for many helpful comments concerning the NMR analysis and P. Lefebvre for his help in the kinetic runs.

Registry No.—**1b**, 3068-88-0; **1c**, 15890-55-8; **1f**, 7379-74-0; **1g**, 43084-06-6; **1h**, 59092-50-1; **1i**, 59092-51-2; **2g**, 4941-92-8; **4f**, 59092-52-3; **4g**, 59092-53-4; **4i**, 59092-54-5; **5**, 59109-99-8; **6**, 59092-55-6; **7**, 59092-56-7; **8**, 59092-57-8; ketene, 463-51-4; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; methacrolein, 78-85-3; α-chloracrolein, 683-51-2; propynal, 624-67-9.

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Heterocyclic *N*-Oxides as Synthetic Intermediates. 4. Reaction of Benzyne with 1,3,4-Oxadiazin-6-one 4-Oxides and Related Compounds[1]

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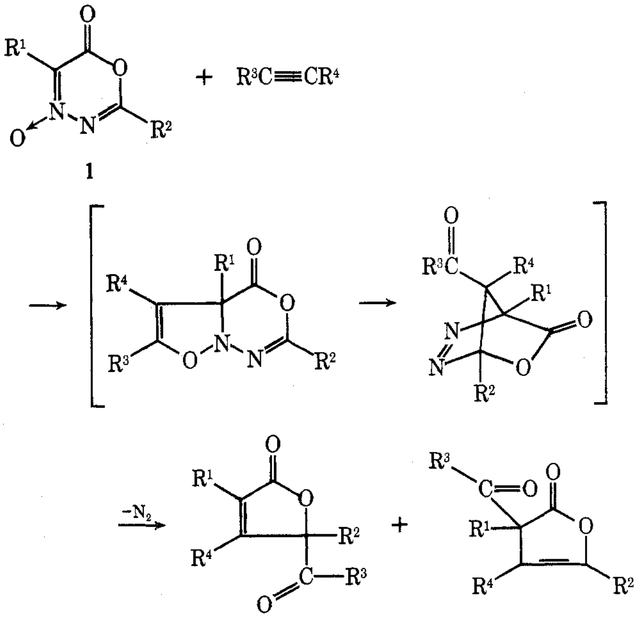
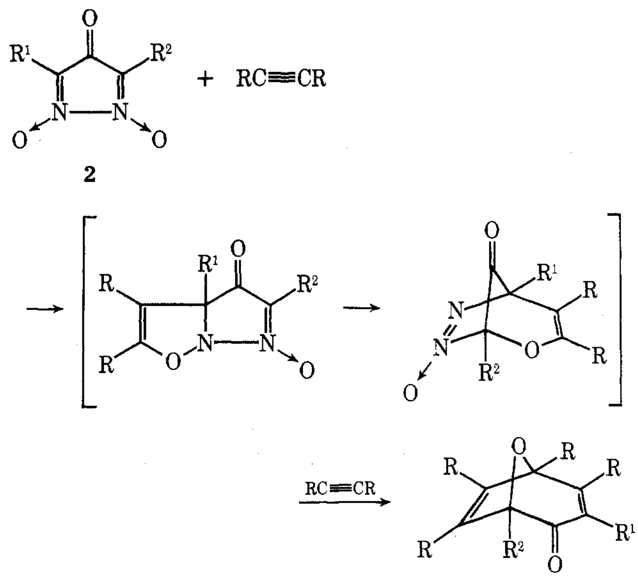
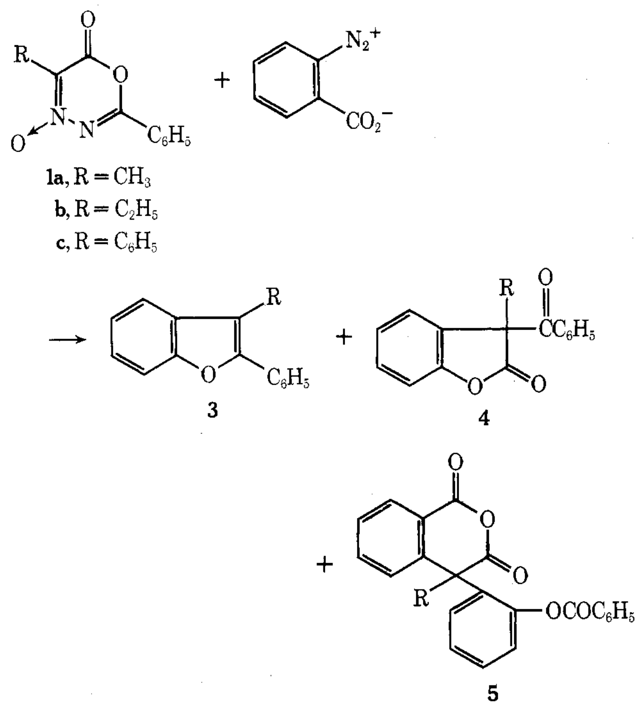
Benzyne, generated from benzenediazonium 2-carboxylate, condenses with 1,3,4-oxadiazin-6-one 4-oxides (**1**) to yield mixtures of substituted benzofurans (**3**) and acylbenzofuranones (**4**). A side product of this reaction, a diaryl homophthalic anhydride (**5**), apparently results from trapping of the benzyne precursor by an intermediate from the primary reaction. A mechanism to rationalize these products is presented and is substantiated in part by isolation of a 1:1 adduct (**10**) from benzyne and 2-methyl-5-phenyl-3,4-diazacyclopentadienone 3,4-dioxide.

