Table IV

Substituent	Rel concn of biphenyl[a]
4-F	4.5
4-Cl	
4-Br	4.9
2,5-Cl_2	19.8
2,4,5-Cl_3	30.5

[a] On the scale of Table III.

Table V

Substituent	Yield, mol %	Mp, °C (acid)	Registry no.	Dec point, °C (Ag salt)
4-F	60	Syrup	369-51-7	220
4-Cl	35	92–93	100-03-8	304
4-Br	89	108	1195-33-1	251
2,5-Cl_2	90	99–101	61558-25-6	224
2,4,5-Cl_3	80	150–152	10439-21-1	218

chloroterphenyl. There was a considerable amount, 14.3 on the scale of Table II, of product of composition $C_{18}H_{11}Cl_3S$, confirmed by high-resolution precise-mass measurement, presumably having the structure $ClC_6H_4SC_{12}H_7Cl_2$, such as might arise from reaction of a chlorophenylthio radical and dichlorobiphenyl. The corresponding compound containing two fewer hydrogen atoms, tentatively pictured as chlorophenyl dichlorodibenzothiophene, also was confirmed by high-resolution precise-mass measurement.

Experimental Section

Benzene- and *p*-toluenesulfinic acids were purchased from Aldrich Chemical Co. The other benzenesulfinates were prepared by the method of Baldwin and Robinson,[8] by reduction of the corresponding benzenesulfonyl chlorides with aqueous sodium sulfite at 0–10 °C (Table V).

Silver salts were prepared by adding filtered solutions of sodium sulfinates to aqueous silver nitrate in 5% excess at 20 °C in dim light, collecting the precipitated silver salt on a filter, washing thoroughly with cold water, and drying in vacuo at 80 °C.

For pyrolysis, the silver salt, 20 mmol, was spread evenly in a Pyrex tube, swept with dry nitrogen, and heated in a furnace. The cooled products were extracted with ether, the ether solutions filtered and evaporated, and the residues analyzed by gas chromatography, 70-eV and low-voltage mass spectroscopy (low resolution), supplemented by high-resolution precise-mass measurements where shown in the tables, and directly coupled gas chromatography–mass spectrometry. Low-resolution mass spectra were measured on a Du Pont Model 21-104 instrument using electrical scanning, with normal and low-voltage electron energies set at 70 and 7.5 eV nominal, and with inlet and source temperatures of 350 and 250 °C, respectively. Directly coupled gas chromatography–mass spectrometry utilized a 5 ft × 0.125 in. stainless steel column packed with 10% SE-30 on Chromosorb W, coupled via a jet-orifice separator to a Du Pont Model 21-491 mass spectrometer; electron energy was 70 eV and ion source temperature was 250 °C. High-resolution measurements were made on a CEC Model 21-110B mass spectrometer with 70-eV electrons and inlet and source temperatures approximating those used for the low-resolution spectra. Mass measurements were obtained via the A.E.I. DS50 system at a resolution of 10 000 (10% valley definition) except in cases where peaks of interest—especially some due to chlorinated species—were poorly resolved from perfluoroalkane reference peaks. In such cases, we resorted to peak matching at a resolution of 20 000. Silver phthalate and silver diphenate upon pyrolysis gave mostly black polymer as did other silver polycarboxylates.[1] The polymer was extracted with acetone; the small amount of distillate was dissolved in acetone, combined with the extract, and analyzed by gas chromatography. Biphenylene was prepared by the method of Logullo, Switz, and Friedman.[9]

Registry No.—Silver benzenesulfinate, 7449-23-2; silver thiophenolate, 22758-12-9.

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The Mechanism of the Photoreaction of 1,2-Benzocyclobutenedione in Ethanol. The Photochemistry of *o*-Carboethoxybenzaldehyde

