (enol OH), 1700 (keto form C=O), 1610 (conj C=O and C=C), 695 cm^{-1} (monosubstituted benzene).

The neutral product on the above reaction was extracted with ether from the alkaline aqueous solution. The residue after drying (Na_2SO_4) and evaporation of the ether extracts was recrystallized from ethanol giving 5 g of **3**: mp 141–142°; ir, 1708 and 1682 (keto form C=O), 1600, 1572, 1490, 1450, and 695 cm^{-1} (monosubstituted benzene); uv max, 204 mμ (ε 11,403), 260 (269), and 295 (116).

2-Benzylcyclohex-2-en-3-ol-1-one Acetate (5a).—A solution of 4 g of 2-benzylcyclohexane-1,3-dione (**2a**) and 280 mg of *p*-toluenesulfonic acid in acetic anhydride (36 ml) was heated for 1 hr. Vacuum distillation afforded 3 g of the acetate (**5a**): bp 178–183° (7 mm); ir, 1750 (ester C=O), 1665 and 1645 (conj C=O and C=C), 690 cm^{-1} (monosubstituted benzene); uv max, 207 (ε 9549), 217 infl (8661), 238 (7440).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; O, 19.65. Found: C, 73.78; H, 6.89; O, 19.95.

2-(4-Acetylbenzyl)cyclohexane-1,3-dione (6a).—The general method used for the rearrangement reaction was as follows.[3] An intimate mixture of the enol ester with an excess of PPA[8] (ten times its weight) was heated in a closed vessel, with ocassional stirring, on the steam bath, until a deep red color was developed. An excess of ice and water, ten times the weight of PPA, was added with stirring to allow the hydrolysis of the excess acid. A precipitate appeared which was worked up as indicated.

A mixture of 2 g of the acetate (**5a**) and PPA was heated for 45 min. The precipitate which appeared after the hydrolysis of the acid was extracted with chloroform. The chloroform solution was dried (Na_2SO_4), concentrated (to approximately 100 ml) and chromatographed on a column of alumina (40 g). The first fractions, eluted with chloroform, contained the recovered benzyl derivative **2a**, 1.5 g. The 4-acetyl derivative **6a** was collected on the remaining fractions, eluted with acetone. It was recrystallized from acetone–ether, acetone–cyclohexane, and then from methanol–water (0.15 g, mp 178°); ir, 3150 broad (enol OH), 1700 sh (keto form C=O), 1670 (aryl ketone C=O), 1620 sh and 1600 cm^{-1} (conj C=O and C=C); uv max, 205 mμ (ε 39,080), 260 (53,740); uv min, 225 mμ (ε 11,327).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.75; H, 6.60; O, 19.65. Found: C, 73.85; H, 6.44; O, 19.79.

2-Benzylcyclohex-2-en-3-ol-1-one Propionate (5c).—To a solution of 20 g of **2a** in 90 ml of warm propionic anhydride, 1.4 g of *p*-toluenesulfonic acid was added. After heating the mixture for 2 hr, vacuum distillation afforded 25 g of the ester **5c**, a pale yellow liquid [bp 168° (7 mm)] which crystallized on cooling to give a colorless solid: mp 35–39°; ir, 1750 (ester C=O), 1665 and 1645 (conj C=O and C=C), 690 and 660 cm^{-1} (monosubstituted benzene); uv max, 207 mμ (ε 12,398), 230 infl (8394), 243 (9169); mass spectrum (70 eV), *m/e* (relative intensity) 258 (1.2), 202 (17.3), 91 (11.8), 57 (100), 29 (58.3).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02; O, 18.58. Found: C, 74.14; H, 7.19; O, 18.47.

