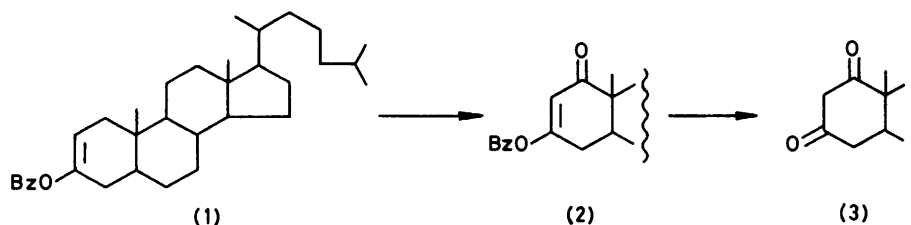


## Sodium Chromate Oxidation of Enol Benzoates. Allylic Oxidation *versus* a Novel Rearrangement

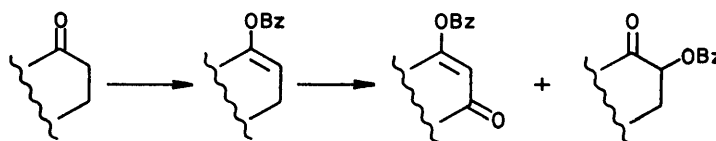
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Various enol benzoates were oxidized with sodium chromate in acetic acid and acetic anhydride. Allylic oxidation (leading to 1-benzoyloxy-3-oxoalk-1-enes) and a novel oxidative rearrangement (leading to  $\alpha$ -benzoyloxy-ketones) in varying yields were the major reactions observed. The implications of these findings are discussed.

WE recently reported<sup>1</sup> that the reaction of some alicyclic enol benzoates on treatment with sodium chromate led to products formed by allylic oxidation. Thus, the enol benzoate of 5 $\alpha$ -cholestan-3-one (1) gave 1-oxo-5 $\alpha$ -cholest-2-en-3-yl benzoate (2); on hydrolysis 5 $\alpha$ -cholestane-1,3-dione (3) was obtained (Scheme 1). This oxidation follows a path different than that of most oxidations of enol esters, which take place on the double bond itself rather than on one of its allylic positions.<sup>2</sup> As this procedure represents a new route for the production of cyclic 1,3-diketones from cyclic monoketones, its scope was investigated.



SCHEME 1



SCHEME 2

We report now that we have applied the above reaction to several types of cyclic enol benzoates. In addition to the allylic oxidation previously found, a rearrangement to an  $\alpha$ -benzoyloxy-ketone was also observed in most cases (see Scheme 2). Such a rearrangement has not been previously reported. The yields and ratios of the allylic oxidation products and the rearranged ones were found to vary greatly, and to depend, apparently, both on steric and electronic factors.

The enol benzoates used in the present study were usually prepared by either boiling the ketone with benzoyl chloride in the inert solvent (method A),<sup>3a,b</sup> or by boiling the corresponding ketone with isopropenyl benzoate in the presence of sulphuric acid (method B).<sup>3b</sup> Method A led, in a few cases, to a reaction mixture in which the separation between the desired product and

benzoic anhydride formed in the reaction was difficult. In these and several other cases a two-step route (method C) was followed. The ketone was first converted into a silyl enol ether,<sup>4</sup> which on heating with benzoyl chloride in the presence of mercury(II) chloride gave the desired enol benzoate.<sup>5</sup> Method C gives better overall yields than methods A and B although it is a two-step one.

The oxidation conditions were identical to those reported previously,<sup>1</sup> namely sodium chromate (in two-fold excess) in acetic acid, acetic anhydride, and carbon tetrachloride. Although we tried to improve the total

yield by choosing other oxidation conditions, none were found. The neutral products of the oxidation were separated by chromatography. The enol benzoates oxidized and the products obtained are given in the Table.

Stereoelectronic factors obviously play an important role in the above reactions. Thus, the enol benzoate of cyclohexanone (4) led mostly to the allylic oxidation product (5) (50%), while only 15% of the rearranged product (6) was isolated; in the case of the enol ester of cycloheptanone (7) the major product was the rearranged one (9); that of cyclopentanone (10) gave both products (11) and (12) in low yield; that of cyclobutanone (13) gave only the rearranged product (14). As cyclopentenones and cyclobutenones represent energetically

<sup>1</sup> R. Mechoulam, K. Luchter, and A. Goldblum, *Synthesis*, 1974, 363.

<sup>2</sup> W. S. Johnson, B. Gastambide, and R. Pappo, *J. Amer. Chem. Soc.*, 1957, **79**, 1991; T. Nambara and J. Fishman, *J. Org. Chem.*, 1962, **27**, 2131; E. J. Bailey, J. Elks, and D. H. R. Barton, *Proc. Chem. Soc.*, 1960, 215.

<sup>3</sup> (a) L. Ruzicka and W. H. Fischer, *Helv. Chim. Acta*, 1936, **19**, 1371; (b) M. Gorodetsky and Y. Mazur, *Tetrahedron*, 1966, **22**, 3607.

<sup>4</sup> H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 1969, **34**, 2324.

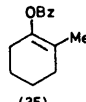
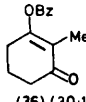
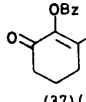
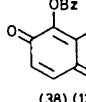
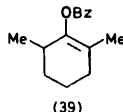
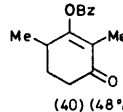
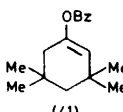
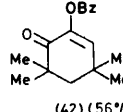
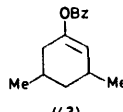
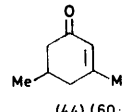
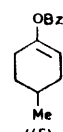
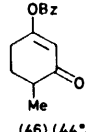
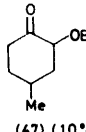
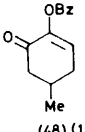
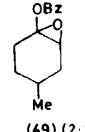
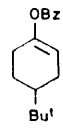
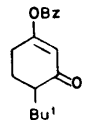
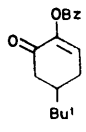
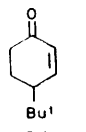
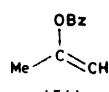
<sup>5</sup> E. N. Kramarova, Y. I. Baukov, and I. V. Lutsenko, *Zhur. obshchei Khim.*, 1973, **43**, 1857.

richer systems than cyclohexenones one can, perhaps, rationalize the yields of the reaction products of (4), (10), and (13) on this basis. However such a relationship is not obvious in the case of the seven-membered enone (8) compared with the six-membered enone (5).

With different enol esters of cyclohexanone the yields of the allylic ketones vary considerably. The yield is highest (50%) in the case of the enol benzoate (4), lower (35%) in the case of the enol cyclohexanoate (15) and lowest (14%) with the *p*-nitrobenzoate (18). In the last

Oxidation of enol esters with sodium chromate <sup>a</sup>

Enol ester	Method of preparation of enol ester <sup>b</sup> (yield)	Oxidation products <sup>b</sup> (yield)
 (4) <sup>f</sup>	B (30%) C (35%)  (5) (50%)	 (6) (15%)
 (7)	B (50%)  (8) (20%)	 (9) (45%)
 (10)	A (32%) B (35%) C (30%)  (11) (10%)	 (12) (13%)
 (13)	B (2.5%)  (14) (10%)	 (14) (10%)
 (15)	A (27%)  (16) (35%)	 (17) (24%)
 (18)	A (15%)  (19a) (14%)	 (19b) (12.4%)
	 (20a) (10.1%)	 (20b) (22%)
 (21)	A (70%) B (40%)  (22) (38%)	 (23a) (19.5%)
	 (23b) (8%)	
 (24)	B (30%)  (25) (40%)	 (26) (50%)
 (27)	A (30%) C (30%)  (28) (45%)	 (29) (47%)
 (30)	A (54%)  (31) (27.7%)	 (32) (37.3%)
	 (33) (12.2%)	 (34) (4.3%)

Enol ester	Method of preparation of enol ester <sup>b</sup> (yield)	Oxidation products <sup>b</sup> (yield)			
 (35)	B (31%)	 (36) (30.1%)	 (37) (17.5%)	 (38) (12.3%)	
 (39)	A (36%)		 (40) (48%)		
 (41)	A (46%)		 (42) (56%)		
 (43)	A (25%) C (50%)		 (44) (60.2%)		
 (45)	A (11%)	 (46) (44%)	 (47) (10%)	 (48) (14.5%)	 (49) (2.2%)
 (50)	A (24%) C (40%)	 (51) (18.6%)	 (52) (31%)	 (53) (21%)	
 (54)	C (48%)	No products identified			

<sup>a</sup> Exact experimental conditions of the reactions as well as physical constants and analyses of all new substances are given in the Experimental section. <sup>b</sup> Method A: benzoyl chloride; method B: isopropenyl benzoate-sulphuric acid; method C: benzoyl chloride-mercury(II) chloride on the silyl enol ether. For details see Experimental section. <sup>c</sup> The oxidation of this compound was described previously.<sup>1</sup> However, on reinvestigation the presence of the rearranged product was observed and the yields were improved.

case it is accompanied by the isomeric oxidation product (19b). In the three cases of aromatic enol benzoates examined, *i.e.* (21), (24), and (27), the yields of the rearranged products are relatively high, but these consist not only of the respective  $\alpha$ -benzoyloxy-ketones (22), (25), and (28), but also of the respective  $\alpha$ -acetoxy-ketones (23a), (26), and (29).  $\alpha$ -Acetoxy-ketones were not observed in reactions of non-aromatic enol benzoates.

