

the expected resonances.²¹ Despite its thermal instability, II can be reduced at 0° in ether with excess LiAlH₄ to give after aqueous work-up and distillation a 76% yield of C₆H₈ hydrocarbons, consisting²⁶ mainly (82%) of tricyclohexane III,² as indicated in Scheme I, contaminated with 18% of bicyclo[3.1.0]hexene.²⁰ Presumably the reaction giving III is analogous to the reduction of 7-chloronorbornadiene, which gives tricyclo[2.2.1.0^{2,7}]hept-5-ene,²⁷ but we have been unable to isolate 3-bromotricyclo[2.2.0.0^{2,6}]hexane.²⁸

This simple synthesis provides tricyclohexane III in much larger quantities than were previously available.² Extending the discovery of Lemal and Shim that hydrogenation of III with palladium catalyst gives mainly methylcyclopentane and some bicyclo[2.1.1]hexane,² and extending discoveries in our laboratory that strained hydrocarbons are dimerized and isomerized by hydrogenation catalysts and related substances in the absence of hydrogen,²⁹ we studied the effects on III of [Rh(CO)₂Cl]₂ and AgX (X = PF₆ or BF₄), catalysts now recognized as particularly effective^{29f,g,30-32} and different.³³ Both transform III into bicyclo[3.1.0]hexene (VI)²⁰ and 4-methylenecyclopentene (VII),³⁶ but the rhodium catalyst gives mainly the latter³⁷ and the

(21) In CCl₄: τ 3.91, 4.26 (H_{2,3}, J = 5.6 Hz, doublets), 5.11 (H₄, multiplet, W_{1/2} = 4.5 Hz),²² 7.33 (H_{1,5}, multiplet), 7.77 (H₆, J = 2.0 Hz, triplet).²⁵

(22) ¹J_{4,5} should be 6 Hz if the protons are cis²³ and 2 Hz if trans.^{23c,24}

(23) (a) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968); (b) E. Ciganek, *ibid.*, **88**, 2882 (1966); (c) E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).

(24) (a) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *ibid.*, **30**, 771 (1965); (b) P. K. Freeman, F. A. Raymond, and M. F. Grostic *ibid.*, **32**, 24 (1967).

(25) Assigned as endo because of the small splitting [cf. W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967); A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965)].

(26) Isolated by glpc (5 ft × 1/4 in. 10% saturated AgNO₃ in benzyl cyanide on 45-60 Chromosorb W regular at 35°), and identified by pmr and ir.

(27) P. R. Story, *J. Amer. Chem. Soc.*, **83**, 3347 (1961). Similarly for 7-chloro- or tosylxynorbornene: S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(28) If much less than a fivefold excess of LiAlH₄ is used, 2-bromo-bicyclo[2.1.1]hexane, the HBr adduct of III, is isolated.

(29) (a) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966); (b) T. J. Katz, J. C. Carnahan, Jr., and R. Boecker, *J. Org. Chem.*, **32**, 1301 (1967); (c) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967); (d) T. J. Katz, N. Acton, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 206 (1969); (e) T. J. Katz and S. Cereface, *ibid.*, **91**, 2405 (1969); (f) T. J. Katz and S. Cereface, *Tetrahedron Lett.*, 2509 (1969); (g) T. J. Katz and S. A. Cereface, *ibid.*, 2561 (1969); (h) T. J. Katz and S. A. Cereface, *J. Amer. Chem. Soc.*, **91**, 6519 (1969); (i) T. J. Katz and S. A. Cereface, *ibid.*, **93**, 1049 (1971).

(30) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, **91**, 218 (1969).

(31) Rhodium: (a) P. G. Gassman and F. J. Williams, *J. Chem. Soc., Chem. Commun.*, 80 (1972); (b) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971), and earlier work referred to therein.

