portions of ether. The ether was washed with 150 ml of 10% aqueous hydrochloric acid, dried ($MgSO_4$), and concentrated by distillation through a 50-cm Vigreux column. The residue was then distilled through a 50-cm Teflon annular spinning-band column to yield 5.0 g (27%) of 3,3,6,6-tetramethylcyclohexadiene. The ir spectrum was in agreement with that of an authentic sample;[20] nmr ($CDCl_3$) δ 5.38 (s, 4, vinyl CH) and 1.01 ppm (s, 12, CH_3).

t-**Butyl Alcohol-O-*d*.**—To 33 g (0.25 mol) of potassium *t*-butoxide under nitrogen was added very carefully 7.0 ml (0.35 mol) of deuterium oxide (Columbia Organic Chemicals, 99.8% *d*). The crude *t*-butyl alcohol-O-*d* was removed by bulb to bulb distillation under vacuum and was then distilled from calcium hydride to yield 15 g (82%) of *t*-butyl alcohol, having isotopic composition[21] 93.0% d_1 and 7.0% d_0.[10,22]

1,1,4,4-Tetramethylcyclohexane-2,3,5,6-*d*$_4$.—A mixture of 1.0 g (44 mg-atom) of sodium and 25 ml of HMPA were stirred at room temperature until a deep blue color appeared. To the solution was then added 0.55 ml (*ca.* 0.5 g, 3.7 mmol) of 3,3,6,6-tetramethylcyclohexadiene and 4 ml of *t*-butyl alcohol-O-*d*. The mixture was stirred overnight and poured into 100 ml of an ice water slush. The aqueous phase was immediately extracted with 25 ml of fluorotrichloromethane and the organic layer was separated, dried ($MgSO_4$), and concentrated by distillation of the solvent through a 20-cm Vigreux column. The 1,1,4,4-tetramethylcyclohexane in the residue was collected using glpc (UC-W98 on Chromosorb W) to yield 0.21 ml of pure product having mass spectral isotopic composition (10 eV) 66.2% d_4, 28.6% d_3, and 5.2% d_2.

Characterization was accomplished by preparation of undeuterated 1,1,4,4-tetramethylcyclohexane using $(CH_3)_3COH$ as the proton source: nmr ($CFCl_3$) δ 1.25 (s, 8, CH_2) and 0.88 ppm (s, 12, CH_3).

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.37.

Registry No.—Hexamethylphosphoramide, 680-31-9; *t*-butyl alcohol, 75-65-0; sodium, 7440-23-5.

Acknowledgments.—We are indebted to Dr. H. O. House for a sample of $\Delta^{9,10}$-octalin, and Drs. Jon Engstrom and F. D. Greene for a sample of tetrahydroindan.

(20) Sadtler Catalogue, spectrum no 30757.

(21) Benzene-free phenylmagnesium bromide was prepared by the addition of 50 ml of toluene to *ca.* 10 mmol of phenylmagnesium bromide in 5 ml of ether and distillation of the mixture until glpc analysis showed that no ether or benzene remained in the resulting toluene suspension of phenyl Grignard reagent. The isotopic composition of the *t*-butyl alcohol-O-*d* was determined by reaction of the Grignard reagent with *t*-butyl alcohol-O-*d*, isolation of a sample of the resulting benzene by distillation, further purification by collection from glpc, and mass spectral isotopic analysis. Less than 1 equiv of *t*-butyl alcohol-O-*d* per equivalent of phenyl Grignard reagent was used to minimize the influence of any deuterium kinetic isotope effect in the hydrolysis on the accuracy of the analysis.

(22) A superior preparation of *t*-butyl alcohol-O-*d* has been published recently: A. T. Young and R. D. Guthrie, *J. Org. Chem.*, **35**, 852 (1970).