It has been shown recently that 1,3,4-oxadiazin-6-one 4-oxides (**1**) react with a variety of acetylenes to produce acylbutenolides.[3] It was proposed that this transformation resulted from a hetero-Cope (3,3) rearrangement within a first-formed 1,3-cycloadduct. A related reaction involving a 1,3 rearrangement had also been investigated between acetylenes and 2,5-disubstituted 3,4-diazacyclopentadienone 3,4-dioxides (**2**).[4] Spurred by these results and those of Abramovitch and co-workers concerning the reactions of other heterocyclic *N*-oxides with benzyne,[5] we now have examined the reactions of this reactive "acetylene" with these two novel heterocyclic systems.





The oxadiazinone reactions proved to be complex and three main products could be isolated and identified when that heterocycle was heated with benzenediazonium 2-carboxylate as the benzyne precursor. In addition a fourth product was sometimes detected but has not been positively identified. (See Experimental Section.)

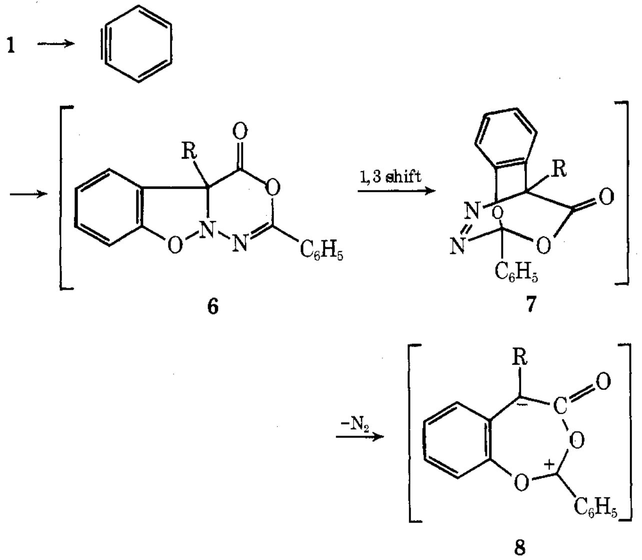

1a, $R = CH_3$
b, $R = C_2H_5$
c, $R = C_6H_5$

3

4

5

The structures of the furans and furanones were established by spectral methods, degradation, and independent synthesis (Experimental Section). The structure of the anhydrides is somewhat less securely established, but the evidence accumulated will be presented in a later section. Mechanistically one can account for these products by schemes similar to those already proposed for the other acetylene reactions.



