306.1371 (calcd for $C_{19}H_{18}N_2O_2$ 306.1368).

1-Benzyl-1,2,3,4-tetrahydro-8-hydroxy-β-carboline-1-carboxylic acid (7b): from serotonin oxalate; 290 mg (90%); mp >230 °C dec; IR (Nujol) 3580, 3500, 3400, 3100, 1622 cm^{-1}; ^{1}H NMR (CF_3COOD) δ 3.1 (br s, 2 H), 3.8 (br m, 4 H), 7.1 (m) and 7.4 (m) (total integration 8 H); mass spectrum (70 eV, relative intensity), *m/e* no M^+, 278 (10), 231 (8), 187 (100), 146 (30), 133 (50), 117 (12), 91 (40), 65 (18); high-resolution mass spectrum (EI) showed weak M^+ and $M - CO_2$, 278.1414 (calcd for $C_{18}H_{18}N_2O$ 278.1419).

1-Benzyl-1,2,3,4-tetrahydro-8-methoxy-β-carboline-1-carboxylic acid (7c): from 5-methoxytryptamine; 315 mg (93%); mp 225 °C dec; IR (Nujol) 3400, 3100, 2400, 1635, 1595 cm^{-1}; ^{1}H NMR (CF_3CO_2D) 3.2 (m, 2 H), 3.8 (m, 2 H), 3.9 (br s, 2 H), 4.05 (s, 3 H), 7.1–7.6 (m, 8 H); mass spectrum (70 eV, relative intensity), *m/e* no M^+, 292 (15), 290 (25), 289 (27), 245 (44), 201 (100 at lower voltages), 199 (10), 145 (20), 123 (35), 91 (100), 65 (40); high-resolution mass spectrum (EI) did not show M^+ but gave $M - (H_2O + H)$, 317.1289 (calcd for $C_{20}H_{17}N_2O_2$ 317.1278).

Derivatization of β-Carbolines. Either **7b** or **7c** (100 mg) was dissolved in MeOH/HCl (2:1) (20 mL) and added to ethereal diazomethane (from 1 g of nitrosomethylurea). After standing at room temperature for 24 h the oil was taken up in 10 mL of MeOH and the process repeated 3–4 times. In this way we obtained 8-methoxy-1-(carbomethoxy)-β-carboline **7d**, the ^{13}C NMR spectrum of which showed the following signals:[23] ($CDCl_3$) δ 26.2 (t), 44.3 (t), 55.5 (q), 55.8 (q), 61.7 (t), 62.2 (s), 100. 3 (d), 111.2 (d), 112.3 (d), 112.4 (s), 126.5 (s), 127.8 (d), 128.2 (s), 128.5 (s), 129.9 (d), 131.6 (s), 136.1 (s) 153.9 (s), 172.0 (s); mass spectrum (70 eV, relative intensity), *m/e* 350 (M^+, 4), 291 (50), 290 (50), 289 (49), 259 (100), 201 (92), 173 (88), 160 (62), 91 (68).

Acknowledgment. We thank Dr. William D. Phillips for the use of the JEOL FX-100 NMR spectrometer in the Department of Chemistry, Washington University, Dr. James Hudson, University of Texas, Austin, for mass spectral measurements, Francis J. Koszyk, Illinois Institute of Technology, for IR and ^{1}H NMR spectra, J. McFarlane for the original synthesis of DNLCA, and C. Latherow for optical rotation measurements. This research was supported by NIH Grant NS-12342 and the National Foundation—March of Dimes.

Registry No. 3a·HCl, 62-31-7; **3b**, 51-41-2; **4**, 127-17-3; **5a**, 57256-22-1; **5a**·HCl, 76480-17-6; *cis*-**5b**, 76480-18-7; *trans*-**5b**, 76480-19-8; **6a**·HCl, 343-94-2; **6b** oxalate, 3036-16-6; **6c**, 608-07-1; **7a**, 17952-61-3; **7b**, 17994-22-8; **7c**, 29573-13-5; **7d**, 76480-20-1; (*E*)-**8**, 76480-21-2; (*Z*)-**8**, 76480-22-3.