The  $\alpha$ -acetoxy-ketones formed in the aromatic series are not the products of an attack of an acetoxy-entity on the  $\alpha$ -benzoyloxy-ketone already formed in the reaction. This was indicated by the attempted reaction of  $\alpha$ -benzoyloxyacetophenone (28) with sodium chromate, acetic acid, and acetic anhydride under the standard

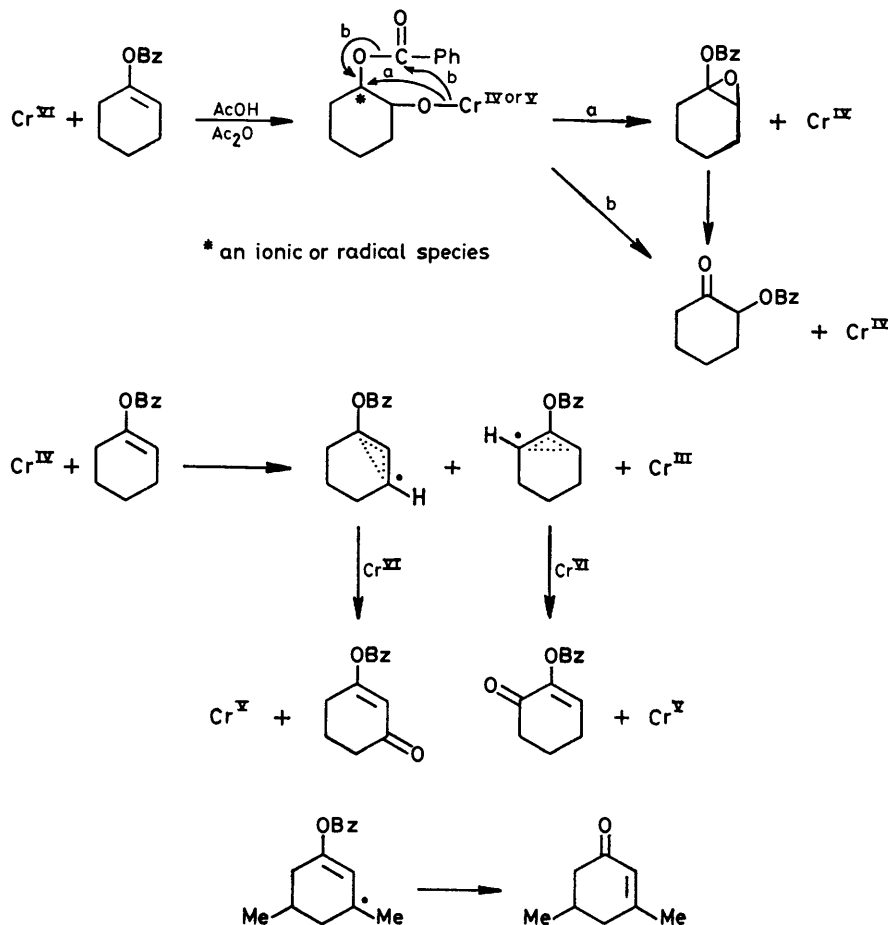
reaction conditions which gave only unchanged starting material.

Alkyl or aryl substituents on the double bond of the enol or on other positions of the alicyclic ring influence the course of the reaction. Thus, 2-phenylcyclohex-1-enyl benzoate (30) gave no rearranged products, but oxidation took place on both allylic positions around the double bond giving the ketones (31) and (32). Oxidation of 2-methylcyclohex-1-enyl benzoate (35) followed essentially the same route giving both allylic ketones (36) and (37). Likewise, no rearrangement products were observed when the ring was substituted by methyl groups on both the 2- and 6-positions, as in compound (39). The only product isolated was the allylic ketone (40).

When one of the allylic positions is fully blocked, as in compound (41), exclusive oxidation at the alternative allylic position takes place giving (42). Partial blocking of one of the allylic positions, as in (43), allows preferential oxidation at C-3 leading exclusively to the ketone (44). Similar, though non-exclusive oxidation, following this path were recorded above [*cf.* compounds (33), (34), and (38)]. The absence of rearranged products in the oxidation of (41) and (43) is unexpected. It may be due,

compound of the latter type, ketone (52), is the main product in the oxidation of the *t*-butyl homologue (50). In this reaction no rearrangement product was isolated. Also the product of oxidation at C-3, ketone (51), is formed in considerably lower yield than the corresponding ketone (46) obtained on oxidation of (45). The alternative oxidation path, mentioned above, leading to 4-*t*-butylcyclohex-2-en-1-one (53) was also followed.

A tentative scheme basically following that proposed



SCHEME 3

in the case of (41), to steric hindrance and, in the case of (43), to the ease of formation of a radical species at C-3 leading to compound (44).

In the cyclohexane series the influence of an alkyl substituent on C-4 on the product composition depends on the nature of the substituent. The presence of a *para*-methyl group [as in compound (45)] leads to a ratio (and absolute amounts) of allylic oxidation product (46) to rearrangement product (47) essentially as in the unsubstituted starting material (4). However, some oxidation also takes place on C-6 leading to (48). A

<sup>6</sup> P. Muller and J. Roček, *J. Amer. Chem. Soc.*, 1974, **96**, 2836.

<sup>7</sup> J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, 1968, **90**, 2986.

<sup>8</sup> W. J. Hickinbottom, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 1955, 1360; M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 1958, 2205.

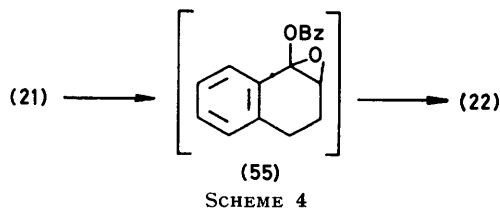
by Roček<sup>6,7</sup> would explain, at least formally, most of our results (Scheme 3).

The mechanism of the rearrangement is as yet obscure. One can postulate the existence of epoxide intermediates or their suggested<sup>8</sup> carbocation precursors. While sodium chromate is not generally considered an epoxidizing reagent, there are cases described in the literature in which isolable epoxides are formed on oxidation with Cr(VI) species.<sup>9</sup> In one case [the oxidation of (45)] we were indeed able to isolate, in a minute yield, the corresponding epoxide (49). The rearrangement of ester epoxides to  $\alpha$ -acyloxy-ketones is known.<sup>10</sup> Some

<sup>9</sup> H. O. House, 'Modern Synthetic Reactions,' Benjamin, Menlo Park, 1972, 2nd edn., pp. 281—283.

<sup>10</sup> R. N. McDonald in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1971, vol. 3, pp. 67—107.

support for the epoxide route was found when, in an attempt to prepare 1,2-epoxy-1-benzoyloxytetrahydronaphthalene (55) from the enol benzoate of  $\alpha$ -tetralone (21) by epoxidation with *m*-chloroperbenzoic acid, the only compound isolated (in 85% yield) was the rearrangement product (22) (Scheme 4).\*

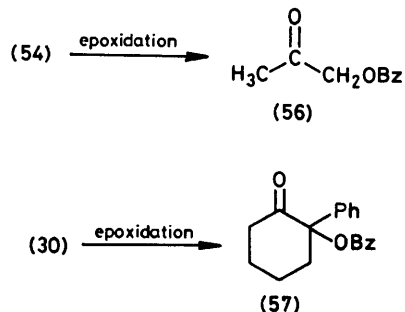


SCHEME 4

By contrast epoxidation of the enol benzoates of acetone (54) and of 2-phenylcyclohexanone (30) yielded the rearranged products (56) and (57) respectively (Scheme 5),† which were not obtained in the oxidation with sodium chromate.

