BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 275—279 (1973)

# The Peracid-oxidation of Tetraphenylallene: The Formation of Hydroxyindanone and Its Oxidative Transformation

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(Received June 17, 1972)

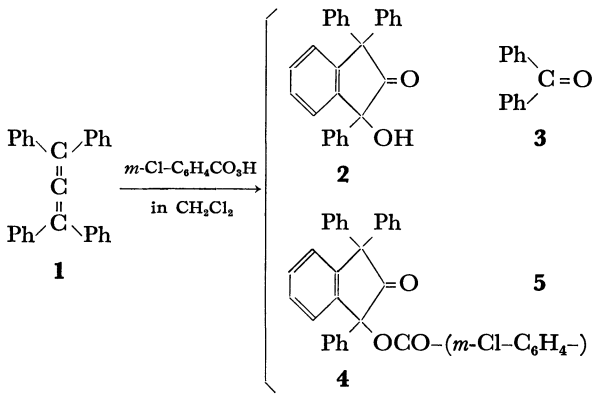
The oxidation of tetraphenylallene (**1**) with *m*-chloroperbenzoic acid has been reported. Under acidic conditions, 1-hydroxy-1,3,3-triphenyl-2-indanone (**2**) was isolated in 45% yield, along with benzophenone (**3**) and the *m*-chlorobenzoate of **2** as minor products. In the presence of sodium carbonate, the oxidation products were 2,2,4,4-tetraphenyloxetanone (**6**), **3**, and 1,3,3-triphenyl-2,3-dihydro-5*H*-indene-2,5-dione (**5**). The prolonged oxidation of **2** with peracetic acid yielded $\alpha,\alpha$-diphenylphthalide (**9a**). The alkaline hydrolysis of **2** induced ring cleavage to give *o*-benzhydrylbenzilic acid (**15b**), whereas acid hydrolysis in ethanol or methanol gave the corresponding ethers, **16a** and **16b** respectively.

The intermediacy of allene oxides has attracted our attention in terms of olefin-epoxidation and valence tautomerism with cyclopropanone.[1] Vorlander[2] was the first to report the synthesis of tetraphenylallene dioxide by the cromic-acid oxidation of tetraphenylallene, but it was proved later[3] that the product was tetraphenyloxetanone instead of the dioxide. Recently Crandall and his co-workers[4] have reported extensive work on the isolation of allene dioxides, cyclopropanones, and oxetanones in the peracid oxidation of alkyl-substituted allenes. More significantly, Greene and Camp[5] have isolated 1,3-di-*tert*-butylallene oxide by using *m*-chloroperbenzoic acid as the effective reagent.

In the present study, we wish to report the peracid oxidation of tetraphenylallene (**1**), where the product formation is largely dependent on the pH of the oxidation mixture. Analogously to the earlier studies,[4] the intermediacy of tetraphenylallene oxide (**7**) and its corresponding spiro-dioxide (**8**), though not isolated, has been demonstrated. On the other hand, however, cationic alkylation on a benzene ring of substrates has taken place predominantly under acidic conditions to give 1-hydroxy-1,3,3-triphenyl-2-indanone (**2**),[6] while under the conditions buffered with sodium carbonate, 2,2,4,4-tetraphenyloxetanone (**6**) and 1,3,3-triphenyl-2,3-dihydro-5*H*-indene-2,5-dione (**5**) have been obtained instead of the indanone (**2**). It has also been found while examining the oxidative susceptibility of the indanone (**2**) to peracids that **2** undergoes a novel Baeyer-Villiger transformation involving the elimination of the benzoyloxy group.

## Results and Discussion

*Oxidation of Tetraphenylallene.* The treatment of tetraphenylallene (**1**) with 2 equivalents of *m*-chloroperbenzoic acid in methylene chloride for 20 hr at 1—3°C (peracid consumption 60%) afforded a yellow




1) a) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968); b) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969).

2) D. Worlander and P. Winstein, *Ber.*, **56**, 1122 (1923).

3) G. B. Hoey, D. O. Dean, and C. T. Lester, *J. Amer. Chem. Soc.*, **77**, 391 (1955). See also **76**, 4988 (1954).

4) a) J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7292 (1968); b) J. K. Crandall, W. H. Machleder, and M. J. Thomas, *ibid.*, **90**, 7346 (1968); c) J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7347 (1968).