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[23] ^{13}C NMR assignments for **7d** are in agreement with a recent study of related 3-(methoxycarbonyl)tetrahydro-β-carbolines.[24] Due to their poor solubility, however, it proved impossible to obtain ^{13}C NMR spectra for the free acids **7a–c**.

[24] Ungemach, F.; Soerens, D.; Weber, R.; DiPierro, M.; Campos, O.; Mokry, P.; Cook, J. M.; Silverton, J.V. *J. Am. Chem. Soc.* **1980**, *102*, 6976. Soerens, D.; Sandrin, J.; Ungemach, F.; Mokry, P.; Wu, G. S.; Yamanaka, E.; Hutchins, L.; DiPierro, M.; Cook, J. M. *J. Org. Chem.* **1979**, *44*, 535.

Neophotosantonin: A [1,5] Hydrogen Shift Isomer of Photosantonin[1]

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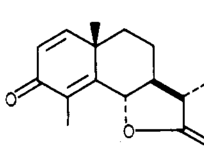
The sesquiterpene α-santonin (**1**), which has proved to be valuable as a chiral synthon,[2] is a well-known prototype of 2,5-cyclohexadienone photochemistry. When exposed to sunlight or irradiated through Pyrex, a neutral solution of **1** in ethanol yields the dienoid ester photosantonin (**2**).[3] Because of its structure, the crowded diene system in **2** is highly twisted (dihedral angle +64° by X-ray crystallography[4]) and is therefore of particular interest in connection with the optical rotatory properties of nonplanar conjugated dienes.[5] For this same reason, although **2** has long been regarded as "the ultimate product"[3a] of this photolysis of **1**, its further photorearrangement under more energetic irradiation into the isomeric structure **3** by an antarafacial [1,5] sigmatropic hydrogen shift should be sterically favored and is now reported. A close analogy for this transformation is the photoisomerization at 254 nm of 1,2-diisopropylidenecyclobutane (**4**) to 1-isopropenyl-2-isopropylcyclobutene (**5**).[6]



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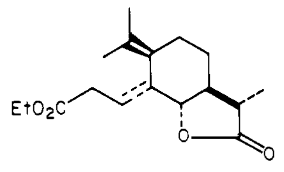

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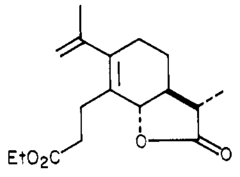

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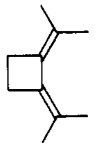

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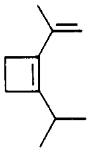
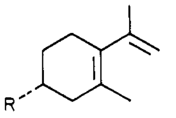
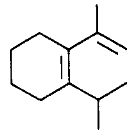


5



6, R = CH_3
7, R = H



8

Best results in the formation of **3**, for which the name "neophotosantonin" is proposed,[7] were obtained by irradiation of **2** in ethanol through a Vycor filter or of **1** in ethanol directly with a quartz-jacketed mercury-vapor lamp. Because of the sensitivity of **3** to further photolysis under these conditions, it was important to avoid overirradiation. In contrast to **2**, which is levorotatory and forms irregular plates, mp 67–68 °C, **3** is dextrorotatory and crystallizes in fine, thin needles, mp 74–75 °C. No evidence for rearrangement of **2** to **3** simply by heating could be detected. Evidently **2**, unlike **4**,[6] is sterically prevented from undergoing the suprafacial process required for a concerted thermal [1,5] sigmatropic hydrogen shift.[8]

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[1] Presented before the Division of Organic Chemistry at the 181st National Meeting of the American Chemical Society, Atlanta, GA., Mar 29–Apr 3, 1981; ORGN 165.