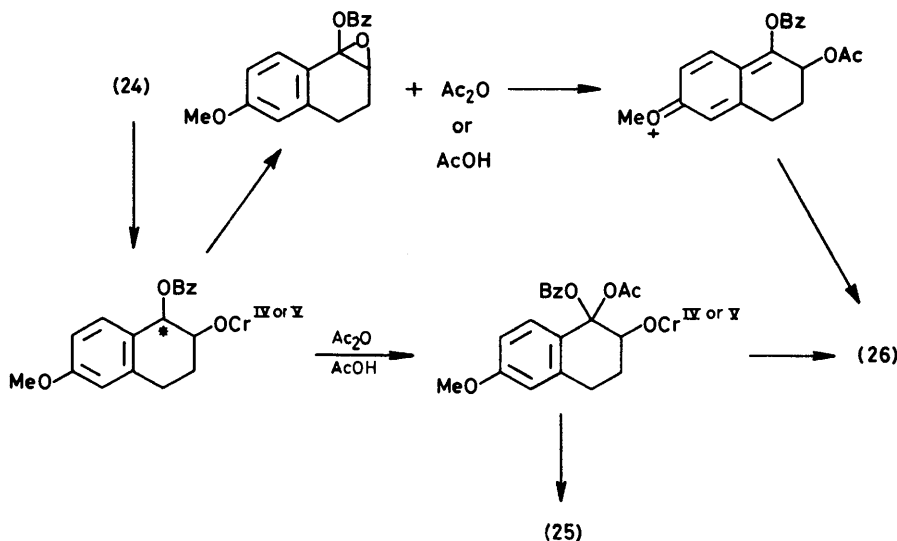
If epoxidation by  $\text{Cr}^{\text{VI}}$  is an electrophilic reaction, as is usually assumed,<sup>8</sup> one would have expected epoxide formation to be facilitated in the case of the alkyl- and aryl-substituted enol benzoates (36), (35), and (39).

One can then formulate the direct formation of rearranged products by the pathways depicted in Schemes 3 and 6 *via* homolytic bond cleavage processes.



SCHEME 5

The formation of  $\alpha$ -acetoxy-ketones (in addition to the  $\alpha$ -benzoyloxy-ketones) in the case of the aromatic enol benzoates can be explained by either an epoxide or a radical mechanism (Scheme 6). In the alicyclic series pathways analogous to those depicted in Scheme 6 are difficult to visualize; indeed no  $\alpha$ -acetoxy-ketones are observed in this series.



SCHEME 6 \* Ionic or radical species

However, no rearrangement (or other evidence of epoxide formation) was noted in these reactions. We tentatively assume therefore that the oxidation at the double bond does not proceed through an epoxide, but through an one-electron transfer to form a radical.<sup>12,13</sup>

\* This reaction represents a simple, high yield modification of a known route to  $\alpha$ -acyloxy-ketones and is being further investigated. The relevant cases described in the literature<sup>10</sup> usually require isolation of the epoxide intermediate, which is then rearranged, under rather drastic conditions. In those cases in which the epoxide was not isolated<sup>11</sup> the yields reported were not high. In our case, the reaction is a direct, high yield one, under mild conditions.

† The experimental details of the epoxidation of compounds (21), (30), and (54) will be described in a separate paper dealing with epoxidation of enol benzoates.

#### EXPERIMENTAL

Unless otherwise stated the following apply. Mass spectra were recorded on a Varian CH-5 instrument at 70 eV. I.r. spectra were recorded for solutions in carbon tetrachloride. U.v. spectra were taken for solutions in ethanol.  $^1\text{H}$  N.m.r. spectra were determined at 60 MHz on Varian T-60, Varian M-360, or high resolution JEOL C 60 H instruments. M.p.s are uncorrected. Column chromatography was done by the dry column method: reaction mixtures to be chromatographed were dissolved in ethyl acetate or chloroform, a quadruple amount of silica

<sup>11</sup> Cf. P. D. Gardner, *J. Amer. Chem. Soc.*, 1956, **78**, 3421.

<sup>12</sup> Ref. 9, p. 281.

<sup>13</sup> J. Roček, personal communication, has suggested the formation of a radical on addition of  $\text{Cr}^{\text{IV}}$  to a double bond.

gel was added and the slurry was evaporated in vacuum to dryness. This mixture was placed over a column of deactivated silica gel for dry column chromatography. The ratio between the silica gel and the organic material was 100 : 1. The silica gel for dry column chromatography was prepared by mixing commercial silica gel (Merck, Woelm, or Hopkin and Williams) with the eluant (ratio of silica gel to eluant 3 : 1). The eluant was determined by t.l.c., being the solvent mixture needed to bring the least polar compound in the organic mixture to a position of  $R_F$  0.5.

All ketones used for the preparation of enol esters were obtained from commercial sources and were purified by distillation or crystallization. A few of the enol esters were purified by chromatography alone and without being brought to analytical purity were used directly for oxidation.

*Preparation of Enol Benzoates.—Method A.* 3,3,5,5-Tetramethylcyclohexanone (7.7 g, 0.05 mol) and benzoyl chloride (7.02 g, 0.05 mol) were refluxed in light petroleum (b.p. 100—120°) (50 ml). The course of the reaction was followed by t.l.c. and g.l.c. After 48 h the reaction mixture was mixed with ether (250 ml). Pyridine was added until no further turbidity was observed, and the organic layer was washed several times with cold 10% hydrochloric acid solution, then with water, saturated aqueous sodium hydrogen carbonate, and saturated sodium chloride solution, dried, and evaporated. The resulting oil (12 g) was purified by chromatography. Elution with 30% ethyl acetate–light petroleum gave 3,3,5,5-tetramethylcyclohex-1-enyl benzoate (41) (6 g, 46%), an oil,  $\lambda_{\max}$  232 nm ( $\epsilon$  10 230),  $\nu_{\max}$  1 742, 1 263, 1 114, and 706  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.08 (6 H, s), 1.1 (6 H, s, allylic  $\text{CH}_3$ ), 1.38 (2 H, s), 2.0 (2 H, t,  $J$  1.9 Hz), 5.15 (1 H, t,  $J$  1.9 Hz), 7.15—7.5 (3 H, m), and 7.83—8.1 (2 H, m),  $m/e$  258 ( $M^+$ , 3%), 243 (6), 136 (2), 121 (1), and 105 (100) (Found: C, 79.25; H, 8.65.  $\text{C}_{17}\text{H}_{22}\text{O}_2$  requires C, 79.05; H, 8.55%).

*Method B.* 2-Methylcyclohexanone (3.2 g, 0.029 mol) and isopropenyl benzoate<sup>14</sup> (4.7 g, 0.029 mol) were heated for 24 h at 160° in the presence of concentrated sulphuric acid (2 drops). The mixture was mixed with ether (100 ml) and washed successively with saturated aqueous sodium hydrogen carbonate, water, and saturated sodium chloride solution, dried, and evaporated. The starting materials were distilled off under reduced pressure, and the resulting dark oil (3.8 g) was chromatographed on a dry column with 15% ethyl acetate in light petroleum as eluant. 2-Methylcyclohex-1-enyl benzoate (35)<sup>3b</sup> (1.9 g, 31%), an oil, was obtained,  $\nu_{\max}$  1 730, 1 278, 1 266, 1 138, 1 115, and 710  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.58br (3 H, s), 1.62—1.92 (4 H, m), 1.92—2.4 (4 H, m, allylic), 7.27—7.62 (3 H, m), and 7.87—8.22 (2 H, m).

*Method C.*<sup>5</sup> A mixture of  $\alpha$ -(trimethylsilyloxy)styrene<sup>4</sup> (10 g, 0.052 mol), benzoyl chloride (7.3 g, 0.052 mol), and mercury(II) chloride (400 mg, 1.5 mmol) was stirred and heated at 75° for 2 h. Equilibration between water and ether was followed by addition of pyridine to the organic layer until no more turbidity was observed. The organic layer was washed successively with 10% hydrochloric acid solution, saturated aqueous sodium hydrogen carbonate, saturated sodium chloride solution, dried, and evaporated. The oily mixture (4.2 g) was chromatographed on a dry

column with 40% ethyl acetate in light petroleum as eluant.  $\alpha$ -(Benzoyloxy)styrene<sup>15,16</sup> (27) (2.26 g, 30% overall yield from acetophenone) was obtained, as a light yellow oil which tended to solidify at room temperature,  $\lambda_{\max}$  235.5 nm ( $\epsilon$  13 700),  $\nu_{\max}$  1 747, 1 242, 1 096, 1 090, and 708  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 5.13 (1 H, d,  $J$  2 Hz), 5.55 (1 H, d,  $J$  2 Hz), 7.16—7.66 (8 H, m), and 8.07—8.27 (2 H, m),  $m/e$  224 ( $M^+$ ), 196, and 105 (base peak). Our reaction temperature is lower than that used by Kramarova *et al.*<sup>5</sup> No decrease in the yields was observed as a result of this change. The silylated enol ketones do not have to be purified before conversion into enol benzoates. This method was applied only towards the end of the work presented in this paper and is under further investigation.