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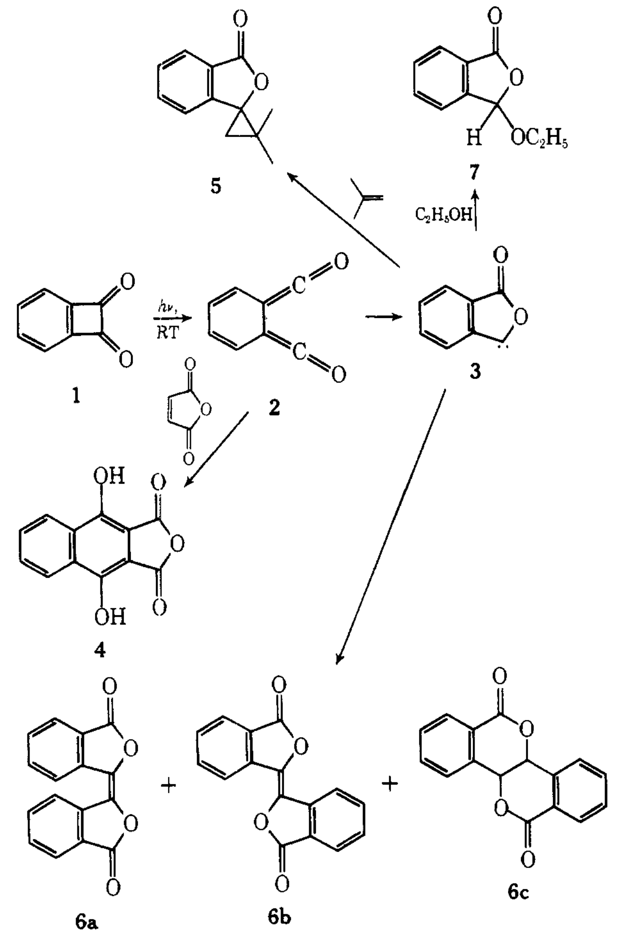
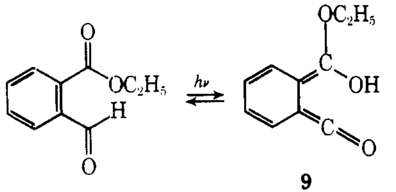
The ultraviolet irradiation of *o*-carboethoxybenzaldehyde (**8**) in ethanol gives the isomeric 3-ethoxyphthalide (**7**). The photoenol **9** of **8** can be trapped by a Diels–Alder reaction with maleic anhydride. Irradiation of **8** in ethanol-d_1 results in deuterium incorporation in **8** via the intermediate photoenol **9**. With the observation that **8** is photochemically isomerized to 3-ethoxyphthalide (**7**), *o*-carboethoxybenzaldehyde (**8**) is proposed as a likely intermediate in the known photoconversion of 1,2-benzocyclobutenedione (**1**) to 3-ethoxyphthalide (**7**).

In 1968 Staab and Ipaktschi reported that the ultraviolet irradiation of benzocyclobutenedione (**1**) at room temperature initially produced bisketene **2** which subsequently isomerized to oxacarbene **3**.[1,2] Chemical evidence was obtained supporting the intermediacy of both **2** and **3**. Specifically, irradiation of **1** with maleic anhydride gave an excellent yield of adduct **4** (presumably via bisketene **2**), irradiation of **1** with isobutylene gave the spirolactone **5** in 65% yield, and irradiation of **1** in inert solvents gave the dimers **6**. In 1971, Chapman, McIntosh, and Barber found that the photolysis of **1** at 77 K as a thin film gave dimers **6** but produced no detectable (by infrared spectroscopy) bisketene **2**.[3a] These workers thus concluded that bisketene **2** was not produced, at least under these experimental conditions, and that carbene **3** arose directly from **1**. Kolc also studied the low-temperature photochemistry of **1** matrix isolated in EPA at 77 K and sim-

Scheme I



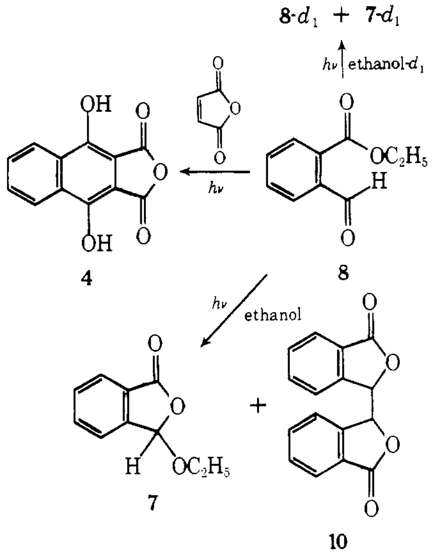
ilarly found no evidence supporting the formation of bisketene **2**.[4] However, Chapman et al.[3b] have subsequently reported that irradiation of **1** matrix isolated in argon at 8 K gave benzyne, carbon monoxide, and bisketene **2**. In their initial investigation, Staab and Ipaktschi also reported that irradiation of dione **1** in ethanol produced dimer **6c** (4% yield) and 3-ethoxyphthalide (**7**, 39% yield).[1] 3-Ethoxyphthalide (**7**) was presumed to arise via the oxacarbene **3**, a postulate in harmony with the formation of dimers **6** and spirolactone **5** and the observations of Chapman et al.[3] However, we envisioned that *o*-carboethoxybenzaldehyde (**8**) and/or its photoenol **9** were



also likely intermediates in the formation of **7** from **1**. We now wish to present evidence that this indeed may be the case and that **7** most likely arises from **1** by a pathway that does not directly involve either **2** or **3**. Our conclusions stem mainly from a study, described herein, of the photochemistry of *o*-carboethoxybenzaldehyde (**8**) and the remarkable similarity between the photochemistry of **8** and benzocyclobutenedione (**1**).