2-(4-Propionylbenzyl)cyclohexane-1,3-dione (6c).—A mixture of 5 g of propionate **5c** and PPA was heated for 45 min. After the addition of ice and water the mixture was extracted with chloroform. The organic extracts were washed with water and evaporated to dryness. The solid yellow residue (4 g) was dissolved in benzene (40 g) and chromatographed on alumina (100 g); 2-benzylcyclohexane-1,3-dione (**2a**) (3.5 g) was recovered in the first fractions, eluted with benzene and chloroform. Rearranged product **6c** was collected in the fractions eluted with acetone (evaporated at room temperature). The product was recrystallized from acetone–ether, giving 165 mg; mp 167–172°; ir, 3150 broad (enol OH), 1700 (keto form C=O), 1670 (aryl ketone C=O), 1620 sh and 1600 cm^{-1} (conj C=O and C=C); uv max, 205 mμ (ε 18,855), 260 (25,313); uv min, 225 mμ (ε 5940); mass spectrum (70 eV), *m/e* (relative intensity) 258 (7.4) 229 (34.4), 55 (45.9), 43 (100), 28 (50).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02; O, 18.58. Found: C, 74.13; H, 7.21; O, 18.74.

2-(2,5-Dimethylbenzyl)cyclohexane-1,3-dione (2b).—To a solution of 3.3 g (0.03 mol) of cyclohexane-1,3-dione in 7 ml of 20% aqueous potassium hydroxide, 4.6 ml (0.03 mol) of 2,5-dimethylbenzyl chloride[9] (**1b**) and 0.3 g of potassium iodide were added; the stirred mixture was kept 1 hr on the steam bath and then cooled at room temperature. Potassium hydroxide (10%, 200 ml) was added to dissolve the solid formed. The aqueous solution was extracted with ether and acidified with hydrochloric acid to pH 4. The precipitate was filtered off under vacuum and

(8) Polyphosphoric acid, Matheson Coleman & Bell (approximately $H_6P_4O_{13}$), was used for the majority of the experiments.

(9) J. C. Bardhan and S. C. Sengupta, *J. Chem. Soc.*, 2525 (1932).

recrystallized from methanol–water yielding 3.0 g of the product **2b**: mp 171°; ir, 3400 broad (enol OH), 1740 and 1710 (keto form C=O), 1610 cm^{-1} (conj C=O and C=C); uv max, 204 mμ (ε 18,884), 263 (15,314); uv min, 233 mμ (ε 3799).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88; O, 13.90. Found: C, 77.98; H, 7.80; O, 13.71.

2-(2,5-Dimethylbenzyl)-3-(2,5-dimethylbenzyloxy)cyclohex-2-en-1-one (4).—The ether extracts from the above reaction were washed with water, dried (Na_2SO_4), and evaporated, giving a solid (670 mg, mp 133°) which was recrystallized from ethanol to obtain the analytical sample of **4** (mp 136°): ir, 1630 and 1600 (α,β-unsat C=O), 880 and 805 cm^{-1} (1,2,4-trisubstituted benzene); uv max, 204 mμ (ε 27,183), 269 (18,953); uv min, 234 mμ (ε 3833).

Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10; O, 9.18. Found: C, 82.43; H, 8.40; O, 9.36.

4 (15 mg) was refluxed with 7 ml of 10% hydrochloric acid and then filtered. The reaction product **2b** was purified (extraction with 10% KOH) obtaining 5 mg, mp 170°. Its ir spectrum was superimposable with that of the condensation product.

2-(2,5-Dimethylbenzyl)cyclohex-2-en-3-ol-1-one Acetate (5b).—A solution of 15 g of **2b** and 800 mg of *p*-toluenesulfonic acid in 40 ml of acetic anhydride was heated at the steam bath for 35 min; the solution was allowed to reach the room temperature and poured into 500 ml of water. The white crowded needles (17 g) of the acetate (**5b**), melting at 70°, were filtered and dried under vacuum. Recrystallization from ether–hexane led to the analytical sample: mp 70°; ir, 1750 (ester C=O), 1665 and 1645 (conj C=O and C=C), 900 and 810 cm^{-1} (1,2,4-trisubstituted benzene); uv max, 203 mμ (ε 15,657), 218 infl (11,164), 238 (9122).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; O, 17.63. Found: C, 75.02; H, 7.03; O, 18.08.