*Oxidation Procedure.*—3,3,5,5-Tetramethylcyclohex-1-enyl benzoate (41) (1.29 g, 0.005 mol) was dissolved in 1 : 1 : 1 acetic acid–acetic anhydride–carbon tetrachloride (48.6 ml). The solution was maintained at 25°, sodium chromate (1.62 g, 0.01 mol; vacuum dried over phosphorus pentoxide at 100° for 24 h) was added at once, and the reaction flask was closed and shaken until all the oxidant had dissolved. The reaction was followed by t.l.c. The starting material disappeared after 60 h, and the mixture was poured into ether (100 ml)–ice (100 g), and stirred for 1 h. After two more extractions of the aqueous solution with ether (2  $\times$  50 ml) the combined organic phase was washed successively with saturated aqueous sodium hydrogen carbonate (3  $\times$  100 ml), water, and saturated sodium chloride solution, dried, and evaporated. Recrystallization of the resulting solid mixture gave 3,3,5,5-tetramethyl-6-oxocyclohex-1-enyl benzoate (42) (760 mg, 56%), needles, m.p. (from ethyl acetate–light petroleum) 126°,  $\lambda_{\max}$  236 nm ( $\epsilon$  10 470),  $\nu_{\max}$  1 736, 1 690, 1 275, 1 268, 1 082, 1 067, and 707  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.27 (12 H, s), 1.88 (2 H, s), 6.36 (1 H, s), 7.3—7.65 (3 H, m), and 7.96—8.23 (2 H, m),  $m/e$  272 ( $M^+$ , 5%), 243 (4), 216 (4), 203 (4), 167 (2), 150 (2), and 105 (100) (Found: C, 74.95; H, 7.4.  $\text{C}_{17}\text{H}_{20}\text{O}_3$  requires C, 75.0; H, 7.35%).

*Oxidation of Cyclohex-1-enyl Benzoate (4).*—The oxidation of cyclohex-1-enyl benzoate (4) was described previously.<sup>1</sup> However, further runs of this oxidation proved to contain a higher yield of the oxidized allylic product 3-oxocyclohex-1-enyl benzoate (5). Column chromatography with 5% ethyl acetate–light petroleum eluted a further oxidation product,  $\alpha$ -benzoyloxycyclohexanone (6) (15%), needles, m.p. 86° (lit.<sup>17</sup> 87°),  $\lambda_{\max}$  232 ( $\epsilon$  12 700), 276sh (960), and 283sh nm (800),  $\nu_{\max}$  ( $\text{KBr}$ ) 1 731, 1 712, 1 280, 1 118, and 715  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.65—2.73 (8 H, m), 5.23—5.65 (1 H, m), 7.26—7.66 (3 H, m), and 8.0—8.2 (2 H, m),  $m/e$  218 ( $M^+$ , 6%) and 105 (100) (Found: C, 71.55; H, 6.55. Calc. for  $\text{C}_{13}\text{H}_{14}\text{O}_3$ : C, 71.55; H, 6.4%).

*Enol Benzoate of Cycloheptanone (7).*—Compound (7) was prepared by method B from cycloheptanone (2.8 g, 0.025 mol). Vacuum distillation of the crude reaction product (1.5 mmHg; 140—145°) followed by dry column chromatography (elution with 20% ether–light petroleum) gave cyclohept-1-enyl benzoate (7) (2.7 g, 50%) an oil,  $\lambda_{\max}$  233 ( $\epsilon$  13 400), 276 (1 400), and 284sh nm (1 040),  $\nu_{\max}$  1 733, 1 272, and 705  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.5—1.9 (6 H, m), 1.85—2.58 (4 H, m), 5.52 (1 H, t,  $J$  6.2 Hz), 7.2—7.55 (3 H, m),

<sup>15</sup> F. G. Young, F. C. Frostick, jun., J. J. Sanderson, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3635.

<sup>16</sup> T. Mitsudo, Y. Watanabe, T. Sasaki, H. Nakanishi, M. Yamashita, and Y. Takegami, *Tetrahedron Letters*, 1975, 3163.

<sup>17</sup> M. Bergmann and M. Greith, *Annalen*, 1926, **448**, 48.

<sup>14</sup> Prepared by the method of N. Nesmeyanov, I. F. Lutsenko, and Z. M. Tumanova, *Izvest. Akad. Nauk S.S.S.R., Khim. Nauk.*, 1949, 601 (*Chem. Abs.*, 1950, **44**, 7225e), or by benzylation of the silyl enol ether of acetone (method C).

and 7.9—8.12 (2 H, m), *m/e* 216 ( $M^+$ , 5%) and 105 (100) (Found:  $M^+$ , 216.115 02.  $C_{14}H_{16}O_2$  requires  $M$ , 216.114 98). It was employed without further purification to analytical purity.

*Oxidation of Benzoate (7)*.—Compound (7) (945 mg, 4.38 mmol) was oxidized over a period of 24 h. Chromatography of the mixture after work-up (847 mg) with 20% ethyl acetate–light petroleum as eluant gave, first,  $\alpha$ -benzoyloxycycloheptanone (9) (460 mg, 45%), needles, m.p. (from ethyl acetate–light petroleum) 56–57° (lit.,<sup>18</sup> 53°),  $\nu_{\max}$ . 1 733, 1 273, and 708  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.5–2.2 (8 H, m), 2.2–2.8 (2 H, m), 5.1–5.4 (1 H, m), 7.2–7.5 (3 H, m), and 7.78–8.1 (2 H, m), *m/e* 232 ( $M^+$ ), 204, 127, 110, and 105 (base peak) (Found:  $M^+$ , 232.109 84. Calc. for  $C_{14}H_{16}O_3$ :  $M$ , 232.109 94). The next compound eluted was 3-oxocyclohept-1-enyl benzoate (8) (200 mg, 20%), an oil,  $\lambda_{\max}$ . 237.5 nm ( $\epsilon$  18 000),  $\nu_{\max}$ . 1 748, 1 677, 1 256, and 709  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.7–2.2 (4 H, m), 2.5–2.8 (4 H, m), 5.84 (1 H, s), 7.3–7.6 (3 H, m), and 7.9–8.2 (2 H, m), *m/e* 230 ( $M^+$ ) and 105 (base peak) (Found:  $M^+$ , 230.097 2.  $C_{14}H_{14}O_3$  requires  $M$ , 230.094 3).

*Enol Benzoate of Cyclopentanone (10)*.—Compound (10) was prepared by method A from cyclopentanone (8.4 g, 0.1 mol). Chromatography of the mixture (14.8 g), by elution with 10% ethyl acetate–light petroleum, gave cyclopent-1-enyl benzoate (10) (6 g, 32%), an oil,  $\lambda_{\max}$ . 232 ( $\epsilon$  12 200) and 270 sh nm (2 500),  $\nu_{\max}$ . 1 740, 1 265, and 707  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.7–2.1 (2 H, m), 2.1–2.7 (4 H, m), 5.51 (1 H, t,  $J$  2.2 Hz), 7.25–7.5 (3 H, m), and 7.9–8.15 (2 H, m), *m/e* 188 ( $M^+$ ) and 105 (base peak) (Found:  $M^+$ , 188.085 4.  $C_{12}H_{12}O_2$  requires  $M$ , 188.083 7), which was employed without further purification.

*Oxidation of Benzoate (10)*.—Compound (10) (1.88 g, 0.01 mol) was oxidized for 96 h. The material obtained (700 mg) was chromatographed with 20% ethyl acetate–light petroleum. Two products were obtained:  $\alpha$ -benzoyloxycyclopentanone (12) (263 mg, 13%), needles, m.p. (from ethyl acetate–light petroleum) 90° (lit.,<sup>19</sup> 90–91°),  $\lambda_{\max}$ . 234 ( $\epsilon$  14 100), 276.5 (1 100), and 284 nm (900),  $\nu_{\max}$ . 1 760, 1 722, 1 260, and 704  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.8–2.8 (6 H, m), 4.92–5.22 (1 H, m), 7.3–7.6 (3 H, m), and 7.9–8.2 (2 H, m), *m/e* 204 ( $M^+$ ) and 105 (base peak) (Found: C, 70.45; H, 5.9. Calc. for  $C_{12}H_{12}O_3$ : C, 70.6; H, 5.9%). Further elution gave 5-oxocyclopent-1-enyl benzoate (11) (200 mg, 10%),  $\lambda_{\max}$ . 235 ( $\epsilon$  10 300), 276 sh (950), and 283 sh nm (740),  $\nu_{\max}$ . 1 750, 1 730, 1 265, 1 240, 1 115, and 706  $cm^{-1}$ ,  $\delta$  ( $CDCl_3$ ) 2.47–2.9 (4 H, m), 7.5–7.73 (4 H, m), and 8.1–8.33 (2 H, m), *m/e* 202 ( $M^+$ ), 173, 149, and 105 (base peak) (Found:  $M^+$ , 202.062 95.  $C_{12}H_{10}O_3$  requires  $M$ , 202.062 99).

*Enol Benzoate of Cyclobutanone (13)*.—Compound (13) was prepared by method B from cyclobutanone (2.8 g, 0.04 mol). Chromatography with 5% ethyl acetate–light petroleum gave cyclobut-1-enyl benzoate (13) (180 mg, 2.5%), an oil,  $\nu_{\max}$ . 1 748, 1 260, 1 082, 1 068, and 708  $cm^{-1}$ ,  $\delta$  ( $CDCl_3$ ) 2.3 (2 H, t,  $J$  3 Hz), 2.9 (2 H, t,  $J$  3 Hz), 5.39 (1 H, s), 7.25–7.6 (3 H, m), and 7.9–8.2 (2 H, m), *m/e* 174 ( $M^+$ ) and 105 (base peak). It was oxidized without further purification.