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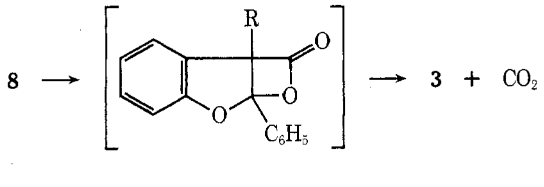
7

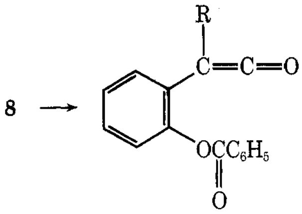
8

In this case a 1,3 rather than a 3,3 rearrangement occurs to preserve the benzene ring. Loss of nitrogen from **7** leads to a dipolar intermediate 8 analogous to that proposed earlier.[4] However, this seven-membered ring does not possess the resonance stabilization of the earlier pyrylium oxide[4] and as a result is a high-energy intermediate for which many decomposition paths may be envisioned.

Collapse to a β-lactone followed by loss of carbon dioxide furnishes the benzofurans.

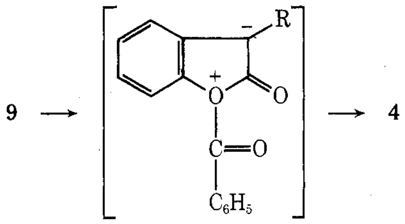


There is ample precedent in the literature for such a "[2 + 2]" cycloreversion.[6] However, a more accessible path involves ring opening to a ketene **9** and the major product-forming path apparently involves just such an intermediate.



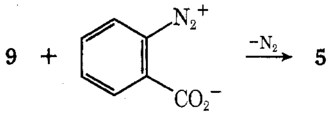
9a, $R = CH_3$
b, $R = C_2H_5$
c, $R = C_6H_5$

It is suggested that intramolecular closure of **9** can generate the benzofuranones.



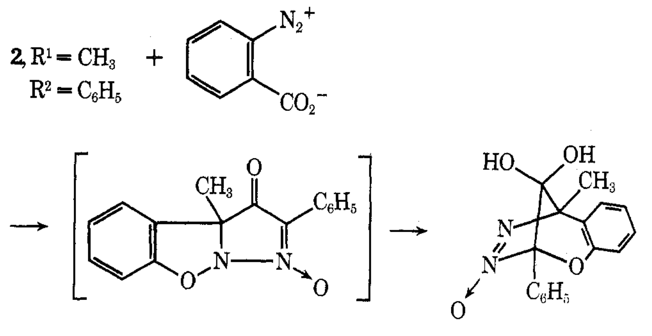
To establish this point *o*-benzoyloxydiphenylacetyl chloride was treated with a tertiary amine, Dabco, to generate ketene **9c**. From this reaction a mixture of **3c** and **4c** was isolated. (It is assumed that **3c** arises by ring closure of the ketene to **8** followed by intramolecular collapse to furan.) This reaction has yet to be explored in depth but at least it has been established that benzofurans and benzofuranones can be obtained from precursors suggested by this benzyne reaction.

Finally, the homophthalic anhydride **5** can be envisioned as arising from the reaction of the ketene with the benzyne precursor either before or after loss of nitrogen but before loss of carbon dioxide. (The existence of benzopropiolactone or its open-chain form has been suggested to account for other reactions.[7]) The interception of such a reactive intermediate demands that the ketene have a reasonable lifetime and it is probably significant that the yield of **5** is best when R = phenyl. (The experimental method employed whereby benzenediazonium 2-carboxylate was continually added to the reaction mixture over a period of time rather than having all reactants mixed at the beginning also helps to account for this result; see Experimental Section.)



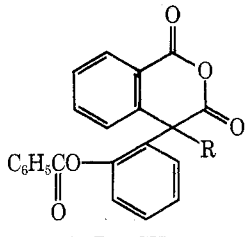
To test this mechanism the reaction of benzenediazonium 2-carboxylate with diphenylketene was examined and diphenylhomophthalic anhydride was isolated in 20% yield.