(32) Silver: (a) L. Friedman, *ibid.*, **89**, 3071 (1967); (b) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *ibid.*, **93**, 1446 (1971); (c) W. Merk and R. Pettit, *ibid.*, **89**, 4787, 4788 (1967); (d) J. Wristers, L. Brener, and R. Pettit, *ibid.*, **92**, 7499 (1970); (e) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971); (f) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masumune, *J. Amer. Chem. Soc.*, **93**, 1043 (1971).

(33) The products of some silver-catalyzed reactions are substrates for rhodium (ref 29f vs. ref 34; ref 35). For different catalysts giving different products see W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **93**, 7345 (1971), and ref 31b.

(34) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

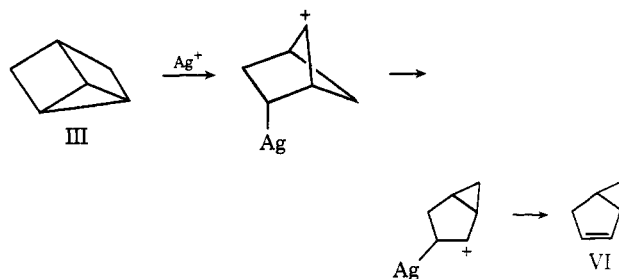
(35) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 6366 (1970).

(36) W. D. Huntsman, J. A. DeBoer, and M. H. Woosley, *ibid.*, **88**, 5846 (1966).

(37) III (0.53 mmol) + [Rh(CO)₂Cl]₂ (0.056 mmol) in CCl₄, 10 min at ambient temperature, gave VII and VI (4:1) in 48% yield, plus a dimer (38%) whose structure is still being determined. [(C₆H₈)₂P]RhCl in CCl₄, 18 hr at 50°, gave the same products.

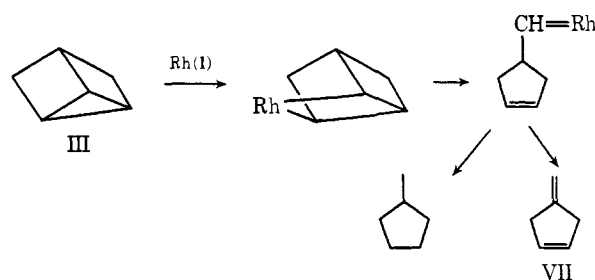
silver mainly the former.³⁸ This is in accord with analogies for the mechanisms depicted in Schemes II³⁹ and

Scheme II



III.^{29d,e,h,31} The latter also provides a particularly

Scheme III



simple explanation for results that have previously been explained only with difficulty, why palladium-catalyzed hydrogenolysis of III gives methylcyclopentane, and of a bicyclo[1.1.0]butane with deuterium gives a 3-methylalkene doubly labeled on the methyl.⁴⁰

Acknowledgments. We are grateful to the National Science Foundation (NSF-GP-30669X) for its support.

(38) III (0.75 mmol) + AgPF₆ (0.22 mmol) in CH₂Cl₂, 20 hr at ambient temperature, gave VI and VII (2:1). AgBF₄ in CDCl₃ gave similar results.

(39) (a) J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971); (b) M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4610 (1971); (c) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

(40) E. Galantay, N. Paoletta, S. Barcza, R. V. Coombs, and H. P. Weber, *ibid.*, **92**, 5771 (1970).

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Intramolecular Photoaddition of Ketenes to Cyclohexenones

Sir:

Considerable attention has been paid in the last few years to the addition of ketenes to double bonds¹ and to the photoaddition of double and triple bonds to α,β -unsaturated ketones.² In general, ketenes are not suffi-

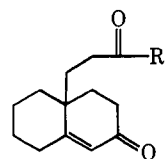
(1) (a) Thap Do Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970); (b) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970); (c) J. E. Baldwin and J. A. Kopecki, *J. Amer. Chem. Soc.*, **92**, 4874 (1970); (d) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (e) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); (f) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., 1970; (g) H. U. Wagner and R. Gompper, *Tetrahedron Lett.*, 2819 (1970).

