aromatic), 7.83 (d, 1 H, aromatic), 8.46 (m, 2 H, aromatic); ^{13}C NMR (D_2O) 36.93, 58.87, 127.81, 134.96, 141.74, 151.11, 152,12, 176.69; IR (KBr disk) broad absorption 3130–2100, 1565, 1447, 1429, 1411, 1346, 1329, 1308, 1153, 853, 718, 685; MS (FAB) [M + 1] *m/e* 167; decomposed at 285 °C; $[\alpha]^{25}$ 9.68 (*c* 1.5, H_2O); chiral LC, 92:8 mixture of *d* and *l* isomers, ee 84%. Anal. C, H, N.

Preparation of *l*-4-Pyridylalanine (5b, *l* Isomer). The *l* isomer of **4b** (3307 mg, 14.90 mmol) was dissolved in 6 N HCl (60 mL) and the resultant mixture heated according to the general procedure. Normal workup and isolation gave 1725 mg (70%) of *l*-4-pyridylalanine as a white powder: ^1H NMR (D_2O) 3.20 (dd, 1 H, CH_2CH), 3.33 (dd, 1 H, CH_2CH), 4.08 (dd, 1 H, CH_2CH), 7.40 (d, 2 H, aromatic), 8.49 (d, 2 H, aromatic); ^{13}C NMR (D_2O) 38.73, 57.97, 128.01, 148.95, 151.74, 176.13; IR (KBr disk) broad absorption 3250–2250, 1609, 1559, 1406, 1360, 1345, 1316, 1217, 1005, 878, 839, 783, 627; MS (FAB) [M + 1] *m/e* 167; chiral LC, ee 96%; decomposed at 290 °C; $[\alpha]^{25}$ −8.3° (*c* 1.8, H_2O); high-resolution MS, calcd (M + H) 167.0821, found 167.0818.

Preparation of *d*-4-Pyridylalanine (5b, *d* Isomer). The *d* isomer of **4b** (348 mg, 1.57 mmol) was dissolved in 6 N HCl (5 mL) and the resultant mixture heated according to the general procedure. Normal workup and isolation gave 37 mg (14%) of *d*-4-pyridylalanine as a white powder: ^1H NMR (D_2O) 3.20 (dd, 1 H, CH_2CH), 3.33 (dd, 1 H, CH_2CH), 4.06 (dd, 1 H, CH_2CH), 7.40 (d, 2 H, aromatic), 8.49 (d, 2 H, aromatic); ^{13}C NMR (D_2O) 38.62, 57.87, 127.92, 148.88, 151.65, 176.02; IR (KBr disk) broad absorption 3250–2250, 1613, 1559, 1541, 1408, 1360, 1345, 1316, 1217, 1005, 839, 783; MS (CI) [M + H] *m/e* 167; chiral LC, 93:7 mixture of *d* and *l* isomers, 86%; decomposed at 280 °C; high-resolution MS, calcd (M + H) 167.0821, found 167.0826.

Acknowledgment. We thank Dr. Ranmali Wijayarathe of the analytical department of G. D. Searle for the chiral LC measurements.

Registry No. **1a**, 626-55-1; **1b**·HCl, 19524-06-2; **2**, 35356-70-8; **3a**, 115167-43-6; **3b**, 131905-72-1; L-**4a**, 95200-94-5; D-**4a**, 95200-93-4; L-**4b**, 131905-73-2; D-**4b**, 131905-74-3; L-**5a**, 64090-98-8; D-**5a**, 70702-47-5; L-**5b**, 37535-49-2; D-**5b**, 37535-50-5; (*R,R*)-[Rh(DIPAMP)(COD)]$^+BF_4^-$, 56977-92-5; (*S,S*)-[Rh(DIPAMP)(COD)]$^+BF_4^-$, 71423-54-6.

Supplementary Material Available: Copies of ^1H and ^{13}C NMR spectra of isomers of **4b** and **5b** (11 pages). Ordering information is given on any current masthead page.