Preferential O$^-$-5 *vs.* O$^-$-6 Cyclization in a Neighboring Group Reaction[1]

H. E. ZAUGG AND R. W. DENET

Organic Chemistry Department, Research Division, Abbott Laboratories, North Chicago, Illinois 60064

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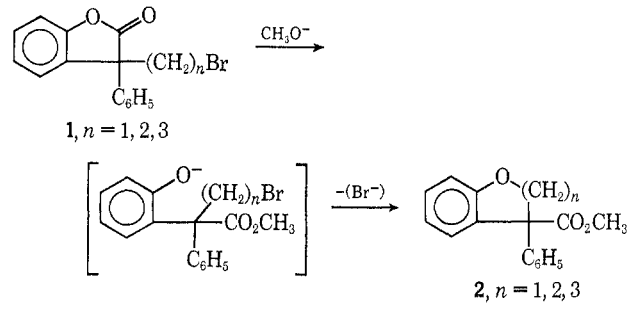
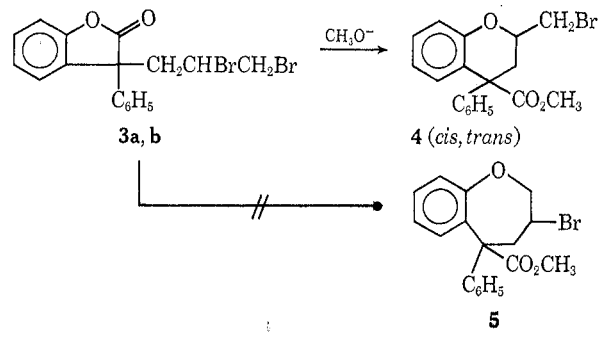
A previous report[2] described the methoxide ion induced rearrangement of the three homologous benzofuranones **1** to the corresponding methyl esters, **2**. The first two members of this series (n = 1, 2) rearrange with extraordinary rapidity (reaction can be conducted under titration conditions), but the third member (n = 3) rearranges more slowly.



It was not surprising, therefore, to find[3] that the dibromide **3** rearranges exclusively by O$^-$-6 cyclization to the chroman derivative **4**. No detectable amounts of the corresponding tetrahydrobenzoxepin **5** (O$^-$-7 cyclization) are found. Furthermore, halide displacement occurs stereospecifically, one diastereomer of **3** giving *cis*-**4** and the other, exclusively, *trans*-**4**.



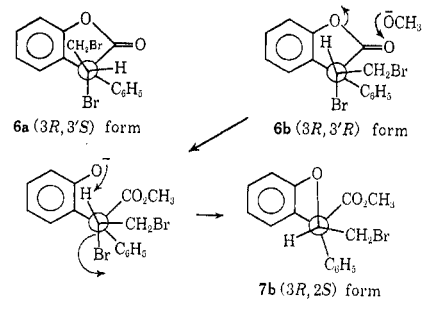
We now find that O$^-$-5 is favored over O$^-$-6 cyclization in this system, and that displacement again is stereospecific. One diastereomer of the dibromide **6a** (mp 109–110°) affords the *trans* bromo ester **7a**, mp 102–103° (82% yield), and the other, **6b** (mp 117–118°), gives the *cis* ester **7b** as an oil which converts to the lactone **8** on distillation.[4] With benzylamine, **7b** (but not **7a**) gives the lactam **9**. The structures shown for these compounds are compatible with their elemental analyses, infrared spectra and nmr spectra. In addition, the complex ABX spin systems observed for the

(1) Paper XIV in the series, "Neighboring Group Reactions." For paper XIII, see H. E. Zaugg and R. J. Michaels, *J. Org. Chem.*, **31**, 1332 (1966).

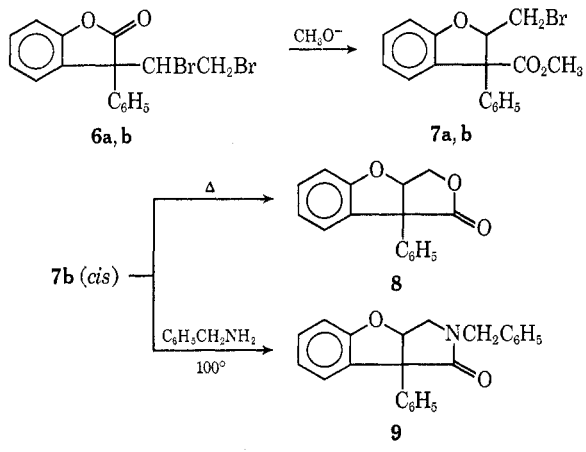
(2) H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *ibid.*, **26**, 4821 (1961).

(3) H. E. Zaugg, R. W. DeNet, and E. T. Kimura, *J. Med. Chem.*, **5**, 430 (1962).