*Oxidation of Benzoate (13)*.—Benzoate (13) (180 mg, 11 mmol) was oxidized for 7 h. After the usual work-up and p.l.c. of the mixture with 10% ethyl acetate–light petroleum,  $\alpha$ -benzoyloxycyclobutanone (14) (20 mg, 10%) was obtained as an oil,  $\nu_{\max}$ . 1 800, 1 730, 1 270, and 705  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.95–2.7 (2 H, m), 2.8–3.2 (2 H, m), 5.75 (1 H, t,  $J$  8.5 Hz), 7.25–7.6 (3 H, m), and 7.9–8.2 (2 H, m). Due to

partial decomposition on distillation, compound (14) could not be prepared for analysis.

*Enol Cyclohexanoate of Cyclohexanone (15)*.—Cyclohexanone (4.9 g, 0.05 mol) was boiled under reflux with cyclohexanecarbonyl chloride (7.3 g, 0.05 mol) following the procedure described in method A. After 60 h the solution was worked up as described. Dry column chromatography with 10% ethyl acetate–light petroleum as eluant gave cyclohex-1-enyl cyclohexanoate (15) (2.7 g, 27%), an oil, u.v. measurement in ethanol shows no absorption above 220 nm,  $\nu_{\max}$ . 1 743, 1 159, and 1 132  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.0–2.3 (19 H, m) and 5.16 (1 H, m), *m/e* 208 ( $M^+$ , 7%), 111 (48), 98 (33), 84 (15), 83 (100), 70 (21), 67 (13), and 55 (68) (Found: C, 75.15; H, 9.55.  $C_{13}H_{20}O_2$  requires C, 75.0; H, 9.65%).

*Oxidation of Cyclohexanoate (15)*.—Cyclohexanoate (15) (1.04 g, 0.05 mol) was oxidized by the standard method. The oily mixture (0.745 g) obtained on chromatography with 20% ethyl acetate–light petroleum gave, first,  $\alpha$ -(cyclohexanoyloxy)cyclohexanone (17) (260 mg, 24%), needles, m.p. (from light petroleum) 54–55°,  $\lambda_{\max}$ . 232 nm ( $\epsilon$  410),  $\nu_{\max}$ . 1 742, 1 732, and 1 165  $cm^{-1}$ ,  $\delta$  ( $CDCl_3$ ) 1.0–2.65 (19 H, m) and 4.8–5.4 (1 H, m), *m/e* 224 ( $M^+$ , 9%), 156 (6), 113 (14), 111 (68), 92 (6), 83 (100), 67 (10), and 55 (41) (Found: C, 69.75; H, 8.8.  $C_{13}H_{20}O_3$  requires C, 69.65; H, 8.95%). The second compound eluted was 3-oxocyclohex-1-enyl cyclohexanoate (16) (390 mg, 35%), an oil,  $\lambda_{\max}$ . 236 nm ( $\epsilon$  12 500),  $\nu_{\max}$ . 1 760, 1 683, and 1 120  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.0–2.7 (17 H, m), and 5.66 (1 H, s), *m/e* 222 ( $M^+$ , 3%), 128 (6), 111 (50), 83 (100), 73 (10), 67 (9), and 55 (55) (Found: C, 70.5; H, 8.4.  $C_{13}H_{18}O_3$  requires C, 70.25; H, 8.1%).

*Enol p-Nitrobenzoate of Cyclohexanone (18)*.—Cyclohexanone (9.8 g, 0.1 mol) and *p*-nitrobenzoyl chloride (18.05 g, 0.1 mol) were refluxed in light petroleum (b.p. 100–120°) (100 ml) during 60 h and worked up as described before (method A). The resulting mixture (26 g) was chromatographed. On elution with 15% ethyl acetate–light petroleum, we obtained cyclohex-1-enyl *p*-nitrobenzoate (18) (3.52 g, 15%), light yellow crystals, m.p. (from ethyl acetate–light petroleum) 92–93°,  $\lambda_{\max}$ . 258 nm ( $\epsilon$  12 500),  $\nu_{\max}$ . 1 732, 1 530, 1 350, 1 275, 1 260, 875, and 860  $cm^{-1}$ ,  $\delta$  ( $CDCl_3$ ) 1.4–1.97 (4 H, m), 1.71–2.5 (4 H, m), 5.45 br (1 H, s), and 8.22 (4 H, s), *m/e* 247 ( $M^+$ , 10%), 219 (3), 150 (100), 134 (5), 120 (44), and 104 (40) (Found: C, 63.35; H, 5.35; N, 5.45.  $C_{13}H_{13}NO_4$  requires C, 63.15; H, 5.25; N, 5.65%).

*Oxidation of p-Nitrobenzoate (18)*.—*p*-Nitrobenzoate (18) (2.47 g, 0.01 mol) was oxidized for 100 h and the solution was worked-up as usual to give a mixture (2.086 g). Chromatography with 40% ethyl acetate–light petroleum gave, first, unchanged starting material (695 mg). Four compounds were eluted in the following order. (1) 3-Acetoxycyclohex-1-enyl *p*-nitrobenzoate (20b) (40 mg, 2.2%) gave an oil,  $\lambda_{\max}$ . 261 nm ( $\epsilon$  9 200),  $\nu_{\max}$ . 1 735, 1 730, 1 530, 1 350, 1 270, 1 240, 872, and 855  $cm^{-1}$ ,  $\delta$  ( $CCl_4$ ) 1.7–2.05 (4 H, m), 2.0 ( $CH_3$ , s), 2.1–2.45 (2 H, m), 5.2–5.45 (3 H, m), 5.6 br (2 H, s), and 8.25 (4 H, s), *m/e* 305 ( $M^+$ ), 150 (base peak), 138, 137, 120, 111, 104, 97, and 96. Due to the low yield an analytical sample could not be prepared. (2)  $\alpha$ -(*p*-Nitrobenzoyloxy)cyclohexanone (20a) (180 mg, 10.1%) gave white needles, m.p. (from ethyl acetate–light petroleum) 125–125.5°,  $\lambda_{\max}$ . 264 nm ( $\epsilon$  12 500),  $\nu_{\max}$ . 1 722, 1 530,

<sup>18</sup> S. David, *Compt. rend.*, 1974, **C278**, 1051.

<sup>19</sup> R. L. Augustine, *J. Org. Chem.*, 1962, **28**, 581.

1 270, 1 117, 1 105, 875, and 825  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.6—2.7 (8 H, m), 5.2—5.55 (1 H, m), and 8.25 (4 H, s),  $m/e$  263 ( $M^+$ , 12%), 219 (4), 150 (100), 134 (22), 120 (18), 113 (43), 104 (50), 96 (22), 92 (18), and 85 (15) (Found: C, 59.45; H, 5.2.  $\text{C}_{13}\text{H}_{13}\text{NO}_5$  requires C, 59.3; H, 4.95%). (3) 6-Oxocyclohex-1-enyl *p*-nitrobenzoate (19b) (220 mg, 12.4%) gave crystals, m.p. (from ethyl acetate–light petroleum) 131—132°,  $\lambda_{\text{max}}$  258 nm ( $\epsilon$  14 200),  $\nu_{\text{max}}$  1 745, 1 690, 1 530, 1 350, 1 265, 1 115, 1 108, 875, and 852  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.98—2.35 (2 H, m), 2.38—2.94 (4 H, m), 6.72 (1 H, t,  $J$  4.5 Hz), and 8.25 (4 H, s),  $m/e$  261 ( $M^+$ , 12%), 150 (100), 120 (35), 104 (22), 97 (11), and 92 (12) (Found: C, 59.5; H, 4.3; N, 5.4.  $\text{C}_{13}\text{H}_{11}\text{NO}_5$  requires C, 59.75; H, 4.2; N, 5.35%). (4) 3-Oxocyclohex-1-enyl *p*-nitrobenzoate (19a) (245 mg, 14%) gave plates, m.p. (from ethyl acetate–light petroleum) 116°,  $\lambda_{\text{max}}$  236 ( $\epsilon$  12 000) and 261 nm (15 250),  $\nu_{\text{max}}$  1 750, 1 680, 1 530, 1 350, 1 258, 1 120, 873, and 852  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 2.0—2.9 (6 H, m), 6.05 (1 H, s), and 8.33 (4 H, s),  $m/e$  261 ( $M^+$ , 17%), 150 (100), 134 (19), 120 (46), 104 (99), and 92 (65) (Found: C, 59.65; H, 4.15; N, 5.65%).