Reformatsky Reaction: Carboxymethylenation of Cyclic Anhydrides and Reactions of Products Thereof†

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Methylidenephthalides 1, which have been prepared by exposing phthalic anhydride to either Perkin (R = H) or Wittig reaction conditions (R = Et),[1-3] are valuable precursors for the preparation of phthalazinone-1-acetic acid, **2** (R = H).[4] Certain derivatives of these acids have been identified as potent aldose reductase enzyme inhibitors targeted for treatment of diabetic complications.[5] In this connection, we were interested in preparing α-substituted phthalazinone-1-acetic acids which required access to α-substituted 3-((alkoxycarbonyl)methylidene)phthalides. The Perkin and Wittig reactions are of little value for the preparation of α,α-disubstituted compounds. However, the easy access to a variety of α-halo esters prompted us to explore the potential of the Reformatsky reaction as a method for the preparation of both 3-((alkoxycarbonyl)-methylidene)phthalides and their α-monosubstituted and α,α-disubstituted derivatives, even though the use of cyclic anhydrides in the reaction was unprecedented.

Scheme I

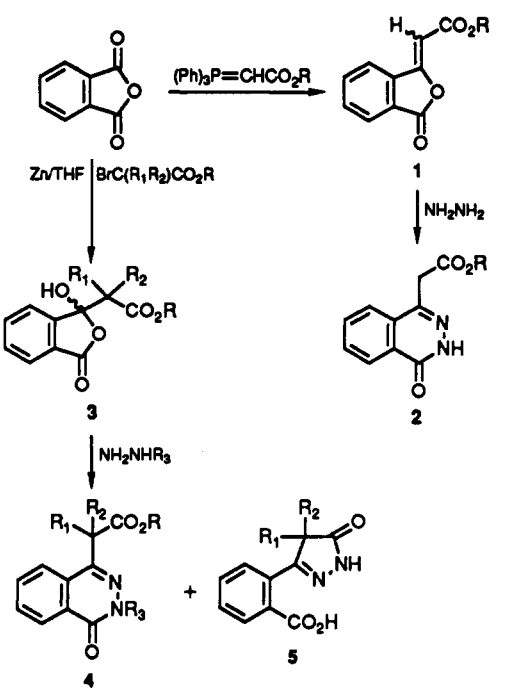
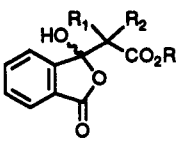


Table I



bromo ester		product R_1	R_2	R_3	yield, %
$BrCH_2CO_2Et$	**3a**	H	H	Et	40
$BrCH_2CO_2t$-Bu	**3b**	H	H	t-Bu	60
$BrCH(CH_3)CO_2Et$	**3c**	CH_3	H	Et	60
$BrCH(Ph)CO_2Et$	**3d**	Ph	H	Et	65
$BrC(CH_3)_2CO_2Et$	**3e**	CH_3	CH_3	Et	76
$BrC(CH_3)_2CO_2t$-Bu	**3f**	CH_3	CH_3	t-Bu	89

Results and Discussion

Exposure of phthalic anhydride and zinc in benzene or tetrahydrofuran to ethyl bromoacetate gave upon work up a crude oily product (Scheme I). Purification of this product by chromatography gave **3a** in low yield (15%). The yield in the Reformatsky reaction is often improved by switching from zinc to a zinc–copper couple.[6] Repetition of the above reaction using zinc–copper couple in tetrahydrofuran did significantly improve the yield (40%) and more importantly gave reproducible yields even when the reaction was run on a large scale. A further increase in the yield of **3a** to 60% was achieved by the addition of

† Dedicated to Professor Ernest Wenkert for his 65th birthday.

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(2) Chopard, P. A.; Hudson, R. F.; Searle, J. G. *Tetrahedron Lett.* **1965**, 2357.
(3) Murphy, P. J.; Brennan, J. *Chem. Soc. Rev.* **1988**, 16.
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0022-3263/91/1956-2587$02.50/0

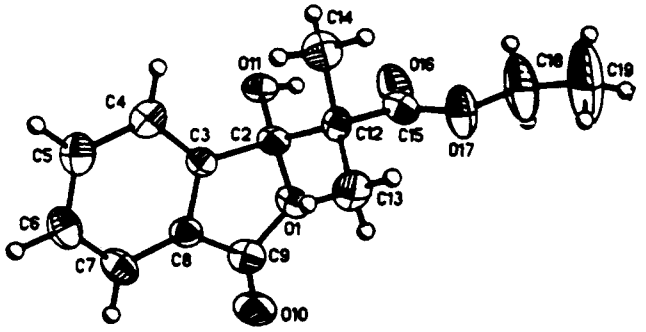
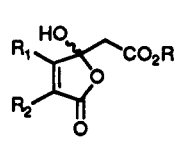


Figure 1.