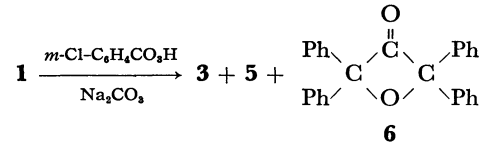
5) R. L. Camp and F. D. Greene, *ibid.*, **90**, 7349 (1968).

6) Acyclic hydroxyketones were the usual products of allene oxidation; *cf.* F. R. LaForge, and F. Acree, Jr., *J. Org. Chem.*, **6**, 208 (1941).

product mixture, which was then chromatographed to give four products: **2** (45%), **3** (3%), **4** (1%), and **5** (<1%), besides the unreacted allene (**1**) (25%).[7]

The structure of the main product (mp 160°C) was determined to be 1-hydroxy-1,3,3-triphenyl-2-indanone (**2**)[8] by the following analyses and by the chemical behavior to be described in the last section of the present paper. The infrared spectrum showed carbonyl (1760 $cm^{-1}$, indicative of a cyclic five-membered ketone) and hydroxyl (3560 $cm^{-1}$) absorptions. The NMR spectrum showed only a complex multiplet of aromatic protons. The elemental analysis ($C_{27}H_{20}O_2$) indicates that the allene ($C_{27}H_{20}$) was oxidized by two atoms of oxygen. Several possible structures other than **2** were also examined, but were ruled out. For example, tetraphenyloxetanone (**6**)[9] was the most expected product by analogy with Crandall's result, but it should show a much higher frequency of $\nu_{C=O}$ than that observed (for the oxetanone (**6**), see the next paragraph). The indanone (**2**) did not form hydrazone with 2,4-dinitrophenylhydrazine nor did it react with hydroxylamine.[10] A similar low reactivity has also been reported for 3-hydroxy-1,3-diphenyl-2-indanone.[11] The second product **3** was identified as benzophenone by comparison with authentic sample. The third product, **4** (mp 216°C), obtained in a low yield, turned out to be $C_{34}H_{23}O_3Cl$. An examination of its infrared spectrum, which shows two carbonyl absorptions at 1770 (strong) and 1730 $cm^{-1}$ (stronger), indicates that a mixed structure with cyclic ketone and *m*-chlorobenzoate functions is preferable to other structures, such as acid anhydrides. The NMR spectrum showed only a complex multiplet of aromatic ring protons and no signal in the other regions. From these data, **4** is assumed to be the *m*-chlorobenzoate of **2**, as has been indicated above. In fact, the formation of **2** was confirmed in the acid hydrolysis of **4**. The minor product **5** was obtained in a trace; its structural determination will be described in the next paragraph.

In order to minimize the influence of *m*-chlorobenzoic acid in the reaction, an excess amount of finely-powdered sodium carbonate was added to the reacting mixture. In this buffered reaction, three products, **3** (10%), **5** (3%), and **6** (5%), were isolated, besides the unreacted allene (48%), after a reaction for 20 hr at 1—3°C (peracid consumption, 46%).

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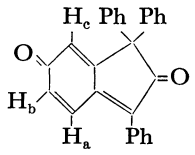
No appreciable formation of any other products was detected, although the isolated yields of the above products were low. It should be noted that the indanone (**2**) was not detected here, but that, instead, tetraphenyloxetanone (**6**) was formed. This implies that the formation of **2** occurred only under acidic conditions. The **6** product (mp 201°C) showed a carbonyl absorption at 1805 $cm^{-1}$ (strained C=O) in its infrared spectrum, and the NMR spectrum showed only the existence of aromatic ring protons. The **5** product (mp 220°C), obtained as orange-yellow crystals, was found to be $C_{27}H_{18}O_2$ by the elemental analysis as well as a study of its mass spectrum ($M^+$ *m/e* 374). The infrared spectrum showed two carbonyl absorptions, at 1725 (s) and 1640 (vs) $cm^{-1}$. The ultraviolet spectrum showed two absorptions, at 367 nm (log ε 4.7) and 260 nm (log ε 4.5), characteristic of the multi-conjugated system involving carbonyl functions, such as *o*-quinone or fuchsone.[12] Its rather distinct NMR signals at τ 2.13 (1H, d, $J$=10 Hz), 3.41 (1H, a pair of doublet, $J_1$=10 Hz, $J_2$=1.5 Hz), and 3.68 (1H, d, $J$=1.5 Hz), in addition to the multiplets of aromatic hydrogens, are quite characteristic of the cyclic conjugating systems with a three-proton arrangement of $-CH_a=CH_b-C=CH_c-$ or $-CH_a=CH_b-CO-CH_c=$.[13] The structural elucidation of this product, based on an analysis of the above data, suggests a cross-conjugated diketone structure depicted below rather than any other available structures:

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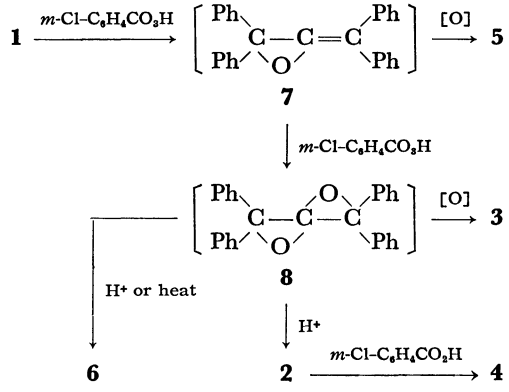
In this structure, *i.e.*, 1,3,3-triphenyl-2,3-dihydro-5*H*-indene-2,5-dione, the three protons on the quinone ring well account for the observed NMR spectrum, in which $H_a$ is shifted downfield due to the diamagnetic anisotropy of the *peri*-phenyl group.

Scheme 1 illustrates the reaction route to accommodate these results. As has been proposed[4] the initial step in this sequence is the formation of allene




Scheme 1

7) Product yields indicated in this paper are those of the isolated and purified products unless otherwise mentioned.

8) Lit. mp 157—159°C by C.F. Koelsch, *J. Org. Chem.*, **3**, 456 (1938).

9) Other structures such as triphenylbenzoylethylene oxide, triphenylvinyl benzoate, phenyl triphenylacrylate, and 2-hydroxy-2,3,3-triphenyl-1-indanone were all ruled out by the analysis.

10) Graf, *Chem. Zentr.*, II, 3337, 3338 (1936).

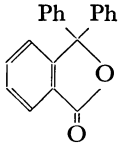
11) S. Ecary, *C. R. Acad. Sci. Paris*, **224**, 1504 (1947).

12) L. C. Anderson and J. W. Steedly, Jr., *J. Amer. Chem. Soc.*, **76**, 5144 (1954).

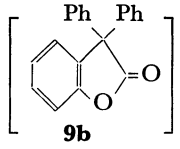
13) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Braunschweig, 1969, p. 340.

oxide (**7**), which is then further oxidized to form **8**. Both oxides are unisolated intermediates, but are likely sources of the isolated products. The failure to isolate the **7** and **8** intermediates can be attributed to the substituent effect of the phenyl group, which is in contrast to that of alkyl homologs.[4,5] Thus, tetraphenylallene is less reactive than the alkyl homologs toward the peracid, as may be seen in the imcomplete and slow conversion of the peracid and the allene (**1**). On the other hand, the **7** and **8** intermediates are much more susceptible to the acid-catalyzed (or thermal) transformation, probably because of the delocalization of cationic species by phenyl groups. The formation of the indanone (**2**) under acidic conditions clearly demonstrates the cationic alkylation of a phenyl ring *via* one of the few possible reaction paths. This route, however, is almost completely suppressed in a buffered reaction, and the oxetanone (**6**) is formed instead. This clear-cut distinction indicates an important role of pH in the product control, regardless of whether **6** is formed thermally or by acid catalysis. The formation of benzophenone, probably closely analogous to the formation of acetone from tetramethylallene,[4] cannot be interpreted well. The most likely precursor, however, seems to be the spirodioxide (**8**), which undergoes further oxidation to give **3** as was observed in the oxidation of **8** with cromic acid.[2] The formation of the *m*-chlorobenzoate (**4**) can be reasonably explained in terms of an acid-catalyzed esterification between **2** and *m*-chlorobenzoic acid. The formation of the diketone (**5**), observed more in the buffered reaction than in the acidic oxidation, reasonably rules out the possible intermediacy of the indanone (**2**) as a precursor of **5**. A plausible explanatory reaction sequence consists of an oxidative ring-hydroxylation of the allene oxide (**7**), followed by some cationic ring-formation and oxidation. However, sufficient evidence is not yet available to support this sequence.