Some evidence that the proposed cycloaddition mechanism is correct was obtained by treating ketonitrone **2**, $R^1 = CH_3$, $R^2 = C_6H_5$, with benzenediazonium 2-carboxylate; a 1:1 adduct could be isolated as the hydrate **10**. The structure of **10** was surmised from its elemental analysis, spectral properties (see Experimental Section), and the similarity of its ir and NMR spectra to those of a similar adduct of **2** with acetylenedicarboxylic ester.[4] Since it is known that thermal loss of nitrous oxide is more difficult than that of nitrogen, the relative stability of **10** is not too surprising. However, the base peak (*m/e* 236) in the mass spectrum of **10** corresponded to the molecular ion less the elements of water and nitrous oxide (298 − 18 − 44 = 236).

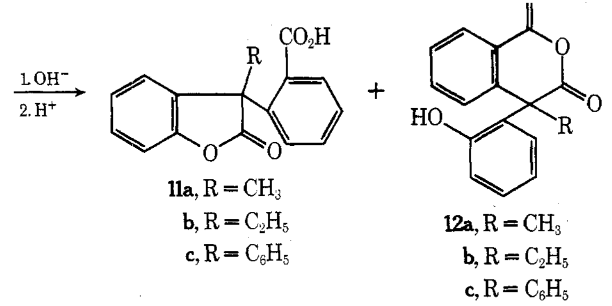


10

Reactions of the Homophthalic Anhydrides. The structure of 5 was suggested by elemental analyses and spectral properties. Attempts to degrade them to simpler compounds, however, led to some unforeseen results. The anhydride could not be selectively hydrolyzed without cleaving the ester and the result of alkaline hydrolysis of **5c** was to produce a mixture of **11c** and **12c**. Hydrolysis of **5a** was cleaner, however, and only **11a** was obtained.



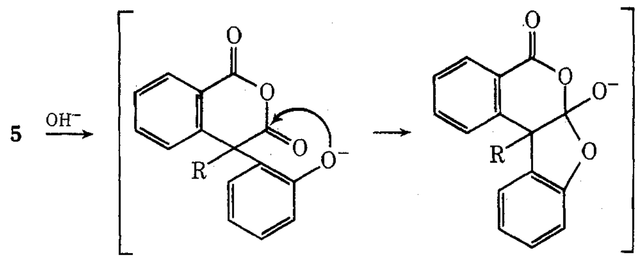
5a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5



11a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5

12a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5

These results suggest that a common intermediate **13** is formed which may partition in different ways depending upon the substituent R. Attempts to capture an intermediate by methylation either with diazomethane or dimethyl sulfate in base produced only the methyl ester of **11**. Although it has not been possible to synthesize **5**, the reactions described seem consistent with the proposed structures.



13

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer Model 137-A Infracord or a Perkin-Elmer 457. NMR spectra were measured on a Varian A-60A spectrometer; mass spectra were measured with an A.E.I. MS 902 mass spectrometer at 70 eV. We are indebted to Mr. Donald Schifferl for these measurements. The elemental analyses were done by Midwest Microlab.

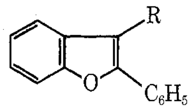
J. T. Baker silica gel (60–200 mesh) was dried at 135 °C for 4 h before use and the column chromatography was monitored by TLC on Baker-flex sheets (silica gel 1B-F).

Reaction of 1,3,4-Oxadiazin-6-one 4-Oxides with Benzyne. Benzenediazonium 2-carboxylate[8] was prepared in an apparatus described by Crews.[9] In all of the following experiments, this precursor was prepared from 1 g (7.3 mmol) of anthranilic acid.

Method A. A magnetically stirred solution of the oxadiazinone oxide[3] (4 mmol) in 1,2-dichloroethane (20–35 ml) was boiled gently on a steam bath. The suspension of benzenediazonium 2-carboxylate in 20 ml of 1,2-dichloroethane was added in several portions over a period of 5 min. The darkened solution was boiled for an additional 15 min. After cooling, the solution was concentrated in vacuo, and the resulting residue was chromatographed on a silica gel column (40 g) with benzene as the eluent.

The benzofuran derivatives **3a–c** were the first products eluted from the column. These derivatives were purified further by microdistillation or recrystallization as outlined in Table I.