[2] For recent applications, see: Edgar, M. T.; Greene, A. E.; Crabbé, P. *J. Org. Chem.* **1979**, *44*, 159–160; Greene, A. E. *J. Am. Chem. Soc.* **1980**, *102*, 5337–5343; Fujimoto, Y.; Miura, H.; Shimizu, T.; Tatsuno, T. *Tetrahedron Lett.* **1980**, *21*, 3409–3412.

[3] For review, see: (a) Kropp, P. J. *Org. Photochem.* **1967**, *1*, 2–4 ff. (b) Schaffner, K.; Demuth, M. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 281–282ff.

[4] Determination in the laboratory of Professor B. Lee, University of Kansas; to be published.

[5] Burgstahler, A. W.; Barkhurst, R. C.; Gawroński, J. K. In "Modern Methods of Steroid Analysis"; Heftmann, E., Ed.; Academic Press: New York, 1973; Chapter 16. Cf.: Moriarty, R. M.; Paaren, H. E.; Weiss, U.; Whalley, W. B. *J. Am. Chem. Soc.* **1979**, *101*, 6804–6810.

[6] Kiefer, E. F.; Tanna, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 4478–4480.

[7] This name is suggested because the term "isophotosantonic lactone" already designates a structurally very different compound produced by acid-catalyzed photolysis of 1.[3]

[8] Cf.: Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187–217; McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270–276.

The structure of **3** was unequivocally established by spectral evidence. Besides features also present in **2** (α-methyl-substituted γ-lactone, primary ethyl ester, and two allylic methylene groups), the ^{1}H and ^{13}C NMR spectra of **3** reveal an isopropenyl group and one less methyl group than in **2**. Moreover, as would be expected, the mass spectrum of **3** is very similar to that of **2**.

Although space-filling molecular models suggest that the diene moiety in **3** might be less skewed than that in **2**, the UV spectrum of **3** shows only end absorption above 200 nm with a slight inflection at 205 nm. In this respect, **3** is like **2**, which also displays only end absorption and a small shoulder near 210 nm. Similar transparency in the UV has been reported for methylisopulegene (**6**)[9] and for diene **8**.[10] On the other hand, evidently owing to their wider exocyclic bond angles and therefore greater ability to approach planarity, the four-membered-ring dienes **4** and **5**,[6] together with two five-membered-ring analogues,[9,11] behave more like typical conjugated dienes and exhibit discrete absorption maxima between 235 and 255 nm.

For additional comparison, diene **7** was synthesized by application of the Wittig reaction to 1-acetyl-2-methylcyclohexene. This diene, like **2**, **3**, **6**, and **8**, appears to have a significantly twisted chromophore, since it shows only end absorption above 200 nm with a small shoulder at 220 nm. On the other hand, the diene moiety in **7** is obviously much more flexible than that in **2** and **3**, since, unlike the latter two compounds (but like **6**[9]), **7** readily gives a Diels–Alder adduct with tetracyanoethylene and is therefore capable of reacting as a normal cisoid conjugated diene.

With respect to their chiroptical properties, **2** and **3** differ markedly. Whereas **2** exhibits a fairly strong negative Cotton effect at 195–210 nm, in conformity with expectations for an exocyclic cisoid diene of this type with a right-handed or *P* helicity,[5] **3** displays a much weaker positive Cotton effect in this region. Since the lactone ring in **3** (and probably also in **2**) would be expected to produce a positive Cotton effect near 210 nm,[12] the chirality contribution of the diene portion of **3** is difficult to assess. Nevertheless, the reversal in Cotton effect in going from **2** to **3** is striking and is clearly worthy of further investigation.[13]

Experimental Section

Melting and boiling points were taken in capillary tubes and are uncorrected. IR spectra were recorded on a Perkin-Elmer 137 Infracord. NMR spectra were determined in $CDCl_3$ with tetramethylsilane as internal reference on Varian A-60A and Bruker WP-80 instruments. Electron-impact mass spectra were obtained at 70 eV with a Varian CH-5 spectrometer. UV spectra were taken in hexane on Cary 14 and Perkin-Elmer 555 spectrophotometers. Optical rotations were measured in ethanol on a Perkin-Elmer 141 polarimeter. CD determinations were made in hexane on a Cary 60 recording spectropolarimeter equipped with a Model 6001 CD accessory unit. Combustion analyses were performed on an HP-185C CHN analyzer by Mr. Tho Nguyen, University of Kansas Department of Medicinal Chemistry microanalyst.