Results and Discussion

Scheme II

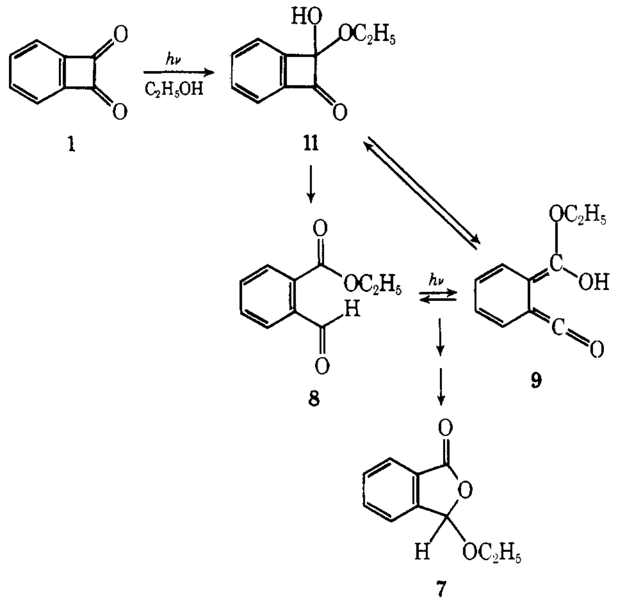


The required *o*-carboethoxybenzaldehyde (**8**)[5] was prepared by the Stevens reduction[6] of ethyl-*o*-cyanobenzoate[7] and was easily purified by vacuum distillation. Our observations on the photochemistry of *o*-carboethoxybenzaldehyde (**8**) are summarized in Scheme II. The photoreactions were analyzed by gas chromatography. Thus the ultraviolet irradiation of aldehyde **8** in ethanol solution gave 3-ethoxyphthalide (**7**,[8] 35% yield) and a dimer, presumably **10**[9,10] (47% yield). A refluxing solution of **8** in ethanol was stable for a period comparable to the irradiation time used above; however, extended refluxing gave rise to the diethyl acetal of **8**. An irradiation of **8** in ethanol-d_1 was stopped at 50% reaction. Both the 3-ethoxyphthalide (**7**) produced and the remaining *o*-carboethoxybenzaldehyde (**8**) were isolated pure by gas chromatography and their isotope distribution was determined by mass spectrometry; **8** contained 46% d_1 and **7** contained 79% d_1, the balance being d_0 in both cases. A solution of **8** and maleic anhydride gave a good yield of adduct **4** upon irradiation. However, irradiation of **8** in isobutylene gave only a trace of the spirolactone **5**, the major product being 3-ethoxyphthalide **7**. The simultaneous irradiation of separate solutions of **1** and **8** in ethanol showed that diketone **1** consistently decomposed about 30% faster than *o*-carboethoxybenzaldehyde (**8**). For example, in one such experiment, the photochemical half-lives of **1** and **8** were 5.5 and 7.2 min, respectively. Plots of log [**1**] and log [**8**] vs. irradiation time in ethanol were linear to about 75% reaction. The photochemical half-life of *o*-carboethoxybenzaldehyde (**8**) was solvent dependent. Approximate half-lives of **8** in several solvents were determined to be as follows: ethanol, 8 min; acetonitrile, 21 min; methylene chloride, 190 min; cyclohexane, >300 min; carbon tetrachloride, >300 min.[12] In each case the only product detected by gas chromatography was 3-ethoxyphthalide (**7**), but no further attempts were made to analyze the products formed in the aprotic solvents above.

We were also able to reproduce the photochemistry of dione **1**, as described by Staab and Ipaktschi and as shown in Scheme I. Thus, irradiation of **1** with maleic anhydride gave the adduct **4** in 67% yield and irradiation with isobutylene gave the spirolactone **5**, although gas chromatography also indicated the presence of other unidentified products in addition to **5**. Irradiation of **1** in ethanol gave 3-ethoxyphthalide (**7**) as the major product, also in agreement with the observation of Staab and Ipaktschi.