*Oxidation of the Enol Benzoate of Acetophenone* (27).—Compound (27) (896 mg, 4 mmol) was oxidized for 60 h. After work-up as usual the oily mixture was purified by chromatography. On elution with 20% ether–light petroleum, we obtained first benzoylmethyl benzoate (28) (430 mg, 45%) as needles, m.p. (from ethyl acetate–light petroleum) 120° (lit.,<sup>20</sup> 118.5°),  $\lambda_{\text{max}}$  239.5 nm ( $\epsilon$  24 100),  $\nu_{\text{max}}$  1 735, 1 714, 1 278, 1 228, 1 124, 710, and 690  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 5.53 (2 H, s), 7.3—7.65 (6 H, m), and 7.83—8.33 (4 H, m),  $m/e$  240 ( $M^+$ ), 210, 118, and 105 (base peak). On further elution we obtained benzoylmethyl acetate (29) (335 mg, 47%), flakes, m.p. (from ethyl acetate–light petroleum) 40.0° (lit.,<sup>20</sup> 40.5°),  $\lambda_{\text{max}}$  242.5 nm ( $\epsilon$  11 900),  $\nu_{\text{max}}$  1 758, 1 712, 1 218, 712, and 690  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 2.1 (3 H, s), 5.16 (2 H, s), 7.2—7.63 (3 H, m), and 7.73—8.0 (2 H, m),  $m/e$  178 ( $M^+$ ), 136, 118, and 105 (base peak).

*Enol Benzoate of  $\alpha$ -Tetralone* (21).—Compound (21), prepared by method B by heating for 20 h, was obtained in 70% yield as an oil,  $\lambda_{\text{max}}$  223 ( $\epsilon$  27 500) and 258 nm (10 500),  $\nu_{\text{max}}$  1 739, 1 260, 1 094, and 705  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 2.25—3.05 (4 H, m), 5.73 (1 H, t,  $J$  4.6 Hz), 7.0 (4 H, s), 7.2—7.52 (3 H, m), and 8.05—8.2 (2 H, m),  $m/e$  250 ( $M^+$ ), 222, and 105 (base peak) (Found: C, 81.6; H, 5.85.  $\text{C}_{17}\text{H}_{14}\text{O}_2$  requires C, 81.6; H, 5.6%).

*Oxidation of Benzoate* (21).—Compound (21) (1.25 g, 0.005 mol) was oxidized for 40 h and worked-up as usual. The mixture (950 mg) was chromatographed with 20% ethyl acetate–light petroleum. Three products were isolated. (1) 1-Naphthyl benzoate (23b) (100 mg, 8%) gave light yellow crystals, m.p. (from ethyl acetate–light petroleum) 57° (lit.,<sup>21</sup> 56.5—57°),  $\lambda_{\text{max}}$  224 ( $\epsilon$  95 000) and 283 nm (9 900),  $\nu_{\text{max}}$  1 745, 1 600, 1 250, and 1 092  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 7.1—7.92 (10 H, m) and 8.0—8.3 (2 H, m),  $m/e$  248 ( $M^+$ ), 182, 160, 118, 115, and 105 (base peak) (Found: C, 82.4; H, 5.0. Calc. for  $\text{C}_{17}\text{H}_{12}\text{O}_2$ : C, 82.25; H, 4.85%). (2) 2-Benzoyloxytetralone benzoate (22) (500 mg, 38%) gave crystals, m.p. (from ethyl acetate–light petroleum) 99.8—100°,  $\lambda_{\text{max}}$  243 nm ( $\epsilon$  19 200),  $\nu_{\text{max}}$  1 728, 1 707, 1 600, 1 262, 1 122, and 707  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 2.3—2.65 (2 H, m), 3.0—3.35 (2 H, m), 5.71 (1 H, characteristic inverted q,<sup>22</sup>

$J$  18 Hz, probably part of ABX sextet), 7.10—7.70 (6 H, m), and 7.90—8.25 (3 H, m),  $m/e$  266 ( $M^+$ , 0.1%), 161 (20), 144 (70), 133 (25), 117 (15), 115 (15), and 105 (100) (Found: C, 76.6; H, 5.15.  $\text{C}_{17}\text{H}_{14}\text{O}_3$  requires C, 76.7; H, 5.25%). (3) 2-Acetoxytetralone (23a) (200 mg, 19.5%) gave needles, m.p. (from ethyl acetate–light petroleum) 75° (lit.,<sup>23</sup> 74.5—75°),  $\lambda_{\text{max}}$  250 ( $\epsilon$  13 300) and 294 nm (1 830),  $\nu_{\text{max}}$  1 750, 1 707, 1 600, 1 235, and 1 221  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 2.08 (3 H, s), 2.1—2.48 (2 H, m), 2.92—3.22 (2 H, m), 5.38 (1 H, characteristic inverted q,<sup>22</sup>  $J$  18 Hz), 7.05—7.5 (3 H, m), and 7.75—8.0 (1 H, m),  $m/e$  205 ( $M^+$  + 1), 161, 144, 133, and 105 (base peak) (Found: C, 70.6; H, 5.8. Calc. for  $\text{C}_{12}\text{H}_{12}\text{O}_3$ : C, 70.6; H, 5.9%).

*Enol Benzoate of 6-Methoxytetralone* (24).—Compound (24) was prepared by method B from 6-methoxytetralone in 30% yield as needles, m.p. (from methanol–ether) 69—70°,  $\lambda_{\text{max}}$  226 ( $\epsilon$  23 000), 274 (13 400), and 333 nm (130),  $\nu_{\text{max}}$  1 750, 1 265, 1 250, 1 138, 1 126, 1 094, and 706  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{C}_6\text{D}_6\text{O}$ ) 2.3—2.9 (4 H, m), 3.71 (3 H, s), 5.63 (1 H, t,  $J$  4 Hz), 6.74—7.1 (3 H, m), 7.5—7.75 (4 H, m), and 8.07—8.25 (2 H, m),  $m/e$  280 ( $M^+$ ), 252, and 105 (base peak),  $m^*$  226.9 (280  $\rightarrow$  252) (Found: C, 77.15; H, 5.45.  $\text{C}_{18}\text{H}_{16}\text{O}_3$  requires C, 77.1; H, 5.7%).

*Oxidation of Benzoate* (24).—Compound (24) (560 mg, 2 mmol) was oxidized in the usual manner and the mixture after work-up (530 mg) was chromatographed with 20% ethyl acetate–light petroleum to give two products. (1) 2-Benzoyloxy-6-methoxytetralone benzoate (25) (236 mg, 40%) gave plates, m.p. (from ethyl acetate–light petroleum) 149°,  $\lambda_{\text{max}}$  273 nm ( $\epsilon$  22 000),  $\nu_{\text{max}}$  1 728, 1 682, 1 600, 1 268, 1 248, 1 124, 1 106, 933, and 704  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 2.2—2.6 (2 H, m), 3.02—3.25 (2 H, m), 3.8 (3 H, s), 5.7 (1 H, characteristic inverted q,  $J$  18 Hz), 6.6—6.9 (2 H, m), 7.25—7.6 (3 H, m), and 7.92—8.2 (3 H, m),  $m/e$  191 ( $M^+$  — 105), 174, 163, 148, 135, and 105 (base peak) (Found: C, 72.75; H, 5.2.  $\text{C}_{18}\text{H}_{16}\text{O}_4$  requires C, 72.95; H, 5.4%). (2) 2-Acetoxy-6-methoxytetralone (26) (234 mg, 50%) gave crystals, m.p. (from ethyl acetate–light petroleum) 99.5—100°,  $\lambda_{\text{max}}$  273 nm ( $\epsilon$  7 500),  $\nu_{\text{max}}$  1 730, 1 675, 1 590, 1 240, 1 072, 938, and 831  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 2.19 (3 H, s), 2.15—2.5 (2 H, m), 2.9—3.15 (2 H, m), 3.8 (3 H, s), 5.5 (1 H, characteristic inverted q,  $J$  18 Hz), 6.6—6.9 (2 H, m), and 7.95 (1 H, d,  $J$  10 Hz),  $m/e$  234 ( $M^+$ ), 191, 174, 163, 148 (base peak), 135, 121, and 120 (Found:  $M^+$ , 234.089 16.  $\text{C}_{13}\text{H}_{14}\text{O}_4$  requires  $M$ , 234.089 20).

*Enol Benzoate of 2-Phenylcyclohexanone* (30).—2-Phenylcyclohexanone (8.7 g, 0.05 mol) gave, on boiling for 48 h following method A, a mixture (14 g). On crystallization 2-phenylcyclohex-1-enyl benzoate (30) (7.5 g, 54%) was obtained as crystals, m.p. (from ethyl acetate–light petroleum) 80—80.5°,  $\lambda_{\text{max}}$  231 ( $\epsilon$  18 000) and 282sh nm (1 600),  $\nu_{\text{max}}$  1 730, 1 492, 1 265, 1 115, and 702  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.66—2.0 (4 H, m), 2.25—2.71 (4 H, m), 7.16—7.55 (8 H, m), and 7.79—8.02 (2 H, m),  $m/e$  278 ( $M^+$ , 10%), 129 (1), 128 (1), 115 (3), and 105 (100) (Found: C, 82.15; H, 6.45.  $\text{C}_{19}\text{H}_{18}\text{O}_2$  requires C, 82.0; H, 6.5%).

*Oxidation of Benzoate* (30).—Benzoate (30) (2.78 g, 0.01 mol), was oxidized for 100 h and worked-up as usual. The mixture (2.9 g) was chromatographed with 30% ethyl acetate–light petroleum and gave, first, unchanged starting material (515 mg). Four compounds followed. (1) 2-

<sup>20</sup> A. L. Stockburn and C. W. Thomas, *Org. Mass Spectrometry*, 1974, **9**, 1027.