(4) Assuming that intramolecular bromide displacement in **6a** and **6b** occurs exclusively with inversion, their relative configurations can be assigned as follows, each structure representing a single mirror image (conversion of **6b** to **7b** is illustrated).

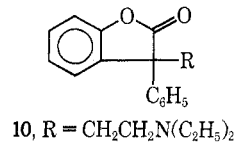


–OCHCH$_2$– group in compounds **7a**, **8**, and **9** have been fitted successfully to theoretical nmr spectra (see the Experimental Section).



6a, b **7a, b** **8** **9**

The dibromides **6** were prepared by a sequence starting from the diethylaminoethylbenzofuranone **10**.[5] Treatment with hydrogen peroxide led to the amine oxide **11** (90%),[6] which, on dry distillation, afforded the vinylbenzofuranone **12** (35–40%). Bromine added readily to **12** to give a mixture of the dibromides **6a** and **b** which were separated by fractional crystallization.



10, R = $CH_2CH_2N(C_2H_5)_2$

11, R = $CH_2CH_2N(C_2H_5)_2$ ↓ O

12, R = CH=CH_2

Experimental Section[7]

Peroxide Oxidation of 3-(β-Diethylaminoethyl)-3-phenyl-2-benzofuranone (10).—To a stirred solution of **10**[5] (freshly distilled) (50 g, 0.162 mol) in ethanol (600 ml) was added 30% hydrogen peroxide (40 ml). After standing at room temperature for 1 week, the product **11** (50 g, 90%) was collected at the filter and dried: mp 177–179° dec; ir (Nujol) no peak at 1790 cm^{-1} (lactone C=O); insoluble in water and all common organic solvents; soluble in DMF and DMSO.

Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34. Found: C, 69.88; H, 7.59.

3-Phenyl-3-vinyl-2-benzofuranone (12).—A 15-g portion of the N-oxide **11** was heated in an oil bath in a round-bottom flask equipped for short-path distillation under reduced pressure (0.5–1.5 mm). When the bath temperature reached 180° distillation began, and continued until 205° was reached and 10.5 g of crude product had been collected: bp 125–175° (0.5–1.5 mm), n^{25}D 1.58. The combined crude product from three such runs was taken up in dry ether (100–150 ml), filtered from insoluble material (2.5 g), washed successively with dilute aqueous HCl and water, and dried ($MgSO_4$). Filtration and removal of the ether by distillation afforded a residual oil (13.5 g) that was distilled under reduced pressure giving the vinyl compound **12** (11.7 g, 38%): bp 130–135° (0.8 mm); n^{25}D 1.5869; ir ($CHCl_3$) 1790 cm^{-1} (lactone C=O); nmr $\left(\begin{matrix}H_A\\R\end{matrix}\!>\!C\!=\!C\!<\!\begin{matrix}H_B\\H_C\end{matrix}\right)$ δ 6.34 (q, 1, J_{AB} = 10 Hz, J_{AC} = 17 Hz, H_A), 5.41 (d, 1, J_{AB} = 10 Hz, J_{BC} < 1 Hz, H_B), 5.24 (d, 1, J_{AC} = 17 Hz, J_{BC} < 1 Hz, H_C).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.13; O, 13.54. Found: C, 81.40; H, 4.89; O, 13.48.

From the cold trap of the original pyrolytic distillation was isolated N,N-diethylhydroxylamine, bp 120–122° (atm), n^{25}D 1.4173, identified by elemental analysis and conversion to its oxalate, mp 134–136° (lit.[8] mp 136–137°).

3-(1′,2′-Dibromoethyl)-3-phenyl-2-benzofuranones (6a and 6b).—To a stirred solution of the vinylbenzofuranone **12** (15.4 g, 0.0652 mol) in chloroform (200 ml) was added dropwise a solution of bromine (10.5 g, 0.0655 mol) in chloroform (100 ml). The reaction was illuminated by a 40-W light bulb during the addition and for 16 hr thereafter. The chloroform was removed by distillation and the thick amber-colored residue (26 g) was triturated with methanol (50–100 ml). After standing for 2 hr the crystallized product (16.2 g, mp 98–102°) was collected at the filter and dried. Two more recrystallizations from methanol gave **6a** (11.5 g, 45%): mp 109–110°; essentially homogeneous by tlc (hexane–ether–acetone, 90:5:5, R_f 0.46); ir ($CHCl_3$) 1800 cm^{-1} (lactone C=O).