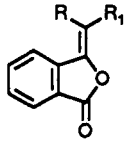
a few drops of dimethylformamide to the reaction mixture.[7a] Addition of trimethyl borate[7b] or the Pd^0 catalyst precursor, $(Ph_3P)_2PdCl_2$, to the reaction had no beneficial effect on the product yield.

We then examined the effect of the bromo ester reagents on the rate and yield of the reaction. As expected, the rate of reaction and/or yield of product increased with alkyl or phenyl substituents on the α-carbon or when ethyl ester was replaced by *tert*-butyl ester. For example, when ethyl 1-bromo-2,2-dimethylacetate was reacted with phthalic anhydride, a high yield (76%) of **3e** was obtained. The hydroxyisobenzofuranones prepared using phthalic anhydride as a substrate are listed in Table I.

The successful reactions with phthalic anhydride prompted us to examine nonaromatic anhydrides as substrates. We found the two anhydrides we tried underwent smooth reaction. Thus, exposure of 3,4,5,6-tetrahydrophthalic anhydride to ethyl bromoacetate and 2,3-dimethylmaleic anhydride to *tert*-butyl bromoacetate gave the desired Reformatsky products, **10** and **11**, in 46% and 89% yield, respectively.



10: R = Et; $R_1R_2 = (CH_2)_4$
11: R = *t*-Bu; $R_1 = R_2$ = Me

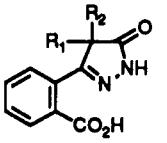


12: R = H, $R_1 = CO_2Et$
13: R = Ph; $R_1 = CO_2Et$

The structure of the Reformatsky product **3a** was confirmed by exposure to concentrated sulfuric acid to give the (*Z*)-phthalide **12**, identical with that reported by Gabriel[8a] and by Castro.[8b] Under the same dehydration conditions **3d** gave the (*E*)-phthalide **13**. A direct confirmation of the structure of the furanone products was deduced by a single-crystal X-ray analysis of **3e** (see Figure 1).[9a,b] It is interesting to note that the distance between the hydroxyl hydrogen and the carbonyl oxygen is 2.02 Å, strongly suggesting an intramolecular hydrogen bond between the two groups. In solution ($CDCl_3$), OH NMR signals of compounds **3a–f** occur between δ 6.25 and 7.24. A downfield shift of nearly 1 ppm between **3a** and **3f** is consistent with intramolecular hydrogen bonding.

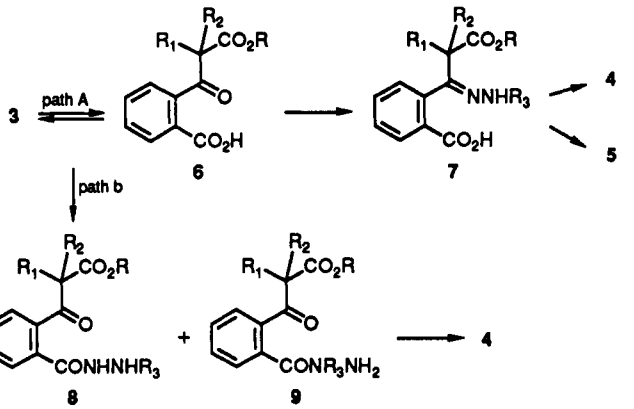
In pursuit of our initial objective, we attempted the transformation of alkyl 1,3-dihydro-1-hydroxy-3-oxoisobenzofuranacetates derived from phthalic anhydride to the corresponding phthalazinone acetic acids **4** (R = H). Exposure of hydroxyfuranones **3** (R = Et) to hydrazine hydrate yielded either a mixture of phthalazinone **4** and pyrazolinone **5** or exclusively **5** depending on R_1 and R_2. When $R_1 = R_2$ = H or R_1 = H and $R_2 = CH_3$, both products were obtained with the ratio of phthalazinone to pyrazolone increasing from 1:1 to 1.5:1. However, pyrazolinone **5** was the exclusive product from **3** (R = Et) when R_1 = H, R_2 = phenyl, and $R_1 = R_2$ = Me. The pyrazolinones that were prepared are listed in Table II.