2-(4-Acetyl-2,5-dimethylbenzyl)cyclohexane-1,3-dione (6b). (a) **From 5b.**—A mixture of 15 g of the acetate **5b** with PPA was heated for 30 min. After the addition of ice and water a beige precipitate (mp 140°) appeared, which was extracted with chloroform. The organic layer was washed with water, dried ($CaCl_2$), and evaporated to a small volume (70 ml). On cooling, the product **6b** crystallized (quantitative yield, mp 183°). Its analytical sample was prepared by crystallization from chloroform (needles mp 186°); ir, 3250 broad (enol OH), 1700 (keto form C=O), 1665 (aryl ketone C=O), 1610 cm^{-1} (conj C=O and C=C), this band was shifted to 1550 cm^{-1} in the KBr pellet spectrum; uv max, 213 mμ (ε 26,866), 262 (27,593); uv min, 232 mμ (ε 8532).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; O, 17.62. Found: C, 74.48; H, 7.60; O, 17.59.

(b) **From 2b.**—Cyclohexane-1,3-dione (mp 105°) was obtained by the Thompson method[10] and transformed into its enol acetate [bp 95° (1 mm)] by the general procedure described above. A mixture of 1.54 g of this acetate, 2.3 g of **2b**, and 50 g of PPA was heated for 1 hr, poured over water, and extracted. The chloroform extracts (dried and concentrated) were chromatographed over 60 g of alumina. In the first fractions eluted with chloroform (2–5), cyclohexane-1,3-dione was recovered (1.1 g, mp 103°). In the latter with the same eluent (8–18) **6b** (1.8 g, mp 171°) was obtained; mixture melting point and ir spectrum were indistinguishable from that of the compound obtained from **5b**. By the usual methods the enol acetate **7** (mp 80°) and the 2,4-dinitrophenylhydrazone (mp 260°) of **6b** were prepared.

2-(2,5-Dimethylbenzyl)cyclohex-2-en-3-ol-1-one Propionate (5d).—A solution of 5 g of 2-(2,5-dimethylbenzyl)cyclohexane-1,3-dione (**2b**) and 500 mg of *p*-toluenesulfonic acid in 50 ml of propionic anhydride was heated for 40 min. On vacuum distillation, 6 g of the propionate **5d** [bp 170° (7 mm)] was obtained; ir, 1750 (ester C=O), 1665 and 1640 (conj C=O and C=C), 880 and 810 cm^{-1} (1,2,4- trisubstituted benzene); uv max, 203 mμ (ε 17,184), 218 infl (12,819), 239 (10,637).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74; O, 16.76. Found: C, 75.66; H, 7.82; O, 16.52.

2-(4-Propionyl-2,5-dimethylbenzyl)cyclohexane-1,3-dione (6d).—A mixture of the propionate **5d** (5 g) with PPA was heated for 1 hr. After the hydrolysis of the excess acid the mixture was extracted with chloroform. The extracts were dried ($CaCl_2$), concentrated, and chromatographed over alumina (60 g). Chloroform eluted from the column the unreacted compound (as **2b**). The propionyl derivative (**6d**, 1 g) was collected in the fractions eluted with acetone (concentrated at room temperature). Recrystallization from acetone–ether gave 350 mg (mp 180–182°); ir, 3200 broad (enol OH), 1700 (keto form C=O), 1665 (aryl ketone C=O), 1610 cm^{-1} (conj C=O and C=C); uv max, 213 mμ (ε 22,339), 261 (22,052); uv min, 232 mμ (ε 6587).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74; O, 16.76. Found: C, 75.26; H, 8.15; O, 16.37.

Registry No.—**2a**, 19755-60-3; **2b**, 19755-61-4; **3**, 739-03-7; **4**, 19755-63-6; **5a**, 19755-64-7; **5b**, 19755-65-8; **5c**, 19755-66-9; **5d**, 19755-67-0; **6a**, 19755-68-1; **6b**, 19755-75-0; **6c**, 19779-36-3; **6d**, 19755-76-1; **7**, 19755-77-2.

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(10) R. B. Thompson, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 278; the commercial Aldrich product, stabilized with sodium chloride, was also used for the condensations.