(2) (a) P. DeMayo, *Accounts Chem. Res.*, **4**, 41 (1971); (b) P. G. Bauslaugh, *Synthesis*, 287 (1970).

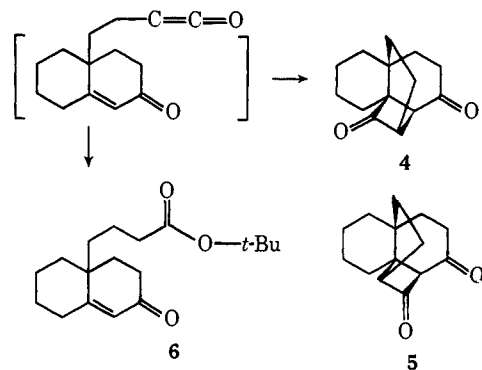
ciently electrophilic to react with unactivated olefins. Therefore, haloketenes were synthesized which do react with olefins under mild conditions.³ Some of the orientational aspects of this process have been studied,⁴ and the reaction has found use in the synthesis of prostaglandins.⁵ During these studies, it was found that even haloketenes failed to react with double bonds conjugated to electron-withdrawing groups.⁶

Several papers dealing with intramolecular addition of ketenes to olefinic bonds have appeared in the literature.⁷ We wish to present the first examples of intramolecular photochemical addition of ketenes to double bonds conjugated to ketones.

The keto acid **1**⁸ was converted to acid chloride **2** with oxalyl chloride and then to diazo ketone **3** (ir (CHCl₃)



- 1, R = -OH
2, R = -Cl
3, R = -CHN₂



2100, 1650 cm⁻¹) by subsequent treatment with excess diazomethane. Irradiation⁹ of a 0.5% solution of **3** in cyclohexane¹⁰ afforded, after chromatography on Florisil, a 40% yield of the diketone **4**:^{11a} mp 78°; ir (CHCl₃) 1785, 1705 cm⁻¹; nmr δ 3.39 ppm (m, 1 H)^{11b}; M⁺ = 218.

In order to determine which of the two possible structures **4** or **5** was obtained, a solution of diketone in

(3) (a) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965); (b) L. Ghosez, R. Montaigne, and P. Mollett, *Tetrahedron Lett.*, 135 (1966).

(4) A. Hassner, V. R. Fletcher, and D. P. G. Hamon, *J. Amer. Chem. Soc.*, **93**, 264 (1971).

(5) E. J. Corey, Z. Arnold, and J. Hutton, *Tetrahedron Lett.*, 307 (1970).

(6) W. T. Brady and O. H. Waters, *J. Org. Chem.*, **32**, 3703 (1967).

(7) (a) R. R. Sauers and K. W. Kelly, *ibid.*, **35**, 3286 (1970); (b) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968); (c) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loesch, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6856 (1969); (d) H. Hart and G. M. Love, *ibid.*, **93**, 6266 (1971); (e) Ch. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22**, 1809 (1966).

(8) D. Becker, D.Sc. Thesis, Israel Institute of Technology, 1968.

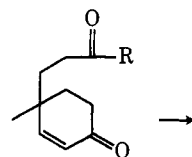
(9) Irradiation was carried out in a Pyrex vessel under nitrogen at room temperature for 2 hr with a 450-W Hanovia lamp. No reaction occurred when a G.E. sunlamp was used.

(10) The commercial cyclohexane used (after shaking with concentrated sulfuric acid and dilute Na₂CO₃ and distillation) was at least 0.01 M benzene.