*Reaction of 1-Hydroxy-1,3,3-triphenyl-2-indanone (2).* The stability of the indanone (**2**) in relation to *m*-chloroperbenzoic acid rules out the possibility that this material is the precursor of **3**, **5**, or **6**. The oxidation of **2** with peracetic acid after a prolonged reaction, however, afforded only one product. Its infrared spectrum showed a carbonyl absorption at 1775 $cm^{-1}$, and both its mass spectrum and elemental analysis ($C_{20}H_{14}O_2$, *m/e* 286) proved it to be either **9a** or **9b**.[14] Compound **9a** has been prepared from phthalic anhydride and phenyllithium,[15] whereas **9b** has been prepared from benzil and phenol.[16] As a result, it has been found that the product was α,α-diphenylphthalide (**9a**)



**9a**



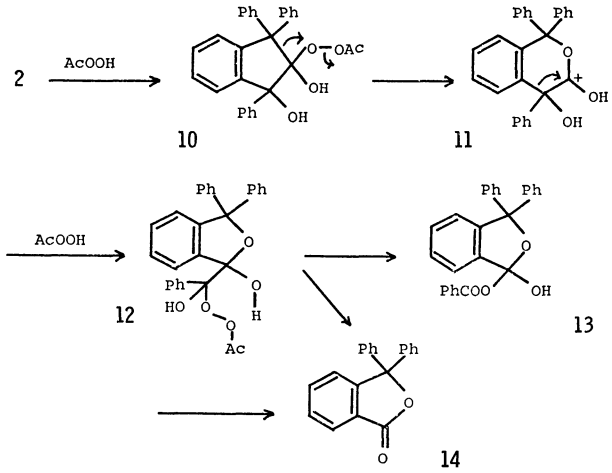
**9b**

14) Lit. mp of **9a** 116°C, see Ref. 15; lit. mp of **9b** 120°C, see Ref. 16.

15) J. M. Wilson, *J. Chem. Soc.*, 2297 (1951).

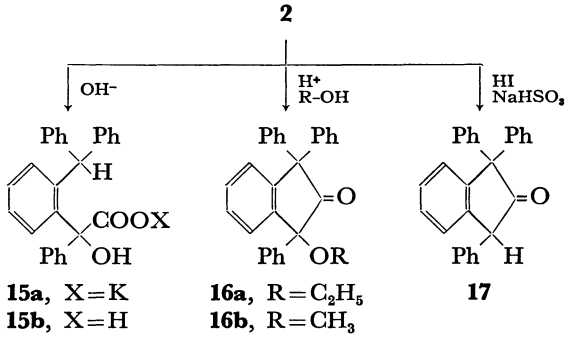
16) V. Liebig and P. Keim, *Ann. Chem.*, **360**, 200 (1908).

(15%); this presents us with a possible reaction scheme in which a novel Baeyer-Villiger-type transformation of α-hydroxyketone is involved (Scheme 2). Additionally, the fact that benzophenone was not formed in this reaction excludes any transformation in which the indanone (**2**) can be the precursor of benzophenone.



Scheme 2

Some supplemental reactions of the indanone (**2**) were carried out in order to determine the structure and reaction behavior of **2** in the oxidation system. The hydrolysis of **2** in aqueous potassium hydroxide gave a white solid of a potassium carboxylate (**15a**). This material was then acidified to yield its free acid (**15b**). The infrared spectrum and the NMR spectrum of **15b** are in good agreement with the structure of *o*-benzhydrylbenzilic acid,[8] and its formation can be interpreted in terms of a hydroxy-anion attack on the carbonyl function, followed by ring cleavage to form the trityl anion.



**15a**, X=K
**15b**, X=H

**16a**, R=$C_2H_5$
**16b**, R=$CH_3$

**17**

The treatment of **2** with ethanolic hydrochloric acid yielded 1-ethoxy-1,3,3-triphenyl-2-indanone (**16a**) in a good yield. The NMR spectrum of **16a**, however, showed a pair of quartets of the ethoxy methylene signal slightly split (by about 3 Hz), whereas the ethoxy methyl appeared unsplit. With the aid of a molecular model, this may be accounted for by a steric inhibition of the free rotation in this rather crowded molecule. Similarly, the methoxy derivative (**16b**) was obtained from a methanolic hydrochloric acid solution in a 73% yield. Somewhat related to the formation of the *m*-chlorobenzoate (**4**), the ether formation may be indicative of a possible nucleophilic displacement on

the position adjacent to the carbonyl. In addition, the tertiary hydroxy group of **2** was readily reduced by treating **2** with hydriodic acid and sodium bisulfite,[17] thus giving 1,1,3-triphenyl-2-indanone (**17**).