Table II



compd	R_1	R_2	yield, %
5a	H	H	30
5b	H	CH_3	42
5c	H	Ph	84
5d	CH_3	CH_3	85

Scheme II



The most plausible pathways for the formation of the observed products are depicted in Scheme II. The increased ratio of pyrazolinone to ethyl 4-oxo-1-phthalazineacetate with increased α-substitution (from $R_1 = R_2$ = H to $R_1 = R_2$ = Me) in **3** when R = Et, the formation of pyrazolinones with a carboxylic acid appendage and the quantitative formation of **4** ($R_1 = R_2$ = H, R = t-Bu, R_3 = benzyl) from **3** ($R_1 = R_2$ = H, R = t-Bu) and benzylhydrazine are consistent with path a. The structure of the benzyl compound was confirmed by transformation to the corresponding known acid.[4] Path b would not be expected to yield **4** (R_3 = benzyl) as the sole product because of the ambiguity of attack associated with the unsymmetrical benzylhydrazine. Whereas alkylation of unsymmetrical hydrazines takes place on the more substituted nitrogen, acylation usually gives mixtures of 1- and 2-monoacyl derivatives.[10] In the present case path b should have given a mixture of **8** and **9** with only **9** capable of leading to the formation of **2** (R_3 = benzyl). Furthermore, pyrazolinone formation via path b would have yielded compounds with a carbohydrazide rather than a carboxylic acid appendage.

The desired phthalazinones, including **4** (R = t-Bu, $R_1 = R_2 = CH_3$, R_3 = H), were obtained as sole products starting from **3**, but by switching from the ethyl ester to the bulkier *tert*-butyl ester. The medicinal chemistry aspects of derivatives of the new 3,4-dihydro-4-oxo-1-

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(9) (a) We thank Dr. J. Bordner of Pfizer X-ray Laboratory for the data. (b) Structure of **3d** has also been confirmed by X-ray analysis and data is available as supplementary material.

(10) *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press Ltd.: New York, 1979; Vol. 2, p 228.

phthalazineacetic acids will be described elsewhere.

Experimental Section

Melting points are uncorrected. Structures of new compounds were confirmed by mass and NMR (300 MHz) spectroscopy. Flash chromatography was performed using silica gel. All new compounds gave satisfactory elemental analysis.

Ethyl 1,3-Dihydro-1-hydroxy-3-oxo-1-isobenzofuranacetate (3a). Procedure a. To a refluxing suspension of zinc–copper couple (31.0 g 0.2 mol) in tetrahydrofuran (50 mL) was gradually added a solution of phthalic anhydride (29.6 g, 0.2 mol) and ethyl bromoacetate (70.5 g, 0.3 mol) in tetrahydrofuran (150 mL). The reaction mixture was refluxed for 2 h and was then cooled and filtered. The filtrate was added to aqueous HCl (200 mL, 10% by volume) and then extracted with EtOAc. The EtOAc layer was washed with water (2 × 50 mL) and evaporated to give a clear colorless oil, which was purified by flash chromatography (CH_2Cl_2–EtOAc, 1:1) to give **3a** (17.7 g, 40%): ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 8 Hz, 3 H), 3.15 (s, 2 H), 4.2 (q, J = 8 Hz, 2 H), 6.25 (b, 1 H), 7.6 (m, 4 H). Compounds **3b–f**, **10**, and **11** were all prepared according to this procedure.

***tert*-Butyl 1,3-dihydro-1-hydroxy-3-oxo-1-isobenzofuranacetate (3b)**: ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9 H), 2.75 (d, J = 15.2 Hz, 1 H), 3.10 (d, J = 15.2 Hz, 1 H), 6.80 (br, 1 H), 7.60 (m, 2 H), 7.70 (m, 1 H), 7.80 (dd, J = 7.6, 2.0 Hz, 1 H).

Ethyl 1,3-dihydro-1-hydroxy-α-methyl-3-oxo-1-isobenzofuranacetate (3c): ^{1}H NMR ($CDCl_3$) δ 0.9, 1.42 (d, J = 7.5 Hz, 3 H), 1.35, 1.40 (t, J = 6.0 Hz, 3 H). 2.85, 3.20 (q, J = 6.0 Hz, 2 H), 6.25, 6.90, (br, 1 H), 7.50–7.80 (m, 3 H), 7.95 (d, J = 6.5 Hz, 1 H).

Ethyl 1,3-dihydro-1-hydroxy-α,α-dimethyl-3-oxo-1-isobenzofuranacetate (3e): mp 73 °C; ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 3 H), 1.32 (t, J = 7.0 Hz, 3 H), 1.60 (s, 3 H), 7.60 (s, 3 H), 4.28 (q, J = 7.0 Hz, 2 H), 7.0 (s, 1 H), 7.50–7.70 (m, 3 H), 7.90 (dd, J = 6.0, 2.0 Hz, 1 H).