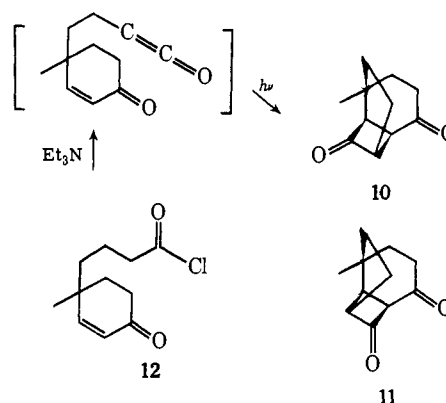
(11) (a) All new compounds gave correct elemental analyses. Also spectral data were in accord with assigned structures. (b) The nmr spectrum of the diketones in CDCl₃ and Eu(DPM)₃ was carried out on a Bruker HF90 using the indor technique. The information obtained from these spectra supports structures **4** and **17**.

1:1 methanol-water, 10% in potassium hydroxide, was refluxed for 5 hr under nitrogen. Since cleavage did not occur under these basic conditions and since no nmr absorption was observed lower than 3.4 ppm, structure **5**, in which the carbonyl groups are in a 1,3 relationship, can be eliminated.¹² When diazo ketone **3** was irradiated in *tert*-butyl alcohol, the major product isolated was the *tert*-butyl ester **6** and no trace of the diketone **4** was found.

In order to examine an additional case, we synthesized keto acid **7** from the appropriate keto ester.¹³ After irradiation of diazo ketone **9** in cyclohexane,¹⁰



- 7, R = -OH
8, R = -Cl
9, R = -CHN₂



it was possible to isolate in 42% yield the diketone **10**:^{11a} mp 78°; ir (CHCl₃) 1790, 1715 cm⁻¹; nmr δ 3.42 (m, 1 H), 3.0 (m, 2 H), 1.14 ppm (s, 3 H); M⁺ = 178. Since this diketone was also stable under basic conditions, it was concluded that **10** rather than **11** represents the correct structure. One of the possible mechanisms was addition of the ketene moiety to the double bond of the α,β-unsaturated ketone in the ground state. In order to exclude this possibility, the acid chloride **12** was prepared from the corresponding acid¹⁴ and treated with triethylamine under a variety of conditions.^{7a,b} In no case was it possible to detect any cyclobutanone in the reaction mixture. The absence of cycloaddition product agrees with previous results in which ketenes failed to react with double bonds conjugated to electron-withdrawing groups.⁶

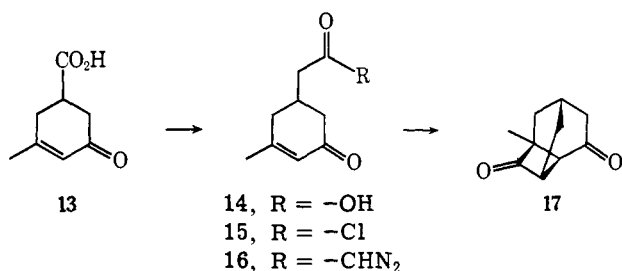
It was found that upon irradiation of diazo ketone **9** in hexane (instead of cyclohexane¹⁰) transparent to light above 200 nm, no trace of diketone **10** was obtained although **9** was completely consumed. Irradiation in hexane containing benzene (0.01 M) produced the photoadduct **10** in the usual yield. It is reasonable to assume that benzene acts as a triplet sensitizer for the enone or the ketene, and it is the excited triplet which reacts.

(12) von H. Wehrli, C. Lehman, P. Keller, J. J. Bonet, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 2218 (1966).

(13) A. J. Birch and J. S. Hill, *J. Chem. Soc. C*, 125 (1967).

(14) D. Becker and J. Kalo, *Tetrahedron Lett.*, 3725 (1971).

An additional system with a different relative location of the reacting sites was synthesized. Keto acid **14** was prepared by an Arndt-Eistert reaction of keto acid **13**.¹⁵ Irradiation of diazo ketone **16** in cyclohexane or



benzene enabled isolation of diketone **17**^{11a} from the reaction mixture in a yield of 24%: mp 74°; ir 1782, 1710 cm⁻¹; nmr δ 3.35 (m, 1 H), 2.60 (m, 1 H), 1.20 ppm (s, 3 H); M⁺ = 164.