With our observation that **8** is photochemically isomerized to **7**, *o*-carboethoxybenzaldehyde (**8**) now can be considered as a possible intermediate in the photoconversion of **1** to **7** (see Scheme III). The observed deuterium incorporation and the formation of adduct **4** establish the reversible formation of photoenol **9** from **8**. Mellows and Sammes have similarly trapped the photoenol of *o*-tolualdehyde with maleic anhy-

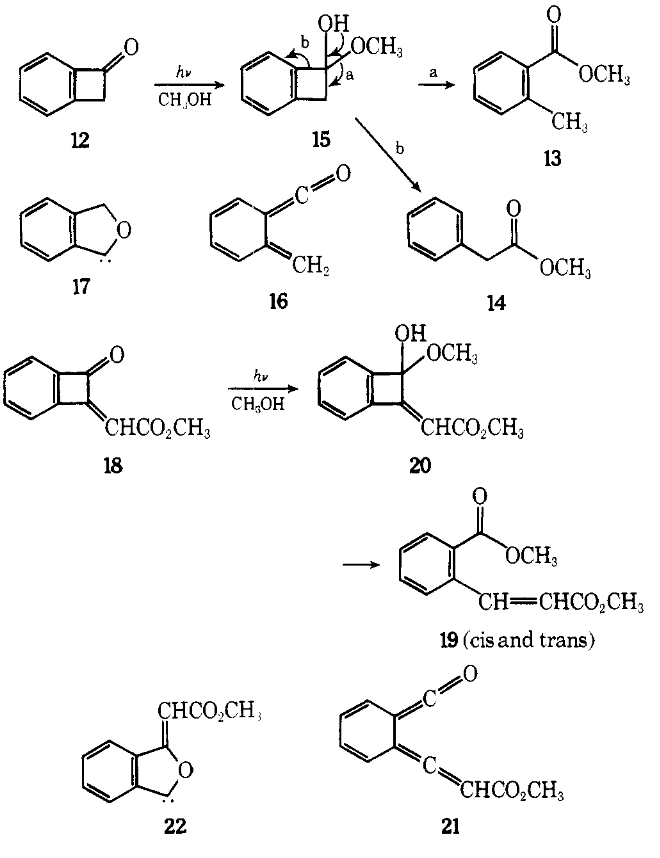
Scheme III



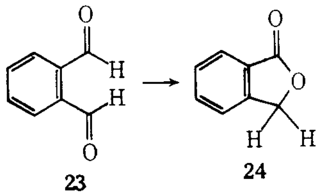
dride.[11] The photoenol **9** can also arise from dione **1** by the addition of ethanol to an excited state of the dione **1**, initially producing **11**; hemiketal **11** can then undergo ring opening to give either **9** and/or **8**. Photoenol **9** may be in equilibrium with **11**; such equilibria have been demonstrated for other benzocyclobutenols.[13]

The mechanism of Scheme III is consistent with the formation of **7** from **1** and also finds analogy in the photochemistry of other benzocyclobutenones. For example, irradiation of benzocyclobutenone (**12**) in methanol produces methyl *o*-toluate (**13**) and methyl phenylacetate (**14**)[14] (Scheme IV); no products attributable to carbene **17** were obtained. Hedaya has proposed that the hemiketal **15**, which is analogous to **11**, may be an intermediate common to both products.[14] Similarly, irradiation of the keto ester **18** in methanol produces cis and trans esters **19**; no products derived from the oxacarbene **22** were detected.[15] The formation of esters **19** from **18** is in accord with the intermediacy of a hemiketal, **20**. The low-temperature photochemistry of **18** is also in agreement with this postulate in that the ketene **21** could not be detected as an intermediate by infrared spectroscopy.[16] Thus all three of the benzocyclobutenones, **1**, **12**, and **18**, can now be envisioned as undergoing photodecomposition in alcohol solution by a common pathway involving hemiketal formation followed by ring opening.[17] In alcohol solution there is no compelling evidence supportive of the intermediacy of either ketenes (e.g., **2**, **16**, **21**) or carbenes (e.g., **3**, **17**, or **22**). In contrast, carbenes are well-established intermediates in the photochemistry of certain alicyclic ketones.[18] An observation by Chapman et al.[3b] is the basis for a further argument against bisketene **2** as an intermediate in the irradiation of benzocyclobutenedione **1** in ethanol at room temperature. Irradiation of **1** in matrix isolated argon–methanol at 8 K gave bisketene **2**, identified by infrared spectroscopy. Warming the matrix resulted in the concurrent disappearance of the infrared bands of **2** and the appearance of the infrared spectrum of dimethyl phthalate. Thus the reaction product of **2** and methanol is dimethyl phthalate. By analogy, if bisketene **2** were generated during the irradiation of dione **1** in ethanol, diethyl phthalate should be formed; however, the latter is not a photoproduct of **1** in ethanol at room temperature.[1]