Photochemical irradiations were conducted in nitrogen-purged, water-cooled ethanol solutions at 40 °C with a quartz-jacketed 450-W Hanovia medium-pressure mercury-vapor immersion lamp inserted in a filter sleeve as indicated and were monitored by IR and ^{1}H NMR spectroscopy. After termination of the photolysis, the solvent was evaporated under reduced pressure, and the product (**2** or **3**) was isolated by chromatography on silica gel (30:1, Mallinckrodt CC-4 SilicAR) with petroleum ether–ether (4:1) and crystallized at −20 °C from CCl_4–hexane. TLC assays were made with cyclohexane–ethyl acetate (1:1) on 0.2-mm Merck silica gel 60 F_{254} precoated slides.

Photosantonin (2) was prepared by irradiation of α-santonin (**1**, Sigma) through a Pyrex filter as reported,[14] except for the scale and type of apparatus. From 5.0 g (0.02 mol) of **1** in 600 mL of absolute ethanol, after 3 h of irradiation, was obtained 2.4 g (40%) of **2** as irregular plates: mp 63–67 °C, (raised to 67–68 °C after three recrystallizations from CCl_4–hexane); homogeneous by TLC (R_f 0.49); IR (CCl_4) 1785, 1735 cm^{-1}; $[\alpha]^{25}{}_D$ −121° (*c* 0.50) (lit.[14] $[\alpha]^{25}{}_D$ −121°); $[\alpha]^{25}{}_{578}$ −122°; $[\alpha]^{25}{}_{546}$ −141°; $[\alpha]^{25}{}_{436}$ −270°; $[\alpha]^{25}{}_{365}$ −471°; UV λ 210 nm (ϵ 8700, sh) (lit.[14] ϵ 8500 at 204 nm in ethanol); CD $\Delta\epsilon^{\mathrm{infl}}{}_{210}$ −12.4, $\Delta\epsilon_{195}$ ca. −25; ^{1}H NMR, as published for photosantonic acid[15] except for additional peaks (in $CDCl_3$) at δ 4.14 (q, J = 7 Hz, 2 H) and 1.23 (t, J = 7 Hz, 3 H) due to the ethoxy group; ^{13}C NMR δ 178.47 (s), 171.61 (s), 139.75 (s), 130.58 (s), 127.73 (s), 111.10 (d), 83.31 (d), 60.43 (t), 54.30 (d), 42.04 (d), 34.15 (t), 30.39 (t), 27.42 (t), 22.02 (q), 19.89 (q), 14.13 (q), 12.37 (q); mass spectrum (probe temperature 49 °C), *m/e* (relative intensity) 292 (M^+, 44), 219 (100), 191 (29), 145 (97), 131 (50), 105 (24), 91 (29), 55 (39), 43 (45).