<sup>21</sup> A. Leman, *Ann. Chim. (France)*, 1938, **9**, 357.

<sup>22</sup> Cf. n.m.r. data in K. Hanaya, *Bull. Chem. Soc. Japan*, 1967, **40**, 1884.

<sup>23</sup> F. Strauss, O. Bernouilly, and P. Mauthner, *Annalen*, 1925, **444**, 179.



Phenyl-*p*-benzoquinone (34) (65 mg, 4.3%) gave orange needles, m.p. (from ethyl acetate) 114–115° (lit.,<sup>24</sup> 113–114°),  $\nu_{\max}$  1 670, 1 658, 1 095, 910, and 695  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 6.88 (3 H, s), and 7.48 (5 H, s), *m/e* 184 ( $M^+$ , base peak), 156, 128, 102, and 82 (Found:  $M^+$ , 184.052 430. Calc. for  $\text{C}_{12}\text{H}_8\text{O}_2$ :  $M$ , 184.052 426). (2) 2-Phenylcyclohex-2-enone (33) (171 mg, 12.2%) gave crystals, m.p. 92–94° (lit.,<sup>25</sup> 94–95°),  $\nu_{\max}$  1 690 and 700  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.76–2.6 (6 H, m), 6.87 (1 H, t,  $J$  4 Hz), and 7.18 (5 H, d,  $J$  1 Hz). These data correspond to those reported.<sup>25</sup> (3) 6-Oxo-2-phenylcyclohex-1-enyl benzoate (32) (886 mg, 37.3%) gave yellow crystals, m.p. (from ethyl acetate–light petroleum) 119°,  $\lambda_{\max}$  232 ( $\epsilon$  17 500) and 275 nm (15 700),  $\nu_{\max}$  1 746, 1 697, 1 263, 1 130, 707, and 698  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 2.06–2.46 (2 H, m), 2.5–3.0 (4 H, m), 7.16–7.6 (8 H, m), and 7.93–8.1 (2 H, m), *m/e* 292 ( $M^+$ ), 117, 115, and 105 (base peak) (Found: C, 77.85; H, 5.6.  $\text{C}_{19}\text{H}_{16}\text{O}_3$  requires C, 78.1; H, 5.5%). (4) 3-Oxo-2-phenylcyclohex-1-enyl benzoate (31) (652 mg, 27.7%) gave yellow crystals, m.p. (from ethyl acetate–light petroleum) 51–52°,  $\lambda_{\max}$  236 ( $\epsilon$  16 800) and 270sh nm (6 000),  $\nu_{\max}$  1 740, 1 685, 1 260, 1 240, 1 160, 705, and 695  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.83–2.93 (6 H, m), 7.05–7.5 (8 H, m), 7.67–7.9 (2 H, m), *m/e* 292 ( $M^+$ , 21%), 117 (6), 115 (8), and 105 (100) (Found: C, 78.2; H, 5.55.  $\text{C}_{19}\text{H}_{16}\text{O}_3$  requires C, 78.1; H, 5.5%).

*Oxidation of 2-Methylcyclohex-1-enyl Benzoate (35).*—Compound (35) (1.08 g, 5 mmol) was oxidized by the usual procedure. The reaction was stopped and worked up after 60 h. A mixture (0.99 g) was obtained. Chromatography with 20% ethyl acetate–light petroleum gave, first, unchanged starting material (130 mg). Three compounds followed. (1) 2-Benzoyloxy-3-methyl-*p*-benzoquinone (38) (132 mg, 12.3%) gave yellow crystals, m.p. (from ethyl acetate–light petroleum) 51°,  $\lambda_{\max}$  242 ( $\epsilon$  12 000) and 330 nm (550),  $\nu_{\max}$  1 754, 1 681, 1 670, 1 255, 1 242, 1 153, and 709  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 2.0 (3 H, s), 6.83 (2 H, s), 7.47–7.77 (3 H, m), and 8.05–8.32 (2 H, m), *m/e* 244 ( $M^+$ , 4.5%), 149 (1), and 105 (100). (2) 2-Methyl-3-oxocyclohex-1-enyl benzoate (36) (308 mg, 30.1%) gave an oil,  $\lambda_{\max}$  241 nm ( $\epsilon$  23 000),  $\nu_{\max}$  1 742, 1 682, 1 265, 1 256, 1 100, and 712  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.7 [3 H, t (homoallylic coupling),  $J$  1.5 Hz], 1.88–2.27 (2 H, m), 2.33–2.83 (4 H, m), 7.43–7.7 (3 H, m), and 8.0–8.27 (2 H, m), *m/e* 230 ( $M^+$ ) and 105 (base peak) (Found:  $M^+$ , 230.0945.  $\text{C}_{14}\text{H}_{14}\text{O}_3$  requires  $M$ , 230.0943). (3) 2-Methyl-6-oxocyclohex-1-enyl benzoate (37) (179 mg, 17.5%) gave an oil,  $\lambda_{\max}$  235 ( $\epsilon$  22 000), 276sh (3 000), and 284sh nm (2 100),  $\nu_{\max}$  1 745, 1 693, 1 265, 1 130, and 710  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.9 (3 H, s), 1.9–2.3 (2 H, m), 2.37–2.73 (4 H, m), 7.47–7.67 (3 H, m), and 8.03–8.27 (2 H, m), *m/e* 230 ( $M^+$ ) and 105 (base peak) (Found:  $M^+$ , 230.094 25.  $\text{C}_{14}\text{H}_{14}\text{O}_3$  requires  $M$ , 230.094 28).

*Enol Benzoate of 2,6-Dimethylcyclohexanone (39).*—2,6-Dimethylcyclohexanone (10.7 g, 0.084 mol) gave by method A, a mixture (21 g). Chromatography with 5% ethyl acetate–light petroleum gave the benzoate (39) (7 g, 36%), an oil,  $\lambda_{\max}$  233 ( $\epsilon$  14 000), 276 (1 450), and 283sh nm (1 100),  $\nu_{\max}$  1 733, 1 280, 1 125, and 712  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.97 (d,  $J$  7 Hz, 6-Me), 1.17–2.83 (7 H, m), 1.53br (s, 2-Me), 7.17–7.63 (3 H, m), and 8.02–8.2 (2 H, m), *m/e* 230 ( $M^+$ , 6%) and 105 (100) (Found: C, 78.2; H, 8.1.  $\text{C}_{15}\text{H}_{18}\text{O}_2$  requires C, 78.25; H, 7.85%).

*Oxidation of the Enol Benzoate of 2,6-Dimethylcyclohexanone (39).*—Benzoate (39) (3.45 g, 0.015 mol) was oxidized for 90 h and worked-up as usual. Chromatography with 30% ethyl acetate–light petroleum gave

unchanged starting material (550 mg), and then 2,6-dimethyl-3-oxocyclohex-1-enyl benzoate (40) (1 500 mg, 48%), an oil,  $\lambda_{\max}$  241 nm ( $\epsilon$  42 000),  $\nu_{\max}$  1 742, 1 684, 1 265, 1 255, 1 110, and 720  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.15 (d,  $J$  7 Hz, 6-Me), 1.58 (d,  $J$  2 Hz, 2-Me), 1.66–3.1 (5 H, m), 7.23–7.66 (3 H, m), and 7.86–8.2 (2 H, m) (Found: C, 72.6; H, 6.8.  $\text{C}_{15}\text{H}_{16}\text{O}_3$  requires C, 73.75; H, 6.55%).

*Enol Benzoate of 3,5-Dimethylcyclohexanone (43).*—The silyl enol ether of 3,5-dimethylcyclohexanone (2.22 g, 0.011 mol), was converted by method C into benzoate (43) (1.8 g, 70%), an oil,  $\lambda_{\max}$  230.5 nm ( $\epsilon$  14 000),  $\nu_{\max}$  1 732, 1 270, 1 140, and 709  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.97br ( $\text{CH}_3$ , s), 1.07 ( $\text{CH}_3$ , d,  $J$  2 Hz), 1.33–2.7 (6 H, m), 5.3br (1 H, s), 7.23–7.6 (3 H, m), and 7.93–8.2 (2 H, m), *m/e* 230 ( $M^+$ , 3%), 122 (22), and 105 (100) (Found: C, 78.2; H, 7.85.  $\text{C}_{15}\text{H}_{18}\text{O}_2$  requires C, 78.25; H, 7.85%).

*Oxidation of Benzoate (43).*—Compound (43) (2.3 g, 0.01 mol) was oxidized for 20 h and worked-up by the usual procedure. Chromatography with 30% ethyl acetate–light petroleum gave 3,5-dimethylcyclohex-2-enone<sup>26</sup> (44) (747 mg, 60.2%), an oil,  $\lambda_{\max}$  235 nm ( $\epsilon$  13 100),  $\nu_{\max}$  1 666 and 888  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.09 (3 H, d,  $J$  5 Hz), 1.96 (3 H, s), 1.65–2.65 (5 H, m), and 5.78br (1 H, s) (Found:  $M^+$ , 124.088 79. Calc. for  $\text{C}_8\text{H}_{12}\text{O}$ :  $M$ , 124.088 81).