Scheme IV



We have not examined the question of how **8** is isomerized to **7**. This process bears a superficial resemblance to the well-studied isomerization of *o*-phthalaldehyde (**23**) to phthalide (**24**) and may well proceed via an analogous mechanism.[9,19–23] In fact, *o*-carboethoxybenzaldehyde (**8**) and *o*-phthalaldehyde (**23**) both undergo photoenolization and produce dimeric photoproducts which differ only in oxidation state, also suggesting a similar mechanism for their photodecomposition. However, the mass spectra of **23** and **24** are practically indistinguishable,[21] whereas the mass spectra of **8** and **7** are easily distinguishable, suggesting that an electron impact induced rearrangement analogous to the photochemical process may occur in the case of **23** but not with **8**.



Experimental Section

All irradiations were performed with a Rayonet photochemical reactor Model RPR-208, producing approximately 120 W of principally 253.7-nm ultraviolet light. All photoreactions were carried out at a temperature of 35 °C. The photochemical reaction vessels consisted of cylindrical quartz vessels ranging in size from 10-mL to 75-mL capacity (1.2–4.0 cm o.d.). These were fitted with a ground glass stopper and a side arm fitted with a rubber septum for withdrawing samples. Infrared spectra were determined with a Perkin-Elmer Model 621 or 237 spectrometer. Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected. NMR spectra were determined in CCl_4 using Me_4Si as an internal standard with either a Varian A-60 or HA-100 spectrometer. Mass spectra were determined using a Hitachi Perkin-Elmer RMU-6E mass spectrometer operating at 70 eV. Gas chromatography analyses were determined with either a 6 ft × 0.125 in. column of 3% neopentyl glycol succinate on Chromosorb W (80/100) (column A), a 12 ft × 0.125 in. column of 3% neopentyl glycol succinate on Chromosorb W (80/100) (column B), or a 6 ft × 0.25 in. column of 3% neopentyl glycol succinate on Chromosorb W (80/100) (column C).

Preparation of *o*-Carboethoxybenzaldehyde (8). Using the method of Slotta,[24] a mixture of anhydrous commercial ether (240

Table I. Photochemical Half-Lives of *o*-Carboethoxybenzaldehyde (8) in Various Solvents[a]

Solvent	$t_{1/2}$
Ethanol[b]	8 min
Acetonitrile[c]	21 min
Methylene chloride[c]	190 min
Cyclohexane[b]	No change in 5 h
Carbon tetrachloride[b]	No change in 5 h

[a] Reactions were followed by GC (column B, 180 °C). [b] *n*-Eicosane was used as a GC internal standard. [c] No GC internal standard was used.

mL) and anhydrous tin(II) chloride[6] (64 g, 0.415 mol) was added to a one-neck round-bottom flask equipped with a reflux condenser and magnetic stirrer. Hydrogen chloride gas was bubbled through the mixture until it was saturated, at which point the two-phase solution became homogeneous. To this was added ethyl *o*-cyanobenzoate[7] (40 g, 0.229 mol) and additional HCl gas was bubbled through the solution for about 15 min. The homogeneous solution was stirred for 2 h and left overnight. Two phases again resulted with the bottom phase full of white crystals. These were filtered and washed with ether to give the intermediate tin salt[6] (95.85 g, 97% yield). The salt was dissolved by heating and vigorous stirring in H_2O; the water was cooled and then extracted with three 100-mL portions of anhydrous ether. The ether layer was washed with 150 mL of 5% $NaHCO_3$ solution. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The resulting oil, containing some white crystals, was vacuum distilled, bp 95–100 °C (0.1 mm), to yield 4.4 g (11%) of **8**: NMR δ 1.35 (t, 3 H), 4.35 (q, 2 H), 7.45–8.00 (m, 4 H), 10.52 (s, 1 H);[25] UV λ_{max} (ethanol) 233 nm (ϵ 5740) and 288 (1160); IR (neat) 1720, 1600, 1280, 1140, 1080, 760 cm^{-1}; mass spectrum *m/e* (rel intensity) 178 (5), 177 (1), 150 (45), 149 (50), 134 (15), 133 (85), 132 (20), 122 (11), 121 (12), 106 (18), 105 (100), 104 (52), 103 (2), 93 (7), 90 (4), 77 (45), 76 (28), 75 (6). Gas chromatography (column A at 180 °C) showed that this material contained approximately 1% of 3-ethoxyphthalide (**7**) as an impurity.