## Experimental

Melting points are uncorrected. Infrared spectra were recorded on a JASCO IRA-1 grating spectrophotometer, NMR spectra were taken on a JEOL 4H-100 spectrometer (100 MHz) unless otherwise stated. Chemical shifts are relative to internal TMS and are given on $\tau$ scale. Mass spectra were obtained with a Shimadzu LKB-9000 mass spectrometer. Combustion analyses were performed by the Microanalytical Laboratory, Kyoto University.

*m-Chloroperbenzoic Acid.* The preparation of *m*-Cl-perbenzoic acid[18] on a laboratory scale was performed starting with *m*-toluidine according to the method indicated in the literatures.[19]

*Tetraphenylallene (1).*[20] Starting with diphenylmethyl bromide (120 g) and 1,1-diphenylethylene (88 g), and after several experimental procedures directed by the literature,[21] a pure solid of **1** (28.5 g, mp 165°C) was obtained.

*Oxidation of 1 with m-Chloroperbenzoic Acid.* To a solution of **1** (13.8 g, 0.04 mol) in methylene chloride (100 ml) was added a solution of 86% *m*-Cl-perbenzoic acid (16.6 g, 0.08 mol) in methylene chloride (250 ml) and the mixture was stirred for 20 hr at 1—3°C (peracid consumption 60%).[22] Then the mixture was washed three times with 10% aqueous sodium carbonate and two times with saturated aqueous sodium chloride. After the organic solution has been dried over anhyd magnesium sulfate, the solvent was removed by flash evaporation to give a yellow oil. Tlc showed two major spots, plus several (mainly three) minor spots. The crude oil was chromatographed on silica gel (Merck 70—325 mesh), first with carbon tetrachloride and then with chloroform. The first eluting fraction contained unreacted **1** (4.1 g, 25% recovery). The second fraction gave a colorless solid of 1,3,3-triphenyl-2-oxodihydro-1-indenyl *m*-Cl-benzoate (**4**), 0.2 g (1%); mp 216°C (ethanol); IR ($CCl_4$) 1770 (strong) and 1730 (stronger) $cm^{-1}$ (both C=O); NMR ($CCl_4$) $\tau$ 2.7—3.2 (m).

Found: C, 79.54; H, 4.59%. Calcd for $C_{34}H_{23}O_3Cl$: C, 79.29; H, 4.50%.

The saponification of **4** with hot hydrochloric acid in dioxane, followed by the removal of the solvents, yielded a crude solid, which showed a tlc spot identical with that of indanone (**2**). The third fraction gave a viscous oil which gradually solidified on standing. The solid was recrystallized from diethyl ether to give 0.4 g (3%) of benzophenone (**3**). The fourth fraction was a viscous yellow oil, from which the diketone (**5**) was isolated (<1%). The physical data of **5** will be given in the next experimental paragraph. The fifth fraction consisted mainly of 1-hydroxy-1,3,3-triphenyl-2-indanone (**2**), which was purified by recrystallization from toluene to give 6.7 g (45%) of **2** as colorless needles; mp 161°C; IR 3560 (OH), 1760 $cm^{-1}$ (C=O); UV $\lambda_{max}^{cyclohexane}$ 320 nm (log $\varepsilon$ 2.5), 278 (3.56), 270 (3.34), 263 (3.31); NMR ($CCl_4$) $\tau$ 2.62—3.02 (m); *m/e* 376 ($M^+$).

Found: C, 86.34; H, 5.32%. Calcd for $C_{27}H_{20}O_2$: C, 86.15; H, 5.36%.