Neophotosantonin (3). Irradiation of 500 mg (1.71 mmol) of **2** in 100 mL of absolute ethanol for 2 h through a Vycor filter yielded 220 mg (44%) of **3** as fine needles: mp 74–75 °C (after two recrystallizations at −20 °C from CCl_4–hexane); homogeneous by TLC (R_f 0.49, indistinguishable from that of **2**); IR (CCl_4) 1785 (γ-lactone CO), 1735 (ester CO), 1635 (C=C) 900 cm^{-1} (=CH_2); $[\alpha]^{25}{}_D$ +62° (*c* 1.00); $[\alpha]^{25}{}_{578}$ +65°; $[\alpha]^{25}{}_{546}$ +74°; $[\alpha]^{25}{}_{436}$ +124°; $[\alpha]^{25}{}_{365}$ +197°; UV λ 205 nm (ϵ 7300, infl); CD $\Delta\epsilon_{210}$ +4.4; ^{1}H NMR δ 4.95, 4.65 (m, 2 H, =CH_2, collapsed to 2 d, J = 2 Hz, by irradiation at δ 1.8), 4.45 (m, 1 H, CHO), 4.13 (q, J = 7 Hz, 2 H, $OC\mathbf{H}_2CH_3$), 2.6–2.4 (br s + m, 3 H, CH_2CO + CHCO), 2.3–1.9 (m, 4 H, 2 =CCH_2), 1.8–1.4 (m, 3 H, CH_2CH), 1.8 (br t, 3 H, CH_2=$CC\mathbf{H}_3$), 1.23 (t, J = 7 Hz, 3 H, $OCH_2C\mathbf{H}_3$), 1.21 (d, J = 6 Hz, 3 H, $C\mathbf{H}_3CHCO$); ^{13}C NMR δ 179.44 (s), 172.94 (s), 144.80 (s), 138.11 (s), 128.84 (s), 113.89 (t), 81.19 (d), 60.25 (t), 48.84 (d), 41.88 (d), 33.49 (t), 29.91 (t), 24.83 (t), 22.93 (t), 22.30 (q), 14.25 (q), 12.43 (q); mass spectrum (probe temperature 49 °C), *m/e* (relative intensity) 292 (M^+, 92), 219 (61), 218 (83), 191 (98), 175 (75), 145 (100), 131 (63), 105 (45), 91 (61), 55 (86), 43 (33), 41 (50). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.89; H, 8.48.

Similar photolysis of 5.0 g (0.02 mol) of **1** in 600 mL of absolute ethanol through a Vycor filter required 10 h and gave only 0.65 g (11%) of once recrystallized **3**, mp 72–74 °C. Without a filter the conversion of **1** into **3** on this scale was practically complete in only 3 h, and the yield of **2**, mp 72–74 °C, was improved to 1.15 g (19%). With a Corex filter the formation of **3** from either **1** or **2** was evident by ^{1}H NMR spectroscopy but was slow compared to production of byproducts. Photochemical reversion of **3** to **2** was not observed, nor was rearrangement of **2** to **3** in the dark detected at temperatures up to 250 °C.

1-Isopropenyl-2-methylcyclohexene (7). The Wittig synthesis of this compound was patterned after the general procedure of Sondheimer and Mechoulam,[16] but conditions were not optimized. To 50 mL of an ether suspension, under nitrogen, of methylenetriphenylphosphorane, generated from 21 mmol of methyltriphenylphosphonium bromide and 20 mmol of *n*-butyllithium, was added, with stirring at 0 °C over a period of 5 min, 2.1 g (15 mmol) of purified 1-acetyl-2-methylcyclohexene[17] in 5

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[9] Wolinsky, J.; Chan, D. *J. Am. Chem. Soc.* **1963**, *85*, 937–940.

[10] Starr, J. E.; Eastman, R. H. *J. Org. Chem.* **1966**, *31*, 1393–1402. For a further example in a comparable photoproduct derived from ψ-santonin, see: Dauben, W. G.; Lightner, D. A.; Hayes, W. K. *J. Org. Chem.* **1962**, *27*, 1897–1898.

[11] Wolinsky, J.; Chollar, B.; Baird, M. D. *J. Am. Chem. Soc.* **1962**, *84*, 2775–2779.

[12] Jennings, J. P.; Klyne, W.; Scopes, P. M. *J. Chem. Soc.* **1965**, 7211–7229.

[13] For this purpose, low-temperature CD determinations on **3** would probably be helpful but are difficult to perform below 220 nm.

[14] Barton, D. H. R.; de Mayo, P.; Shafiq, M. *J. Chem. Soc.* **1958**, 3314–3319.

[15] van Tamelen, E. E.; Levin, S. H.; Brenner, G.; Wolinsky, J.; Aldrich, P. E. *J. Am. Chem. Soc.* **1959**, *81*, 1666–1678.