Photochemical additions of double bonds to α,β -unsaturated ketones have been studied intensively and numerous cases of intramolecular additions are known.¹⁶ The structures of such products have been determined, but it is not always clear what factors govern the orientation of addition. In the photochemical cycloaddition of allenes to cycloalkenones,¹⁷ the direction of the addition was such that oxidation of the exocyclic double bond led to a 1,3-diketone.

Thus, we have presented three examples of intramolecular photochemical addition of ketenes to double bonds conjugated to ketones. It was found that the direction of addition in the cases studied in this work was such that the products contained the carbonyl groups in a 1,4 relationship, as opposed to the addition of allenes. It was shown that without excitation of the enone system no cycloaddition occurred.

- (15) D. D. Phillips and A. W. Johnson, *J. Org. Chem.*, **21**, 587 (1956).
 (16) (a) G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.*, **79**, 4741 (1957); (b) C. H. Heathcock and R. A. Badger, *Chem. Commun.*, 1510 (1968); (c) W. F. Erman and T. W. Gibson, *Tetrahedron*, **25**, 2493 (1969).
 (17) (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) P. E. Eaton, *Tetrahedron Lett.*, 3695 (1964); (c) K. Wiesner, S. Üyeyo, A. Philipp, and Z. Valenta, *ibid.*, 6279 (1968).

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 Received February 24, 1972

Two Syntheses of the 2,4a-Ethano-2,3,4,4a-tetrahydroxanthene System

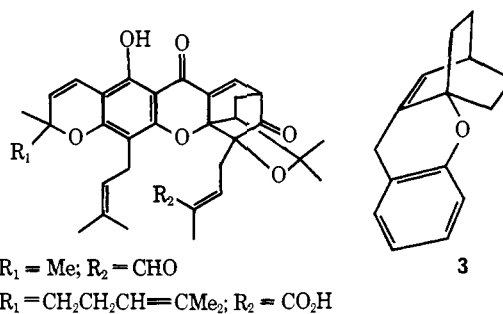
Sir:

The naturally occurring compounds morellin (**1**)¹ and gambogic acid (**2**)² and their relatives have a nucleus consisting of the 2,4a-ethano-2,3,4,4a-tetrahydroxan-

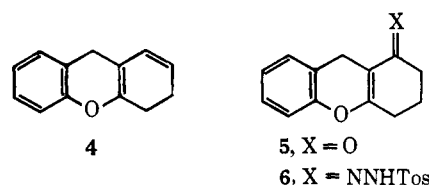
(1) G. Kartha, G. N. Ramachandran, H. B. Bhat, P. M. Nair, V. K. V. Raghavan, and N. Venkataraman, *Tetrahedron Lett.*, 459 (1963); F. M. Nair and K. Venkataraman, *Indian J. Chem.*, **2**, 402 (1964); H. B. Bhat, P. M. Nair, and K. Venkataraman, *ibid.*, **2**, 405 (1964); C. G. Karanjgaonkar, P. M. Nair, and K. Venkataraman, *Tetrahedron Lett.*, 687 (1966).

(2) P. Yates, S. S. Karmarkar, D. Rosenthal, G. H. Stout, and V. F. Stout, *ibid.*, 1623 (1963); W. D. Ollis, M. V. J. Ramsay, I. O. Sutherland, and S. Mongkolsuk, *Tetrahedron*, **21**, 1453 (1965); S. A. Ahmad, W. Rigby, and R. B. Taylor, *J. Chem. Soc. C*, 772 (1966); M. Amorosa and G. Giovanninetti, *Ann. Chim. (Rome)*, **56**, 232 (1966); G. Cardillo and L. Merlini, *Tetrahedron Lett.*, 2529 (1967).