Anal. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05; Br, 40.35; O, 8.08. Found: C, 48.54; H, 3.04; Br, 40.55; O, 8.30.

The filtrate from the original methanol trituration was concentrated to dryness and the residue (9.5 g) was taken up in a minimum quantity of benzene, decolorized with charcoal, and treated with 4–5 volumes of hexane. Refrigeration for several days yielded **6b** (2.8 g, 11%), mp 116–118°. A sample was recrystallized again from a benzene–hexane mixture: mp 117–118° (mmp with **6a**, 85–90°); homogeneous by tlc (hexane–ether–acetone, 90:5:5, R_f 0.35); ir ($CHCl_3$) 1800 cm^{-1} (lactone C=O).

Anal. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05; Br, 40.35; O, 8.08. Found: C, 48.26; H, 2.81; Br, 40.04; O, 8.11.

Methyl *trans*-2-Bromomethyl-2,3-dihydro-3-phenyl-3-benzofurancarboxylate (7a).—To a stirred suspension of **6a** (2.5 g, 0.0063 mol), mp 109–110°, in methanol (60 ml), containing phenolphthalein indicator, was added dropwise a solution of sodium methoxide (from 0.15 g, 0.0065 g-atom of Na) in methanol (30 ml). Initial reaction was rapid as shown by the nearly instantaneous decolorization of the indicator after the addition of each drop. The rate slowed considerably, however, near the end of the addition (1.5 hr). The basic mixture was stirred overnight at room temperature and crystallized product (1.1 g, mp 101–102°) was collected at the filter and dried. The filtrate was concentrated to dryness and the residue was taken up in a mixture of ether and water. On drying and concentrating the ether layer a glassy residue (1 g) was obtained which crystallized (0.7 g, mp 99–100°) on trituration with methanol to give a total yield of 1.8 g (82%). Two recrystallizations from methanol afforded 1.58 g of pure **7a**: mp 102–103°; ir ($CHCl_3$) 1730 cm^{-1} (ester C=O); nmr δ 7.1 (m, 9, ArH), 5.62 (m, 1, J_{AX} = 10.3 Hz, J_{BX} = 3.2 Hz, –OCH_X–), 3.82 (s, 3, OCH_3), 3.15 (m, 1, J_{AB} = 11 Hz, J_{BX} = 3.2 Hz, $BrCH_B$–), 2.80 (m, 1, J_{AB} = 11 Hz, J_{AX} = 10.3 Hz, $BrCH_A$–).

Anal. Calcd for $C_{17}H_{15}BrO_3$: C, 58.81; H, 4.35; Br, 23.01; O, 13.83. Found: C, 58.77; H, 4.38; Br, 22.75; O, 13.81.

Methyl *cis*-2-Bromomethyl-2,3-dihydro-3-phenyl-3-benzofurancarboxylate (7b) and 3,4-Benzo-2,7-dioxa-5-phenylbicyclo[3.3.0]-octan-6-one (8).—When the foregoing procedure was applied to the dibromide **6b** (3.0 g), mp 117–118°, an oil (2.6 g) was obtained that resisted attempts at crystallization. Its infrared spectrum showed that the lactone carbonyl group (1800 cm^{-1}) in **6b** had been converted entirely to an ester group (1740 cm^{-1}). Other spectral details also resembled those of the isomeric bromo ester **7a**. However, when the oil (**7b**) was distilled under reduced pressure, the distillate [1.7 g, bp 160–162° (0.5–1 mm)] exhibited (ir) the partial conversion to still another carbonyl compound. A second distillation [1.2 g, bp 155–157° (0.5 mm)] effected complete conversion to this material which solidified and was recrystallized twice from ether–hexane to afford 0.75 g (39% yield from **6b**) of the lactone **8**: mp 91–92°; ir ($CHCl_3$) 1775 cm^{-1} (lactone C=O); nmr δ 7.1 (m, 9, ArH), 5.42 (m, 1, J_{AX} = 2.6 Hz, J_{BX} = 5.4 Hz, $ArOCH_X$–), 4.68 (m, 1, J_{AB} = 11.1 Hz,

(5) A. W. Weston and W. B. Brownell, *J. Amer. Chem. Soc.*, **74**, 653 (1952).