Table I. Benzofuran Derivatives[a]



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Registry no.	Compd	R	Bp (0.3 Torr) or (mp), °C	Yield,[b] %
4521-08-8	**3a**[10]	CH_3	76–78 (bath)	7.5
59092-74-9	**3b**	C_2H_5	90–92 (bath)	6
13054-95-0	**3c**	C_6H_5	(120–122)[c] (CH_3OH)	1

[a] Biphenylene appears to be an impurity in all of these derivatives and it was not possible to obtain satisfactory elemental analyses of **3b**. [b] The yields are based on reacted oxadiazinone oxide and represent purified products. [c] Lit.[11] mp 123 °C.

The benzofuranones **4a–c** were the next compounds eluted from the column. These derivatives were also purified further by distillation or recrystallization as shown in Table II.

The third component eluted from the column was dissolved in a minimal amount of hot benzene and Skellysolve B was added to precipitate a solid. Several recrystallizations from the same solvent mixture yielded the homophthalic anhydride derivatives **5a–c** as colorless, crystalline solids. The physical properties of these derivatives are tabulated in Table III.

In the case of **5a**, the filtrate from the first recrystallization was concentrated in vacuo to leave a yellow solid. This solid was purified on a neutral alumina column (1 × 10 cm) with methylene chloride as the eluent. The yellow band was collected. After two recrystallizations from anhydrous methanol, it yielded bright yellow prisms (19 mg): mp 136–137 °C; ir (KBr) 1620, 1605, 1550, 1255, 1200, 1145, 830, 824, 783, 760, 695 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 1.68 (s, 3 H), 6.0–6.8 (m, 4 H),. 7.3–7.7 (m, 9 H); MS *m/e* rel intensity) 284 (100), 256 (25), 242 (32), 241 (100), 239 (40).

Anal. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.64; N, 0.0. Found: C, 87.81; H, 5.61; N, 0.0.

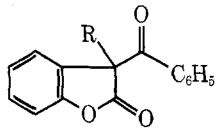
The final compounds eluted from the columns were identified as the unreacted oxadiazinone oxides **1a–c**.

Method B. The suspension of benzenediazonium 2-carboxylate in 25 ml of methylene chloride was added to an ice-cold solution of 2,5-diphenyl-1,3,4-oxadiazin-6-one 4-oxide (**1c**,[3] 4 mmol) in 35 ml of methylene chloride. This mixture was heated under reflux for 5 h and worked up as in method A. A comparison of the two methods is shown in Table IV.

3-Methyl-2-phenylbenzofuran was prepared according to Takagi and Ueda[10] with slight modification.

A mixture of 3-formyl-2-phenylbenzofuran[10] (5 mmol), 85% hydrazine hydrate (14.2 mmol), and potassium hydroxide (14.4 mmol) in 15 ml of diethylene glycol was refluxed for 1 h. The condenser was removed and the pot temperature was raised to 215 °C. The condenser was replaced and reflux was continued for an additional 3.5 h. The cooled mixture was diluted with H_2O and extracted with ether. The ether layers were washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo. By distillation of the crude product under vacuum through

Table II. Benzofuranone Derivatives



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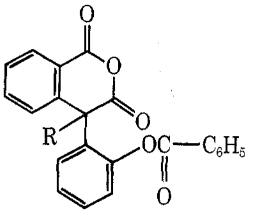
Registry no.	Compd	R	Bp (bath), °C (Torr)	Mp, °C	Yield,[c] %	Ir, cm^{-1}[d] Lactone C=O	Ir, cm^{-1}[d] Ketone C=O
59092-75-0	**4a**	CH_3[a]	106–108 (0.4)		36	1810	1680
59092-76-1	**4b**	C_2H_5[a,b]	148–150 (0.35)		30	1810	1680
59092-77-2	**4c**	C_6H_5		192–193[e]	15	1810	1675

[a] A small amount of the deacylated benzofuranone is a contaminant, as seen in the elemental analyses. This deacylation occurred on the silica gel column. [b] Calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26. Found: C, 75.82; H, 5.23. [c] The yields are based on reacted oxadiazinone oxide and represent purified products. [d] Measured as a KBr pellet or as a film. [e] Lit.[12] mp 186 °C.