*Enol Benzoate of 4-Methylcyclohexanone (45).*—4-Methylcyclohexanone (10 g, 0.09 mol) was enol-esterified by method A. Work-up and chromatography with 2.5% ethyl acetate–light petroleum gave benzoate (45) (2.1 g, 11%), an oil,  $\lambda_{\max}$  230 ( $\epsilon$  12 900), 273 (1 360), and 280sh nm (1 040),  $\nu_{\max}$  1 733, 1 268, 1 130, and 707  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.98 (d,  $J$  4 Hz,  $\text{CH}_3$ ), 1.3–2.53 (7 H, m), 5.27–5.5 (1 H, m), 7.17–7.53 (3 H, m), and 7.73–8.13 (2 H, m), *m/e* 216 ( $M^+$ , 5%), 123 (2), and 105 (100) (Found: C, 77.55; H, 7.35.  $\text{C}_{14}\text{H}_{16}\text{O}_2$  requires C, 77.8; H, 7.4%).

*Oxidation of Benzoate (45).*—Compound (45) (1.08 g, 0.005 mol) was oxidized for 48 h by the usual procedure. Chromatography with 5% ethyl acetate–light petroleum gave, first, starting material (260 mg). Four compounds followed. (1) 1,2-Epoxy-4-methylcyclohexyl benzoate (49) (20 mg, 2.2%) gave an oil,  $\lambda_{\max}$  232.5 ( $\epsilon$  5 500) and 274 nm (500),  $\nu_{\max}$  1 725, 1 280, 1 232, 1 168, 930, 900, and 709  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.83–2.42 (10 H, m), 3.22br (1 H, s), 7.2–7.6 (3 H, m), and 7.88–8.16 (2 H, m), *m/e* 232 ( $M^+$ ), 127, 110, and 105 (base peak). (2) 4-Methyl-3-oxocyclohex-1-enyl benzoate (46) (400 mg, 44%) gave crystals, m.p. (from ethyl acetate–light petroleum) 74.5°,  $\lambda_{\max}$  242 nm ( $\epsilon$  22 400),  $\nu_{\max}$  1 745, 1 682, 1 260, 1 245, 1 132, and 707  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.15 (d,  $J$  6.5 Hz,  $\text{CH}_3$ ), 1.63–2.5 (3 H, m), 2.5–2.97 (2 H, m), 5.88 (1 H, d,  $J$  <1 Hz), 7.28–7.82 (3 H, m), and 7.92–8.22 (2 H, m), *m/e* 230 ( $M^+$ , 2%), 149 (1), and 105 (100) (Found: C, 72.9; H, 5.95.  $\text{C}_{14}\text{H}_{14}\text{O}_3$  requires C, 73.05; H, 6.1%). (3) 5-Methyl-2-oxocyclohexyl benzoate (47) (90 mg, 10%) gave crystals, m.p. (from ethyl acetate–light petroleum) 94.5–95°,  $\lambda_{\max}$  233 ( $\epsilon$  16 100), 277sh (1 460), and 283sh nm (1 170),  $\nu_{\max}$  1 740, 1 727, 1 280, 1 268, 1 118, and 708  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.83–2.67 (7 H, m), 1.05 (d,  $J$  5.5 Hz,  $\text{CH}_3$ ), 5.37 (1 H, q,  $J_{\text{AX}}$  12,  $J_{\text{BX}}$  3 Hz), 7.12–7.58 (3 H, m), and 7.83–8.25 (2 H, m), *m/e* 232 ( $M^+$ , 11%), 204 (2), 127 (25), 110 (22), and 105 (100) (Found:  $M^+$ , 232.1105.  $\text{C}_{14}\text{H}_{16}\text{O}_3$  requires  $M$ , 232.1099). (4) 4-Methyl-6-oxocyclohex-1-enyl benzoate (48) (130 mg, 14.5%) gave crystals, m.p. (from ethyl acetate–light

<sup>24</sup> P. Brassard and P. L'Écuyer, *Canad. J. Chem.*, 1958, **36**, 700.

<sup>25</sup> B. Miller and H. S. Wong, *Tetrahedron*, 1972, **28**, 2369.

<sup>26</sup> H. S. French, *J. Amer. Chem. Soc.*, 1952, **74**, 514.

petroleum) 81—82°,  $\nu_{\max}$ . 1 745, 1 705, 1 265, 1 142, 1 118, and 708  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 1.1br ( $\text{CH}_3$ , d,  $J < 4$  Hz), 1.83—2.83 (5 H, m), 6.55br (1 H, t,  $J$  4 Hz), 7.27—7.63 (3 H, m), and 7.92—8.23 (2 H, m),  $m/e$  230 ( $M^+$ , 10%) and 105 (100) (Found: C, 73.35; H, 6.1.  $\text{C}_{14}\text{H}_{14}\text{O}_3$  requires C, 73.05; H, 6.1%).

*Enol Benzoate of 4-t-Butylcyclohexanone* (50).—4-t-Butylcyclohexanone (10 g, 0.065 mol) was enol-esterified according to method A for 100 h. The usual work-up and chromatography with 20% ethyl acetate–light petroleum resulted in *benzoate* (50) (4 g, 24%), crystals, m.p. (from ethyl acetate–light petroleum) 97°,  $\lambda_{\max}$ . 230.5 ( $\epsilon$  13 000), 272sh (1 450), and 279sh nm (1 100),  $\nu_{\max}$ . 1 733, 1 269, 1 130, and 705  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CDCl}_3$ ) 0.88 (s,  $\text{Bu}^t$ ), 1.2—2.4 (7 H, m), 5.27—5.48 (1 H, m), 7.22—7.45 (3 H, m), and 7.8—8.0 (2 H, m),  $m/e$  258 ( $M^+$ , 4%), 136 (1), and 105 (100) (Found: C, 79.05; H, 8.55.  $\text{C}_{17}\text{H}_{22}\text{O}_2$  requires C, 79.05; H, 8.6%).

*Oxidation of Benzoate* (50).—Compound (50) (2.58 g, 0.01 mol) was oxidized for 85 h and worked-up as usual. The mixture obtained (2.2 g) was chromatographed with 5% ethyl acetate–light petroleum and starting material (850 mg) was first recovered. Three compounds followed.

<sup>27</sup> F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, 1966, **31**, 351.

(1) 3-Oxo-4-t-butylcyclohex-1-enyl benzoate (51) (320 mg, 18.6%) gave crystals, m.p. (from ethyl acetate–light petroleum) 60°,  $\lambda_{\max}$ . 238.5 nm ( $\epsilon$  21 000),  $\nu_{\max}$ . 1 740, 1 682, 1 260, 1 245, 1 080, and 705  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.96 (s,  $\text{Bu}^t$ ), 1.6—2.46 (3 H, m), 2.63 (2 H, t,  $J$  5.5 Hz), 5.76 (1 H, s), 7.3—7.53 (3 H, m), and 7.85—8.03 (2 H, m),  $m/e$  272 ( $M^+$ , 13%), 215 (100), and 105 (99) (Found: C, 75.0; H, 7.25.  $\text{C}_{17}\text{H}_{20}\text{O}_3$  requires C, 75.0; H, 7.35%). (2) 6-Oxo-4-t-butylcyclohex-1-enyl benzoate (52) (569 mg, 31%) gave crystals, m.p. (from ethyl acetate–light petroleum) 125—126° (lit.,<sup>27</sup> 126—126.5°),  $\lambda_{\max}$ . 232.5 ( $\epsilon$  19 000), 274 (1 100), and 281sh nm (860),  $\nu_{\max}$ . 1 748, 1 700, 1 265, 1 128, and 705  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.95 (s,  $\text{Bu}^t$ ), 1.63—2.66 (5 H, m), 6.4—6.66 (1 H, m), 7.23—7.63 (3 H, m), and 7.83—8.23 (2 H, m),  $m/e$  274 ( $M^+$ , 4%), 169 (7), 133 (7), 105 (100), and 96 (11) (Found: C, 75.25; H, 7.6%). (3) 4-t-Butylcyclohex-2-enone<sup>28</sup> (53) (356 mg, 21%) had  $\nu_{\max}$ . 1 688  $\text{cm}^{-1}$ ,  $\delta$  ( $\text{CCl}_4$ ) 0.95 (s,  $\text{Bu}^t$ ), 1.86—2.58 (5 H, m), 5.9 (1 H, q,  $J_1$  11,  $J_2$  2.5 Hz, 2-H), and 6.85 (1 H, q,  $J_1$  11,  $J_2$  1.5 Hz, 3-H).

[7/072 Received, 14th January, 1977]

<sup>28</sup> E. W. Garbisch, jun., *Chem. and Ind.*, 1964, 1715; *J. Org. Chem.*, 1965, **30**, 2109.