***tert*-Butyl 1,3-dihydro-1-hydroxy-α,α-dimethyl-3-oxo-1-isobenzofuranacetate (3f)**: mp 86–87 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 3 H), 1.50 (s, 12 H), 7.24 (s, 1 H), 7.60 (m, 2 H), 7.70 (m, 1 H), 7.85 (dd, J = 7.0, 2.0 Hz, 1 H).

Ethyl 1,3,4,5,6,7-hexahydro-1-hydroxy-3-oxo-1-isobenzofuranacetate (10): mp 75–76 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 8 Hz, 3 H), 1.70 (br, 4 H), 2.20 (br, 3 H), 2.40 (br, 1 H), 2.60 (br, 1 H), 2.82 (br, 1 H), 4.25 (q, J = 8 Hz, 2 H), 6.32 (br, 1 H).

***tert*-Butyl 1,3-dihydro-1-hydroxy-4,5-dimethyl-3-oxo-1-isofuranacetate (11)**: mp 95 °C; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9 H), 1.80 (s, 3 H), 1.95 (s, 3 H), 2.48 (d, J = 16.5 Hz, 1 H) 2.80 (d, J = 16.5 Hz, 1 H), 6.55 (s, 1 H).

Procedure b. A slurry of zinc–copper couple (15 g, 0.2 mol) in THF (25 mL) and DMF (1 mL) was heated to 70 °C. To this mixture was added phthalic anhydride (14.8 g, 0.1 mol) and ethyl bromoacetate (35.2 g, 0.15 mol) dissolved in THF (75 mL) containing DMF (2 mL). After 3 h, the reaction was worked up as above to give the desired product **3a** (13.3 g, 60%).

(*Z*)-3-((Ethoxycarbonyl)methylidene)phthalide (12). Ethyl 1,3-dihydro-1-hydroxy-3-oxo-1-isobenzofuranacetate (**3a**; 2.36 g, 10 mmol) was dissolved in concentrated sulfuric acid (5 mL) and allowed to stand at room temperature for 5 min. The solution was then slowly poured into ice–water (50 mL), and the resulting white precipitate was collected, washed with water (3 × 25 mL), and then air-dried (2.07 g, 95%), mp 132–134 °C.[7a]

Using the above conditions and starting from **3d** (3.12 g), **(*E*)-3-((α-ethoxycarbonyl)benzylidene)phthalide (13)** was obtained (2.62 g, 89%): mp 75 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, J = 7 Hz, 3 H), 4.3 (q, J = 7 Hz, 2 H), 6.55 (d, J = 8 Hz, 1 H), 7.3–7.6 (m, 7 H), 8.0 (d, J = 8 Hz, 1 H).

2-(4,5-Dihydro-4,4-dimethyl-5-oxo-1*H*-pyrazol-3-yl)benzoic acid (5d). Hydrazine hydrate (0.25 mL, 5 mmol) was added to a solution of ethyl α,α-dimethyl-3-dihydro-1-hydroxy-3-oxo-1-isobenzofuran acetate **3e** (1.18 g, 5 mmol) in EtOH (5 mL), and the mixture was refluxed for 4 h. Reaction monitoring by TLC showed formation of one very polar product. Upon quenching the reaction with ice–water (20 mL) and adjusting the pH to about 2, a white precipitate was obtained (0.91 g, 85%): mp 232–234 °C; m/z 232.2384; ^{1}H NMR (DMSO-d_6) δ 1.3 (s, 6 H), 7.5 (m, 2 H), 7.8 (m, 2 H).

2-(4,5-Dihydro-5-oxo-1*H*-pyrazol-3-yl)benzoic acid (5a): mp 203 °C; ^{1}H NMR (DMSO-d_6) δ 5.85 (s, 1 H), 7.22 (m, 2 H), 7.60 (m, 2 H).

2-(4,5-Dihydro-4-methyl-5-oxo-1H-pyrazol-3-yl)benzoic acid (5b): mp 234–236 °C; ^{1}H NMR (DMSO-d_6) δ 1.70 (s, 3 H), 7.3–7.6 (m, 3 H), 7–8 (dd, J = 6 and 2 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 168.06, 158.92, 140.15, 132.35, 131.17, 131.01, 130.95, 129.63, 128.16, 97.01, 6.93.