Table III. Homophthalic Anhydrides[a]



5

Registry no.	Compd	R	Mp, °C	Yield,[b] %	Ir,[c] cm^{-1} Anhydride C=O	Ir,[c] cm^{-1} Ester C=O
59092-78-3	**5a**	CH_3	226–228	3	1785, 1740[d]	1740[d]
59092-79-4	**5b**	C_2H_5	198–200	1	1790, 1745	1745
59092-80-7	**5c**	C_6H_5	239–241	20	1780, 1740	1740

[a] Derivatives 5a and 5c were analyzed and gave satisfactory elemental analyses.[e] The molecular ions were present in the mass spectra but the base peak in all of them was *m/e* 105 ($C_6H_5CO^+$). [b] The yields are based on reacted oxadiazinone oxide and represent purified products. [c] Measured as KBr pellets. [d] In the case of 5a, high-resolution infrared spectroscopy resolved the two bands at 1740 cm^{-1}. [e] Calcd for $C_{23}H_{16}O_5$ (**5a**): C, 74.19; H, 4.30. Found: C, 73.95; H, 4.33. Calcd for $C_{28}H_{18}O_5$ (**5c**): C, 77.42; H, 4.15. Found: C, 77.02; H, 4.19.

Table IV

Compd	Method A (yield, %)	Method B (yield, %)
3c	1	Trace
4c	15	10
5c	20	12.5

a short path distilling head, 3-methyl-2-phenylbenzofuran (872 mg, 84%) was obtained as a colorless oil, bp 127–128 °C (0.3 Torr), mp 32–34 °C. The spectral properties of this oil were identical with those reported[10] and with those of **3a**.

3-Benzoyl-3-phenyl-2(3*H*)-benzofuranone was prepared according to Löwenbein and Simonis.[12]

Sodium (0.11 g) was added to a suspension of 3-phenyl-2(3*H*)-benzofuranone[13] (5 mmol) in 20 ml of anhydrous ether. This mixture was heated under reflux until the sodium was dispersed. Benzoyl chloride (4.7 mmol) was added to this mixture dropwise at room temperature. Then the mixture was heated under reflux for 15 min and suction filtered, and the filter cake was washed with 50 ml H_2O and air dried. Recrystallization from benzene yielded the product as white prisms (48%), mp 191–193 °C (lit.[12] mp 186 °C). Mixture melting point and spectral properties of this solid confirmed the structure of **4c**.

Deacylation of 3-Benzoyl-3-methyl-2(3*H*)-benzofuranone. A solution of 180 mg (0.7 mmol) of **4a** in benzene was placed on a silica gel column, prepared from 2 ml of H_2O and 10 g of silica gel, for 12 h. Elution of the column with 50 ml of C_6H_6 yielded a pale yellow oil (95 mg; 90%). Microdistillation of this oil under vacuum yielded 3-methyl-2(3*H*)-benzofuranone as a clear oil, bp (bath) 61–63 °C (4 Torr). Spectral properites of this oil were identical with those reported by Elix and Ferguson.[14]

Anal. Calcd for $C_9H_8O_2$: C, 72.97; H, 5.41. Found: C, 72.67; H, 5.41.

Treatment of Diphenylketene with Benzenediazonium 2-Carboxylate. Using method A above, 4 mmol of diphenylketene yielded a red semisolid after concentration in vacuo. This residue was dissolved in hot methanol and cooled in an ice bath to yield a yellow solid, from which 250 mg (19%) of 1,1-diphenylhomophthalic anhydride was obtained as white prisms (ethyl acetate): mp 230–232 °C (lit.[15] mp 228–229 °C); ir (KBr) 1790, 1750, 1295, 1250, 1150, 1025, 764, 757, 723, 702 cm^{-1}; MS *m/e* (rel intensity) 270 (100), 241 (26), 239 (22), 165 (17); no parent peak visible at 70 eV.

Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.25; H, 4.46. Found: C, 80.09; H, 4.46.