[16] Sondheimer, F.; Mechoulam, R. *J. Am. Chem. Soc.* **1957**, *79*, 5029–5033.

[17] Turner, R. B.; Voitle, D. M. *J. Am. Chem. Soc.* **1951**, *73*, 1403–1410. Cf.: Erskine, R. L.; Waight, E. S. *J. Chem. Soc.* **1960**, 3425–3431.

J. Org. Chem. **1981**, *46*, 1743–1745

mL of dry tetrahydrofuran. The resulting dense white precipitate was stirred at 20 °C for 6 h, after which the ether was removed by slow distillation and replaced with 30 mL of THF. Stirring at gentle reflux was continued for 36 h with little change in appearance. The mixture was then cooled, diluted with 100 mL of water, and extracted with three 25-mL portions of pentane. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated on the steam bath under atmospheric pressure. Passage of the residue through 40 g of basic alumina (Woelm, activity grade I) with pentane, followed by short-path distillation, afforded 0.85 g (42%) of diene **7** as a colorless oil with a pinene-like odor: bp 174–176 °C (740 mm); homogeneous by GLC (90 °C on a 6 mm × 2 m 15% Carbowax–Chromosorb W column); IR (neat) 1645, 1375, 895 cm^{-1}; UV λ 220 nm (ϵ 3600, sh); ^1H NMR δ 4.87, 4.57 (m, 2 $=CH_2$, collapsed to 2 d, $J = 2$ Hz, by irradiation at δ 1.76), 2.0 (m, 4 H, 2 $CH_2C=$), 1.76 (m, 3 H, $CH_3C=CH_2$), 1.7–1.4 (m, 4 H, CH_2CH_2), 1.62 (m, 3 H, $CH_3C=$); ^{13}C NMR δ 147.66 (s), 134.25 (s), 126.30 (s), 112.04 (t) ($=CH_2$), 31.38 (t), 29.44 (t), 23.31 (t) (2 CH_2), 22.22 (q), 20.34 (q); mass spectrum (inlet temperature 154 °C), *m/e* (relative intensity) 136 (M^+, 68), 121 (76), 108 (8), 107 (32), 93 (100), 79 (60), 67 (20), 41 (24), 28 (28). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.79; H, 11.79.

Addition of 136 mg (1.0 mmol) of **7** in 1 mL of THF to 128 mg (1.0 mmol) of freshly sublimed tetracyanoethylene in 1 mL of THF at 22 °C gave an immediate purple color which faded after 5 min to light yellow. After 8 h the solvent was evaporated and the light tan residue passed through 10 g of silica gel with 50 mL of pentane–ether (5:1). Crystallization of the product at 0 °C from pentane–ether (1:1) gave 120 mg (45%) of coarse, colorless plates, mp 115–117 °C. Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 73.01; H, 6.00; N, 21.50.

Under the same conditions, neither **2** nor **3** gave any color change with tetracyanoethylene, and on standing at 20–25 °C only slow reaction, leading to a mixture of products, could be detected by TLC.

Acknowledgment. I am indebted to Professor R. S. Givens for use of his photochemical apparatus and thank him, together with Professors R. G. Carlson, G. W. Everett, and J. Wolinsky, for generous advice and assistance. This work was supported in part by the National Science Foundation (CHE-7823856).

Registry No. **1**, 481-06-1; **2**, 23811-40-7; **3**, 76480-14-3; **7**, 76480-15-4; 1-acetyl-2-methylcyclohexene, 2047-97-4; tetracyanoethylene, 670-54-2; 4,8a-dimethyl-1,1,2,2-tetracyano-1,2,3,5,6,7,8,8a-octahydronaphthalene, 76480-16-5.