2-(4,5-Dihydro-4-phenyl-5-oxo-1*H*-pyrazol-3-yl)benzoic acid (5c): mp >280 °C; ^{1}H NMR (DMSO-d_6) 7.3–.7.5 (m, 3 H), 7.6–7.8 (m, 5 H), 8.0 (dd, J = 6, 2 Hz, 1 H).

***tert*-Butyl 3,4-Dihydro-4-oxo-3-benzyl-1-phthalazineacetate (4, R = t-Bu, = R_1 = R_2 = H, R_3 = CH_2Ph).** A mixture of **3b** (1.32 g, 5.0 mmol), EtOH (10 mL), triethylamine (1.67 mL, 12.0 mmol), and benzylhydrazine dihydrochloride (1.17 g, 6.0 mmol) was gently refluxed for 18 h. The solution was evaporated to dryness, and the residue was treated with dilute HCl (2.0 mL) and then extracted with EtOAc (2 × 10 mL). The organic extract was dried and evaporated, and the resulting solid was crystallized from isopropyl ether to obtain the desired compound (1.68 g, 96%): mp 103 °C; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9 H), 3.86 (s, 2 H), 5.4 (s, 2 H), 7.25 (m, 3 H), 7.45 (m, 2 H), 7.7 (m, 3 H), 8.45 (dd, J = 6.0, 2.0 Hz, 1 H).

***tert*-Butyl α,α-Dimethyl-3,4-dihydro-4-oxo-1-phthalazineacetate (4, R = t-Bu, R_1 = R_2 = Me, R_3 = H).** Anhydrous hydrazine (0.36 mL, 12 mmol) was added to a solution of *tert*-butyl α,α-dimethyl-3-dihydro-1-hydroxy-3-oxo-1-isobenzofuran acetate (**3f**; 1.46 g, 5.0 mmol) in absolute EtOH (10 mL), and the mixture was then gently refluxed for 20 h. Upon cooling, the mixture was cautiously diluted with water and then acidified to pH 2.0 with dilute HCl. The resulting solid was collected and crystallized from isopropyl ether to give the desired product (0.99 g, 52%): mp 202–203 °C; ^{1}H NMR (DMSO-d_6) δ 1.28 (s, 9 H), 1.57 (s, 6 H), 7.66 (d, J = 7.5 Hz, 1 H), 7.9 (m, 2 H), 8.33 (d, J = 7.5 Hz, 1 H).

Single-Crystal X-ray Analysis of Ethyl 1,3-Dihydro-1-hydroxy-α,α-dimethyl-3-oxo-1-isobenzofuranacetate (3e). A representative crystal of **3e** ($C_{14}H_{16}O_5$, d_{calc} = 1.32 g cm^{-3}) with appropriate dimensions 0.08 × 0.17 × 0.28 mm was surveyed, and a 1-Å data set (maximum sin θ/λ = 0.5) was collected on a Nicolet R3M/μ diffractometer. Atomic scattering factors were taken from ref 11. All crystallographic calculations were facilitated by the SHELXTL system.[12] All diffractometer data were collected at room temperature. Crystal parameters were as follows: cell dimensions, a = 7.961 (2) Å, B = 8.754 (2) Å, c = 19.172 (5) Å, α = 90.00°, β = 97.28 (2)°, γ = 90.00°; V = 1325.3 (5) Å space group, $P2_1/n$; molecules/unit cell, 4, and linear absorption factor = 8.01 cm^{-1}. Refinement parameters were as follows: number of reflections, 1353; nonzero reflections ($I > 3.0\sigma$), 1135; R index, 0.056; GOF, 1.65; scale factor, 1.629 (5); secondary extinction factor, 19 (2) × 10^{-3}. A trial structure was obtained by direct methods. This trial structure refined routinely. Hydrogen positions were calculated wherever possible. The methyl hydrogens and the hydrogen on oxygen were located by different Fourier techniques. The hydrogen parameters were added to the structure factor calculations but were not refined. The shifts calculated in the final cycle of least-squares refinement were all less than 0.1 of their corresponding standard deviations. The final R index was 0.056. A final difference Fourier revealed no missing or misplaced electron density. The refined structure was plotted using the SHELXTL plotting package (Figure 1).

Acknowledgment. We thank Prof. E. J. Corey for helpful discussions.

Supplementary Material Available: Crystal parameters and structure diagram of **3d**, atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths and bond angles, and hydrogen atom coordinates for both **3d** and **3e**, and elemental analyses for new compounds (13 pages). Ordering information is given on any current masthead page.

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