Photoreaction of *o*-Carboethoxybenzaldehyde (8) in Ethanol. A mixture of **8** (495 mg, 2.78 mmol) and absolute ethanol (75 mL) was placed in a quartz vessel. The vessel was flushed with nitrogen, closed, and irradiated for 3 h. The solvent was evaporated in vacuo and the residue was vacuum distilled at 75–80 °C (0.5 mm) to give a clear liquid (193.6 mg) that solidified on standing (mp 45–60 °C). This distillate was recrystallized from cyclohexane to give 174.3 mg (35%) of 3-ethoxyphthalide (**7**): mp 65–66 °C (lit.[8] mp 66 °C); NMR δ 1.27 (t, 3 H), 3.87 (split quartet, 2 H), 6.30 (s, 1 H), 7.40–7.90 (m, 4 H); UV λ_{max} (ethanol) 208 nm (ϵ 8100), 231 (11 000), 275 (1390), and 283 (1290); mass spectrum *m/e* (rel intensity) 178 (2), 177 (2), 150 (10), 149 (13), 134 (40), 133 (100), 105 (50), 104 (6), 91 (7), 90 (20), 77 (32), 76 (12), 51 (22), and 50 (10); IR (KBr) 2980, 1790, 1370, 1290, 1150, 1090, 1050, 940, and 750 cm^{-1}. The spectra of this material were identical with that of 3-ethoxyphthalide prepared by refluxing *o*-carboxybenzaldehyde in sulfuric acid and ethanol.[8]

The residue from the distillation was recrystallized from acetone to give 233.9 mg (47%) of **10**[10] as colorless crystals: mp 260–265 °C; IR (KBr) 1760, 1600, 1470, 1290, 1210, 1050, 760, and 690 cm^{-1}; mass spectrum *m/e* (rel intensity) 266 (1), 264 (1), 177 (2), 149 (4), 134 (10), 133 (100), 105 (13), 77 (14), 76 (3), and 51 (8). In a similar experiment, a solution of **8** (60 mg, 0.34 mmol), ethanol (10 mL), and *n*-eicosane (7.0 mg) (as a GC internal standard) was irradiated for 3 h. Quantitative analysis by gas chromatography, using the *n*-eicosane as an internal standard, showed that the yield of 3-ethoxyphthalide (**7**) was 36% and that 2.4% of the *o*-carboethoxybenzaldehyde (**8**) was unreacted.

Thermal Reaction of *o*-Carboethoxybenzaldehyde (8) in Ethanol. When a solution of **8** (86 mg, 0.48 mmol) and absolute ethanol (10 mL) was refluxed in the dark for 3 h, no 3-ethoxyphthalide (**7**) was formed as determined by GC (column C at 170 °C). However, another product peak was noticeable and reflux was continued for an additional 39 h. A portion of this new compound was then purified by preparative GC (column C at 170 °C) to provide the diethyl acetal of **8**: IR (neat) 3440, 2998, 2950, 1729, 1608, 1587, 1454, 1374, 1343, 1292, 1270, 1204, 1142, 1122, 1072, 1031, and 759 cm^{-1}; NMR δ 1.25 (m, 9 H), 3.55 (quartet, 4 H), 4.30 (q, 2 H), 6.18 (s, 1 H), 7.20–7.85 (m, 4 H); mass spectrum *m/e* (rel intensity) 224 (7), 207 (45), 177 (35), 149 (65), 133 (100), 105 (33), 77 (20), 76 (8), and 75 (7).

Photoreaction of Benzocyclobutenedione (1) in Ethanol. Following the procedure of Staab,[1] a quartz vessel was charged with benzocyclobutenedione (**1**, 45 mg, 3.4 mmol), absolute ethanol (10 mL), and octadecane (7 mg); the latter was used as a GC internal standard. After irradiation under nitrogen for 3 h, GC (column A, 180 °C) showed that 3-ethoxyphthalide (**7**) was formed in a 68.5% yield.