(6) The structure assigned to **11** is uncertain. Microanalysis indicates the addition of the elements of one molecule of water to those required for structure **11**. Since lactone carbonyl absorption is not readily detectable in the infrared (Nujol), the true structure may be more accurately represented as the corresponding hydroxy acid.

(7) Melting points and boiling points are uncorrected. Spectra were recorded on a Perkin-Elmer Model 521 infrared spectrophotometer and on a Varian A-60 nmr spectrometer. Chemical shifts (all in $CDCl_3$) are expressed in δ values relative to tetramethylsilane in solution.

(8) W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 800 (1899).

J_{BX} = 5.4 Hz, $-CH_BOCO-$), 4.55 (m, 1, J_{AB} = 11.1 Hz, J_{AX} = 2.6 Hz, $-CH_AOCO-$).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80; O, 19.03. Found: C, 76.33; H, 4.84; O, 19.05.

7-Aza-3,4-benzo-7-benzyl-2-oxa-5-phenylbicyclo[3.3.0]octan-6-one (9).—A sample of the mixed bromo esters **7a** and **7b** (1.8 g of an oil obtained from the mixed dibromides **6**) was treated with benzylamine (10 ml) and heated on the steam bath for 16 hr. Excess amine was removed by distillation (<100°) under reduced pressure. The residue was treated with dry ether and the insoluble benzylamine hydrobromide (0.8 g, mp 220–223°) was removed by filtration. The filtrate was washed with dilute HCl and water and solid product (0.45 g, mp 165–167°) was recovered from the concentrated extract. One recrystallization from ethanol afforded pure lactam **9**: mp 167–168°; ir ($CHCl_3$) 1635 cm^{-1} (lactam C=O); nmr δ 7.1 (m, 14, ArH), 5.16 (m, 1, J_{AX} = 4.6 Hz, J_{BX} = 7.6 Hz, $-OCH_X-$), 4.77 (d, 1, J_{CD} = 14.5 Hz, $C_6H_5CH_CN-$), 4.37 (d, 1, J_{CD} = 14.5 Hz, $C_6H_5CH_DN-$), 3.71 (m, 1, J_{AB} = 12 Hz, J_{BX} = 7.6 Hz, ring-CH_B-N-), 3.52 (m, 1, J_{AB} = 12 Hz, J_{AX} = 4.6 Hz, ring-CH_A-N-).

Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61; N, 4.11; O, 9.37. Found: C, 80.74; H, 5.60; N, 4.29; O, 9.50.

When a sample of the pure *trans*-bromo ester **7a**, mp 102–103°, was submitted to the foregoing procedure, none of the lactam **9** was detectable (ir) in the product. Instead, a liquid amino ester was produced from which a crude solid hydrochloride could be derived. However, this salt resisted all attempts at purification for more precise characterization.

Registry No.—**6a**, 25236-51-5; **6b**, 25236-52-6; **7a**, 25282-55-7; **7b**, 25236-53-7; **8**, 25236-54-8; **9**, 25236-55-9; **12**, 25236-56-0.

Acknowledgments.—We are indebted to Mrs. Evelyn Baker for the tlc tests of purity, to Mrs. Ruth Stanaszek for the nmr spectra, to Dr. Milton Levenberg for calculations of some of the theoretical nmr spectra, to Mr. Victor Rauschel for the microanalyses, and to Mr. Wm. Washburn for the infrared spectra.

Concerning the "Conjugation" of Cyclopropyl with an Adjacent Activated Olefinic Group. An Electrochemical Approach

MANUEL M. BAIZER, JOHN L. CHRUMA, AND PIERRE A. BERGER

Central Research Department and Physical Science Center, Monsanto Company, St. Louis, Missouri 63166