*Oxidation of 1 with m-Chloroperbenzoic Acid in the Presence of Sodium Carbonate.* To a solution of **1** (13.8 g, 0.04 mol) in methylene chloride (100 ml), we added 100 g of finely-pulverized sodium carbonate. To this suspension was then added 17.2 g (0.08 mol) of *m*-Cl-perbenzoic acid (assay 83%) dissolved in methylene chloride (250 ml), after which the mixture was stirred at 1—3°C for 20 hr (peracid consumption 45%). The inorganic salts were filtered out, and the filtrate was washed three times with 10% aqueous sodium carbonate and two times with saturated aqueous sodium chloride, and dried over anhyd. magnesium sulfate. The solvent was then removed by flash evaporation to give a yellow oil (4 tlc spots, but none of **2**, on a silica gel plate). The oil was chromatographed (silica gel, carbon tetrachloride and chloroform eluent). The first eluting fraction contained unreacted **1** (6.7 g, 48%). The second fraction consisted mainly of 2,2,4,4-tetraphenyloxetanone (**6**); 0.8 g (5%); mp 198—201°C (diethyl ether); IR ($CCl_4$) 1805 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\tau$ 2.77 (m).

Found: C, 86.05; H, 5.46%. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.35%.

The third fraction was proved to consist mainly of **3**, as in the previous experimental paragraph. The fourth fraction was a deep yellow oil, the same component as the third chromatographed fraction obtained in the preceding experimental paragraph. This was purified by preparative tlc (silica gel), followed by recrystallization from ethanol, to give orange-yellow crystals of 1,3,3-triphenyl-2,3-dihydro-5*H*-indene-2,5-dione (**5**); 0.5 g (3%); mp 219—220°C; IR ($CCl_4$) 1725 and 1640 $cm^{-1}$ (C=O); NMR (THF) $\tau$ 2.13 (1H, d, $J$=10 Hz), 2.32 (2H, m), 2.50 (3H, m), 2.73 (10H, m), 3.41 (1H, q, $J_1$=10 Hz, $J_2$=1.5 Hz), 3.68 (1H, d, $J$=1.5 Hz); UV $\lambda_{max}^{cyclohexane}$ 367 nm (log $\varepsilon$ 4.7), 260 (4.5); *m/e* 374 ($M^+$).

Found: C, 86.06; H, 4.81%. Calcd for $C_{27}H_{18}O_2$: C, 86.60; H, 4.85%.

*Oxidation of 2 with Peracetic Acid.* Peracetic acid was prepared by adding 90% hydrogen peroxide (10.8 ml, 0.40 mol) to a cold solution of acetic anhydride (44.9 g, 0.44 mol) in methylene chloride (100 ml); the mixture was then kept overnight in a refrigerator (peracid concentration $1.8\times10^{-3}$ mol/g[22]). About 20 ml (40 mmol) of the above peracid solution and **2** (0.75 g, 2 mmol) dissolved in chloroform (30 ml) were mixed, and this mixture was stirred at 10—15°C for 11 days (peracid consumption 15%). The organic mixture was then washed three times with 10% aqueous sodium carbonate and two times with saturated aqueous sodium chloride, and then dried over anhyd. magnesium sulfate. The solvents were removed by flash evaporation to give a crude solid, which was chromatographed (silica gel, carbon tetrachloride eluent) to give **9a** (0.08 g, 15%) in addition to the unreacted **2** (0.5 g, 70% recovery). **9a**: colorless prismen crystal (diethyl ether); mp 117—118°C; mmp (with an authentic sample, see below) 117°C; IR ($CCl_4$) 1775 $cm^{-1}$ (C=O); NMR ($CCl_4$) 2.46 (4H, m), 2.73 (10H, m).

*α,α-Diphenylphthalide (9a).* To a warm ethereal solution of phenyllithium prepared from lithium metal (9.36 g, 1.35 mol) and bromobenzene[14] (101 g, 0.64 mol), was added a solution of phthalic anhydride (20 g, 0.135 mol) in anhyd.

17) L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston and Maruzen Co. Ltd., Tokyo, 1964, p. 93. See also Ref. 7 where the mp of **17** is reported 100—109°C.

18) Belg. 632—597, Oct. 21, 1963.

19) a) C. S. Marvel and S. M. McElvain, "Organic Syntheses," Coll. Vol. 1, p. 170. b) H. T. Clarke and E. R. Taylor, "Organic Syntheses," Coll. Vol. II, p. 135.

20) W. Tadros, A. B. Sakla, and A. A. A. Helmy, *J. Chem. Soc.*, 2687 (1961).

21) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, p. 226.

22) Determined by the method of; C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

dioxane (150 ml) over a 2 hr period. After the mixture has been heated for another hour, the mixture was hydrolyzed by 100 ml of water and the organic layer was dried over anhyd magnesium sulfate. The flash evaporation of the solvent then afforded a crude oil, which was distilled *in vacuo* to give a yellow oil; bp 200°C/4 mmHg. The treatment of the oil in hot ethanol separated **9a** (colorless crystals), 2 g (6%); mp 117°C; IR ($CCl_4$) 1775 $cm^{-1}$ (C=O).

*Preparation of 3,3-Diphenylcoumaran-2-one (**9b**).* A mixture of benzil (50 g), phenol (50 g), and zinc chloride (50 g) was treated according to a procedure previously reported.[15] After following the work-up procedure, an oily material (*ca.* 1 g) was obtained. IR (liq. film) 1805 $cm^{-1}$ (C=O).

*o-Benzhydrylbenzilic Acid (**15b**).* Compound **2** (1.1 g, 3 mmol), dissolved in ethanol (20 ml), was heated with 20% aq potassium hydroxide (2 ml) under a solvent reflux for 5 hr. On cooling, a white solid separated; this was recrystallized from ethanol to give potassium *o*-benzhydrylbenzilate (**15a**); 1.2 g (95%); mp 297°C; IR (nujol dispersion) 3570 and 3350 (OH), 1605 $cm^{-1}$ (COOK).

Found: C, 70.66; H, 5.22%. Calcd for $C_{27}H_{21}O_3K$ (1.47 $H_2O$): C, 70.65; H, 5.25%.

An aqueous solution of **15a** was acidified with concd hydrochloric acid to give a precipitate of **15b**; 0.95 g (85%); mp 188°C (ethanol); IR (nujol dispersion) 3530 and 1695 $cm^{-1}$ (COOH); NMR (acetone-$d_6$) $\tau$ 2.53 (2H, m), 2.90 (15H, m), 3.31 (2H, m), 3.86 (1H, s).

Found: C, 82.53; H, 5.52%. Calcd for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62%.

*1-Ethoxy-1,3,3-triphenyl-2-indanone (**16a**).* A mixed solution of **2** (1.1 g, 3 mmol) and concd hydrochloric acid (5 ml) in ethanol (20 ml) was heated under reflux for 5 hr. After cooling, a white solid of **16a** separated from the solution; 0.9 g (73%); mp 166°C (cyclohexane); IR ($CCl_4$) 1760 (C=O) and 1085 $cm^{-1}$ (C–O); NMR ($CCl_4$) $\tau$ 2.96 (19H, m), 6.74 and 6.76 (2H, a pair of q, $J$=7 Hz), 8.86 (3H, t).

Found: C, 86.70; H, 5.98%. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.95%.

*1-Methoxy-1,3,3-triphenyl-2-indanone (**16b**).* A treatment of **2** (1.1 g, 3 mmol) with methanol similar to the above-described procedure used for **16a** gave **16b** (0.9 g, 78%); mp 168°C; IR ($CCl_4$) 1760 (C=O) and 1085 $cm^{-1}$ (C–O); NMR ($CDCl_3$, 60 MHz) $\tau$ 2.90 (19H, m), 6.82 (3H, s).

Found: C, 86.41; H, 5.47%. Calcd for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68%.

*1,3,3-Triphenyl-2-indanone (**17**).* A solution of **2** (1.1 g, 3 mmol) and 47% hydriodic acid (4 ml) in glacial acetic acid (15 ml) was heated for 1 min under solvent reflux.[16] After cooling, the solution was decolorized with 5% aq sodium bisulfite to give a colorless precipitate of **17**; 0.7 g (65%); mp 133—134°C (diethyl ether); IR ($CCl_4$) 1760 $cm^{-1}$ (C=O); NMR ($CCl_4$, 60 MHz) $\tau$ 2.85 (19H, m), 5.33 (1H, s).

Found: C, 89.67; H, 5.69%. Calcd for $C_{20}H_{20}O$: C, 89.97; H, 5.59%.

The authors wish to thank Mr. Takeda of the Shimadzu Co. for his help in taking the mass spectra. Thanks are also due to Mr. Takayuki Kida for the NMR measurement.