Photolysis of *o*-Carboethoxybenzaldehyde (8) in Ethanol-d_1. A solution of *o*-carboethoxybenzaldehyde (**8**, 47 mg, 2.6 mmol) in ethanol-d_1 (5 mL) was irradiated until about 50% of **8** disappeared as indicated by GC (column A, 180 °C). Pure samples of both *o*-carboethoxybenzaldehyde (**8**) and 3-ethoxyphthalide (**7**) were then obtained from the reaction mixture by preparative GC. The isotopic distribution of **8** was calculated[26] from the mass spectrum of the sample as 53.7% d_0 and 46.3% d_1; that of the 3-ethoxyphthalide (**7**) was calculated to be 21.4% d_0 and 78.6% d_1.

Photochemical Half-Lives of Benzocyclobutenedione (1) and *o*-Carboethoxybenzaldehyde (8) in Ethanol. The photochemical half-lives of **1** and **8** were determined by the simultaneous irradiation of solutions of **1** and **8** in ethanol. The identical reaction vessels were constantly rotated inside the photoreactor to assure equal exposure to the light. Aliquots were periodically withdrawn and analyzed by GC, using *n*-eicosane as an internal standard. Plots of log [**1**] and log [**8**] vs. time were linear to about 75% reaction. In a typical run, a solution of benzocyclobutenedione (**1**, 20.3 mg, 1.54 mmol) and *n*-eicosane (4.2 mg) in absolute ethanol (10 mL) and a solution of *o*-carboethoxybenzaldehyde (**8**, 22.2 mg, 1.24 mmol) and *n*-eicosane (5.2 mg) in absolute ethanol (10 mL) were simultaneously irradiated for 80 min. A few microliters of each solution were withdrawn with a syringe every few minutes and analyzed by GC. Photochemical half-lives obtained in three such runs follow.

	Run 1	Run 2	Run 3
$t^{1/2}{}_1$	15	5.5	9.5
$t^{1/2}{}_8$	21	7.2	12
$t^{1/2}{}_8/t^{1/2}{}_1$	1.4	1.3	1.3

No attempts were made to control temperature or light intensity from run to run.

Photolysis of *o*-Carboethoxybenzaldehyde (8) with Maleic Anhydride. A mixture of **8** (148 mg, 0.83 mmol), maleic anhydride (209 mg, 2.1 mmol), methylene chloride (11 mL), and cyclohexane (39 mL) was irradiated under nitrogen for 12 h. The residue was scraped off the sides of the reaction vessel and washed with H_2O to give 171 mg (90%) of **4** as yellow crystals: mp 280 °C dec (lit.[1] mp 280 °C); IR (KBr) 3420, 1810, 1740, 1630, 1300, 1245, 985, 900, and 745 cm^{-1}; mass spectrum *m/e* (rel intensity) 231 (15), 230 (100), 213 (12), 212 (88), 185 (12), 184 (96), 158 (16), 157 (7), 129 (23), 128 (70), 105 (6), 104 (12), 102 (43), 101 (29), 100 (7), 89 (8), 77 (14), 76 (24), 75 (31), 74 (20), 51 (25), 50 (18), and 39 (6). The MS and IR of this material were identical with those of an authentic sample of **4** prepared from **1** by the procedure of Staab and Ipaktschi.[1]

Photolysis of *o*-Carboethoxybenzaldehyde (8) with Isobutylene. A solution of **8** (176 mg, 0.99 mmol), isobutylene (4 g, 72 mmol), methylene chloride (17 mL), and cyclohexane (50 mL) was irradiated in a quartz reaction vessel for 21 h. The solvent was evaporated under reduced pressure, and the residue was extracted three times with hot petroleum ether (60–110 °C). The extracting solvent was evaporated and the remaining oil was vacuum distilled, bp 90–95 °C (0.4 mm). GC analysis (column B, 180 °C) showed the distillate to be a 99:1 mixture of **7** and **5**. A sample of **5** was purified by preparative GC (column C, 180 °C): IR (neat) 1760, 1620, 1480, 1290, 1110, 1030, 1010, 920, and 720 cm^{-1}; NMR δ 1.28 (d, 1 H), 1.32 (s, 3 H), 1.43 (s, 3 H), 1.6 (d, 1 H), 7.1–8.0 (m, 4 H); mass spectrum *m/e* (rel intensity) 188 (8), 173 (8), 134 (9), 133 (100), 105 (12), 104 (6), 77 (14), 76 (6), and 51 (8). The MS and IR of this sample were identical with those of an authentic sample of **5** prepared from **1** by the procedure of Staab and Ipaktschi.[1]

Photolysis of *o*-Carboethoxybenzaldehyde (8) in Various Solvents. A solution of *o*-carboethoxybenzaldehyde (**8**, 64 mg, 0.36 mmol) in each of the solvents of Table I (10 mL) was irradiated and the half-life of *o*-carboethoxybenzaldehyde (**8**) in each solvent was determined (Table I). The only product detected using GC (column B, 180 °C) was 3-ethoxyphthalide (**7**).