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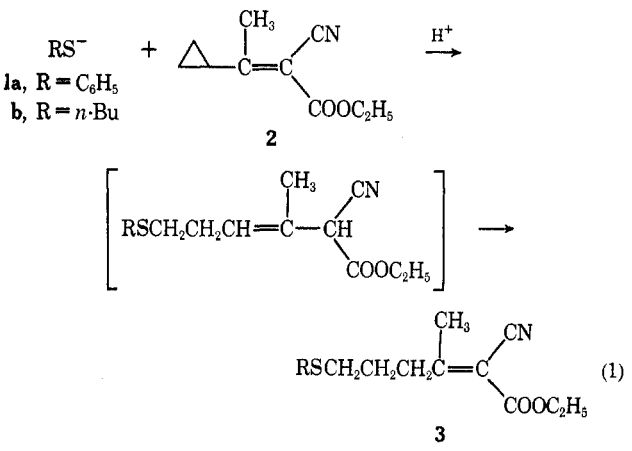
The possibility of conjugation between a cyclopropyl group and a carbon double bond has gained much attention.[1] While the data from uv spectroscopy indicated an affirmative answer for the excited state,[2] the interpretation of the results of hydrogenating such systems catalytically[3] or by sodium in liquid ammonia[4] is ambiguous. The report[1] that mercaptide ion (**1**) reacted with ethyl 2-cyano-3-cyclopropyl-2-butenoate (**2**) to yield a product (**3**) resulting from a formal 1,6 addition was rationalized as resulting from nucleophilic attack upon a conjugated system including the cyclopropyl group. Attempts to use a variety of secondary amines as nucleophiles failed.

(1) J. M. Stewart and D. R. Olsen, *J. Org. Chem.*, **33**, 4534 (1968), and references cited therein.

(2) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).

(3) E. F. Ullman, *ibid.*, **81**, 5386 (1959); M. T. Wuesthoff and B. Rickborn, *J. Org. Chem.*, **33**, 1311 (1968).

(4) H. M. Walborsky and J. B. Pierce, *ibid.*, **33**, 4102 (1968).



(1)

Since it is well known that extension of the conjugation of activated olefins[5] leads to a substantial anodic shift in the reduction potential of the olefins[6] and since reductive coupling in such a system is largely through the ω position,[5] it would be interesting to compare the behavior of **2** and its 3-*n*-propyl (**4**) analog,[7] ethyl 2-cyano-3-methyl-2-hexenoate, under electrolytic conditions and to assess by this means the contribution of the cyclopropyl group to conjugation. While **4**, because of steric conditions, would not be expected to undergo reductive coupling at the 3 position, **2** could reductively couple if opening of the cyclopropyl ring made available an unhindered position.

Polarographic studies (Table I) showed that the cyclopropyl group, even when adjacent to an electron-withdrawing group (**6**, **7**) is not electroreducible. The substances $RC(CH_3)=C(CN)COOC_2H_5$ were, as expected, reducible; however, changing R from ethyl (**5**) to *n*-propyl (**4**) to cyclopropyl (**2**) had virtually no effect upon the half-wave potential. This shows that only the activated olefinic group is involved in the reduction.

Compounds **2**, **4**, and **5** showed only one reduction wave in anhydrous DMF or in 10% aqueous DMF.[8] That this was a one-electron wave was demonstrated unequivocally for **4** which is capable at most of undergoing a two-electron reduction under these conditions: addition of phenol, a more effective proton donor than water, to the polarographic solution virtually doubled the wave height. The same result was then also observed with **2**. The ability of the first reduction species, an anion radical, to escape protonation by water in many cases is not a new phenomenon (*cf.* ref 10). The failure to obtain a second reduction wave for **2** and **4** as well as the complete irreversibility of the reduction of even **4** in DMF (exhibited in cyclic voltammetry at the fastest practical sweep rates, 20 V/sec) remain unexplained.[11] They indicate an extremely rapid follow-

(5) M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 226 (1964).

(6) Compare, *e.g.*, the half-wave potentials (V. *vs.* saturated calomel electrode) of the following pairs: acrylonitrile, −1.9, 1-cyano-1,3-butadiene, −1.5; ethyl acrylate, −1.8, ethyl sorbate, ~−1.5; benzalfluorene, −1.67, cinnamylidenefluorene, −1.46.

(7) The uv maximum of **2** ($\lambda_{max}^{CH_3CN}$ 257 mμ, log ϵ 3.99) showed an auxochromic shift with respect to **3** ($\lambda_{max}^{CH_3CN}$ mμ, log ϵ 3.87) of +25 $\Delta\lambda$; this is similar to the results with other cyclopropyl olefinic esters.[2]

(8) A similar one-wave reduction was obtained for ethyl 2-cyanosorbate.[9]

(9) J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 743 (1969).

(10) J. Simonet and M. Morenas, *C. R. Acad. Sci., Ser. C*, **269**, 42 (1969).

(11) Under these conditions diethyl fumarate showed completely reversible anion radical formation.