Alkaline Hydrolysis of 5c. A suspension of 250 mg (0.58 mmol) of **5c** in 12 ml of 5% NaOH was refluxed for 10 h. The solution was then acidified in an ice bath with 5% HCl. The white solid isolated after suction filtration was dried in vacuo at 67 °C for 4 h. This solid (184 mg, 97%) was an admixture of **11c** and **12c**: mp 238–250 °C; ir (KBr) 1800, 1775, 1730, 1695, 1465, 1290, 1230, 1130, 1070, 760, 720, 705 cm^{-1}. The carbonyl bands at 1775 and 1730 cm^{-1} were assigned to the anhydride moiety in **12c** and the bands at 1800 and 1695 cm^{-1} were assigned to the lactone and the carboxylic acid, respectively, in **11c**.

The acidic filtrate from the hydrolysis was extracted with ether (5 × 25 ml). The dried (Na_2SO_4) ether solution was evaporated in vacuo to yield 67 mg (95%) of benzoic acid as confirmed by a mixture melting point determination with an authentic sample.

Treatment of 11c and 12c with Diazomethane. A solution of 124 mg (0.38 mmol) of the solid admixture **11c** and **12c** in 16 ml of CH_2Cl_2 and 8 ml of CH_3OH was treated dropwise with an ethereal solution of diazomethane until the yellow color persisted. Concentration in vacuo left a solid, which yielded 102 mg (79%) of 3-(*o*-carbomethoxyphenyl)-3-phenyl-2(3*H*)-benzofuranone as white plates (CH_3OH): mp 145–147 °C; ir (KBr) 1800, 1725, 1470, 1450, 1425, 1285, 1265, 1235, 1145, 1085, 1065, 1055, 962, 952, 775, 760, 715, 700 cm^{-1}; NMR (acetone-d_6-Me_4Si) δ 3.53 (s, 3 H), 6.9–7.9 (m, 13 H); MS *m/e* (rel intensity) 344 (77), 284 (100), 268 (65), 257 (55), 255 (75), 251 (90).

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.74; H, 4.65. Found: C, 76.73; H, 4.90.

Treatment of 11c and 12c with Dimethyl Sulfate. A stirred solution of 184 mg (0.56 mmol) of **11c** and **12c** in 0.7 ml of 10% Na_2CO_3 and 2 ml of absolute C_2H_5OH was cooled in an ice bath. Dimethyl sulfate (52 μl, 0.56 mmol) was added dropwise from a syringe and stirring continued for 15 min. The ice-cold mixture was treated four more times with dimethyl sulfate while the pH was kept at 8 with 10% Na_2CO_3. After the final addition, the mixture was stirred overnight at room temperature and finally heated on a steam bath for 0.5 h. The pH was again adjusted to 8 and the white solid filtered and washed with liberal amounts of H_2O. This solid was purified on a silica gel column (10 g) with $CHCl_3$ as the eluent. The isolated solid was recrystallized from CCl_4 to yield 66 mg (35%) of the methyl ester of **11c** as white plates. A mixture melting point with the product from the diazomethane reaction was not depressed.

Alkaline Hydrolysis of 5a. Using the same procedure as for **5c**, 29.8 mg (0.08 mmol) of **5a** in 2 ml of 5% NaOH yielded 19 mg (88%) of a biege solid which was recrystallized from chloroform–hexane mixtures to yield 3-(*o*-carboxyphenyl-)-3-methyl-2(3*H*)-benzofuranone (**11a**) as white needles: mp 214–215 °C; ir (KBr) 2800–2500, 1800, 1695, 1475, 1460, 1400, 1255, 1230, 1140, 1090, 1075, 1030, 904, 895, 763, 702 cm^{-1}; NMR (acetone-d_6–Me_4Si) CH_3 δ 1.87; MS *m/e* (rel intensity) 268 (73), 224 (42), 195 (84), 194 (100), 165 (58).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.68. Found: C, 71.07; H, 4.96.