Registry No.—**1**, 6383-11-5; **4**, 5211-68-7; **5**, 5211-71-2; **7**, 16824-02-5; **8**, 34046-43-0; **8** diethyl acetal, 61634-64-8; *dl*-**10**, 21947-39-7; *meso*-**10**, 21947-73-9; ethanol, 64-17-5; maleic anhydride, 108-31-6; isobutylene, 115-11-7.

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Pyrolytic and Photochemical Wolff Rearrangement of Diazoindanones. Synthesis of 2-Carboalkoxybenzocyclobutenones

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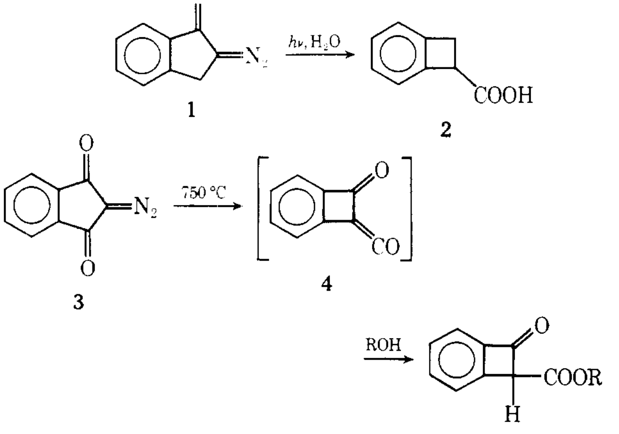
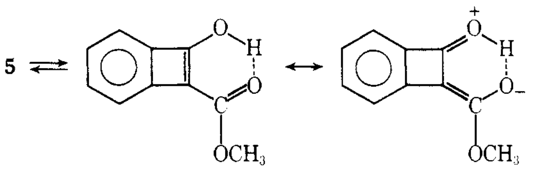
2-Carboalkoxybenzocyclobutenones **5–8** were prepared by the vapor phase pyrolysis of 2-diazo-1,3-indandione (**3**) with alcohols. Similarly the vapor phase pyrolysis of 2-diazo-1-indanone (**1**) with methanol gave methyl benzocyclobutene-1-carboxylate (**24**). These reactions are unusual examples of uncatalyzed thermally induced Wolff rearrangements leading to strained cyclic systems and suggest that the gas phase pyrolysis of cyclic α-diazo ketones may be of use in the synthesis of other strained ring systems. However, the vapor phase pyrolysis of 2-diazo-1,3-indandione (**3**) with water, ammonia, or *tert*-butylamine gave only ring-opened homophthalate derivatives. Ultraviolet irradiation of 2-diazo-1-indanone (**1**) with methanol also yielded methyl benzocyclobutene-1-carboxylate (**24**) as well as 2-methoxy-1-indanone (**26**). In contrast to its pyrolysis, the photolysis of 2-diazo-1,3-indandione (**3**) in methanol gave dimethyl homophthalate (**14**) as the major product.

The ring contraction of diazoindanones has proven to be a useful synthesis of several benzocyclobutene derivatives.[1] For example, the photolysis of aqueous solutions of 2-diazo-1-indanone (**1**) provided an early synthesis of benzocyclobutene-1-carboxylic acid (**2**).[2,3] More recently, Cava and Spangler reported that the gas phase pyrolysis of 2-diazo-1,3-indandione (**3**), under conditions in which the intermediate keto ketene (**4**) could be trapped by methanol, gave 2-carbomethoxybenzocyclobutenone (**5**).[4] The synthesis of **5** from **3** provided the first example of the formation of a strained ring system by an uncatalyzed thermal Wolff rearrangement. We now wish to record the experimental details of this synthetically useful process, to provide examples of other β-keto esters (**6–8**) which can be prepared in this way, to point out some limitations of the process, and to compare the gas phase pyrolysis of diazoindanones **1** and **3** with their solution photochemistry. The β-keto ester **5** is of interest in that its enol tautomer **9** is a benzocyclobutadiene derivative which might be expected to be stabilized not only by intramolecular hydrogen bonding but also by a "push-pull" resonance effect of



5, R = CH_3
6, R = $CH(CH_3)_2$
7, R = $C(CH_3)_3$
8, R = $C(CH_3)_2CH{=}CH_2$



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