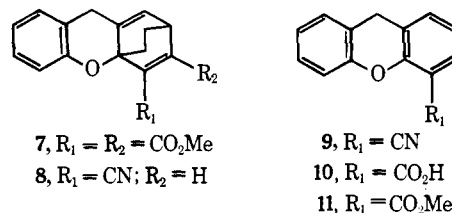
thene system (**3**). We describe two novel synthetic routes to this system.³



The first involves the Diels-Alder reaction of dienophiles with 3,4-dihydroxanthene (**4**). The diene **4**,⁴ mp 32–34° [$\lambda_{\text{max}}^{\text{CCl}_4}$ 5.92 (m) μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 290 (6400), 298 (sh, 6000), 314 (sh, 3700) nm; δ^{CDCl_3} 2.29 (d, $J = 2$ Hz, 4 H), 3.29 (s, 2 H), 5.56 (m, 1 H), 5.68 (d, $J = 9$ Hz, 1 H), 6.96 (m, 4 H)], was prepared from the dihydroxanthene-**5** by treatment of its tosylhydrazone **6**, mp 219–



220°, with methyl lithium. Reaction of **4** with dimethyl acetylenedicarboxylate gave the adduct **7**, mp 92–96° [$\lambda_{\text{max}}^{\text{CCl}_4}$ 5.70, 5.78, 5.97 (w), 6.09 (w) μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 269 (2100), 278 (1700), 305 (650) nm; δ^{CDCl_3} 1.70 (m, 4 H), 3.48 (br s, 2 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 4.17 (d of t, $J = 6$, 3 Hz, 1 H), 6.11 (d of t, $J = 6$, 2 Hz, 1 H), 7.04 (m, 4 H)]. Reaction of **4** with propionitrile gave the adduct **8**, mp 75–78° [$\lambda_{\text{max}}^{\text{CCl}_4}$ 4.54 (m) μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 270 (1600), 276 (1400) nm; δ^{CDCl_3} 1.62 (m, 4 H), 3.40 (d of d, $J = 17$, 1.5 Hz, 1 H), 3.51 (d of d, $J = 17$, 2 Hz, 1 H), 3.71 (m, 1 H), 5.95 (d of t, $J = 6$, 2 Hz, 1 H), 7.14 (m, 5 H)]. The structures of these adducts follow from their pmr spectra and the conversion of **8** at 163° to 4-cyanoxanthene (**9**), mp 91–93° [$\lambda_{\text{max}}^{\text{CCl}_4}$ 4.49 (w) μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 252 (7000), 279 (2100), 307 (4200) nm; δ^{CDCl_3} 4.04 (s, 2 H), 7.29 (m, 7 H)], further characterized as the corresponding acid **10**, mp 185–186° (lit.⁶ mp 183°) [$\lambda_{\text{max}}^{\text{CHCl}_3}$ 3.04 (m), 5.76, 5.86 (sh) μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 248 (8200), 279 (2400), 303 (2800) nm], and methyl ester **11**, mp



48–49° [$\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.82 μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 248 (8200), 278 (2300), 305 (3200) nm; δ^{CDCl_3} 3.94 (s, 3 H), 3.99 (s, 2 H), 7.11 (m, 6 H), 7.72 (d of d, $J = 7$, 2 Hz, 1 H)].

(3) Very recently another synthesis has been reported by A. J. Quilinan and F. Scheinmann, *Chem. Commun.*, 966 (1971).

(4) Acceptable elemental analyses have been obtained for all compounds characterized by melting point; parent peaks for these compounds have been observed in their low-resolution mass spectra.

(5) Prepared by condensation of 1,3-cyclohexanedione with *o*-hydroxybenzyl alcohol in HMPA; cf. P. Yates, D. J. Bichan, and J. E. McCloskey, *Chem. Commun.*, in press.

(6) S. Akagi and T. Iwashige, *J. Pharm. Soc. Jap.*, **74**, 610 (1954).