Diastereoselection in the Decarbalkoxylation Reaction. Effect of Nonbonded Ring Oxygens in the Reactions of Geminal Diesters

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Received October 27, 1980

In connection with our interest in diastereoselective reactions of geminal carboxylic acids[1] and their derivatives, we have investigated the extremely useful decarbalkoxylation method of Krapcho and co-workers.[2] Of particular interest was the possibility that nonbonding electron pairs might produce a dramatic change in the stereoselectivity of the reaction. To test this possibility, the anancomeric compounds, 5,5-bis(carboethoxy)-2-isopropyl-1,3-dioxane, **1**, and diethyl 4-*tert*-butylcyclohexane-1,1-dicarboxylate, **4**, were synthesized and decarboethoxylated.

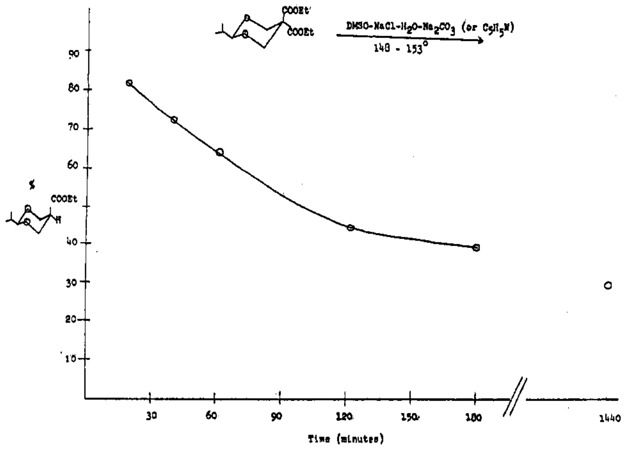

Figure 1.

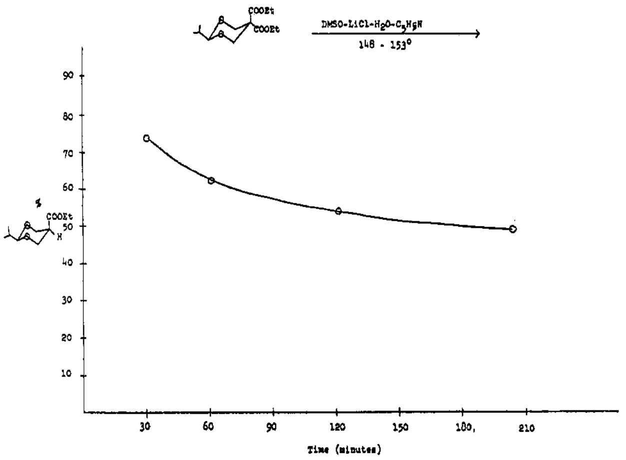

Figure 2.

Table I. Decarbalkoxylation of Geminal Diesters

diester	solvent	product composition, %
1	Me_2SO	86.6 ± 0.52
	DMF	86.9 ± 0.52
1 ($R_2 = R_3 = COOCH_3$)	Me_2SO	86.7 ± 0.52
4	Me_2SO	53.2 ± 0.25
	DMF	52.9 ± 0.25

1, X = O; $R_1 = CH(CH_3)_2$; $R_2 = R_3 = COOC_2H_5$
4, X = CH_2; $R_1 = C(CH_3)_3$; $R_2 = R_3 = COOC_2H_5$

2, X = O; $R_1 = CH(CH_3)_2$; $R_2 = COOC_2H_5$; $R_3 = H$
3, X = O; $R_1 = CH(CH_3)_2$; $R_2 = H$; $R_3 = COOC_2H_5$
5, X = CH_2; $R_1 = C(CH_3)_3$; $R_2 = COOC_2H_5$; $R_3 = H$
6, X = CH_2; $R_1 = C(CH_3)_3$; $R_2 = H$; $R_3 = COOC_2H_5$

Heating **1** with NaCl in wet Me_2SO at 148–153 °C resulted in the evolution of CO_2. The relative concentrations of **2** and **3** were not invariant as a function of time; the initial high preference for the axial isomer disappeared at long reaction times, with the thermodynamically more

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[1] (a) Banks, H. D. *J. Org. Chem.* **1973**, *38*, 4084. (b) Banks, H. D.; Jacobs, W. **1975**, *40*, 790.

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