***o*-Benzoyloxydiphenylacetic acid** was prepared according to Arventi.[11]

3-Phenyl-2(3*H*)-benzofuranone[13] (3.2 g, 15.25 mmol) in 12 ml of 5% NaOH was added to a solution of 10.5 g of Na_2CO_3 in 65 ml of H_2O. This mixture was boiled until the mixture was homogeneous. This mixture was stirred mechanically while 2.25 ml (19.4 mmol) of benzoyl chloride was added dropwise at room temperature over a period of 45 min. The resulting mixture was then diluted with 150 ml of H_2O and acidified with 10% H_2SO_4. The resulting suspension was then boiled gently for a few minutes and after cooling, the crystalline mass was suction filtered and washed with 100 ml of warm H_2O. Recrystallization of this solid from glacial acetic acid yielded 3.02 g (62%) of *o*-benzoyloxydiphenylacetic acid in two crops; mp 148–151 °C (lit.[11] mp 152 °C); ir (KBr) 2725, 2600, 1735, 1690, 1255, 1210, 1175, 1090, 1060, 1025, 763, 732, 704 cm^{-1}.

***o*-Benzoyloxydiphenylacetyl chloride** was prepared in the usual manner starting with 1 g (3 mmol) of the carboxylic acid. The resulting yellow oil was used immediately: ir (KBr) 1805, 1735 cm^{-1}.

Dehydrochlorination of *o*-Benzoyloxydiphenylacetyl Chloride. The acid chloride was dissolved in 15 ml of dry C_6H_6. Dabco (387 mg, 3.46 mmol) was added and the mixture was refluxed for 21 h under a $CaSO_4$ drying tube. The salts were removed by filtration and the filtrate evaporated in vacuo to yield an orange semisolid. This residue was purified on a silica gel column (40 g) with benzene as the eluent. The first fractions yielded 2,3-diphenylbenzofuran (**3c**), 592 mg (73%). The second component was identified as **4c** (27 mg, 3%) by comparison of the ir spectrum with that of an authentic sample.

Treatment of 2-Methyl-5-phenyl-3,4-diazacyclopentadienone 3,4-Dioxide[16] with Benzenediazonium 2-Carboxylate. Using method A, the ketonitrone **2** (4 mmol) yielded a red residue after evaporation of volatiles. This residue was dissolved in 10 ml of ethyl acetate and treated with 1 ml of H_2O. After stirring for 1 h at room temperature, the ethyl acetate solution was decanted through a cone of Na_2SO_4. The ethyl acetate was evaporated in vacuo and the resulting residue was slurried in hot benzene.[17] After cooling, suction filtration yielded 655 mg (55%) of a beige powder. This powder was recrystallized from ethyl acetate–hexane mixtures to yield **10** as beige plates in several crops: mp 183–185 °C dec; ir (KBr) 3400, 1510 ($N{=}N{\rightarrow}O$), 1445, 1215, 1125, 1080, 1015, 850, 757 cm^{-1}; NMR (acetone-d_6–Me_4Si) δ 1.87 (s, 3 H), 5.82 (s, 1 H), 6.28 (s, 1 H), 7.0–7.65 (m, 7 H), 7.7–7.9 (m, 2 H); MS *m/e* (rel intensity) 236 (100), 135 (77), 208 (27), 207 (32), 105 (41), 77 (36), 44 (27), 28 (27), 18 (>100); the parent peak was faintly present at 70 eV.

Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.45; H, 4.70; N, 9.40. Found: C, 64.66; H, 4.80; N, 9.40.

Registry No.—**1a,** 28969-38-2; **1b,** 28969-39-3; **1c,** 28969-37-1; **2** ($R^1 = CH_3$; $R^2 = C_6H_5$), 16901-38-5; **10,** 59092-81-8; **11a,** 59092-82-9; **11c,** 59092-83-0; **12c,** 59092-84-1; benzyne, 462-80-6; benzenediazonium 2-carboxylate, 1608-42-0; 3-formyl-2-phenylbenzofuran, 37883-64-0; 3-methyl-2(3*H*)benzofuranone, 32267-71-3; diphenylketene, 525-06-4; 1, 1-diphenylhomophthalic anhydride, 14596-73-7; 3-(*o*-carbomethoxyphenyl)-3-phenyl-2(3*H*)-benzofuranone, 59092-85-2; *o*-benzoyloxydiphenylacetic acid, 59092-86-3; *o*-benzoyloxydiphenylacetyl chloride, 59092-87-4.

References and Notes

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(17) The benzene filtrate was separated on silica gel to yield a small amount of starting heterocycle and also a small amount of an unidentified orange oil.