(s, 1, NH), 7.44–7.10 (m, 5, aromatic), 5.39 (s, 2, $BzCH_2$), 4.75 (s, 1, C=CH), 4.11 (q, J = 7 Hz, ethyl CH_2), 3.43 (s, 2, NH_2), 1.84 (s, 3, CH_3), 1.25 (t, J = 7 Hz, ethyl CH_3).

Anal. Calcd for $C_{15}H_{19}N_5O_2$: C, 59.79; H, 6.35; N, 23.24. Found: C, 59.77; H, 6.38; N, 22.90.

4*H*,6*H*-1-Benzyl-7-methyl-1,2,3-triazolo[5,4-*b*][1,4]diazepin-5-one (11).—To a solution of 0.1 g (0.004 mol) of sodium in absolute alcohol was added 1.0 g (0.003 mol) of **10**. The yellow solution was refluxed for 5 hr. Concentration *in vacuo* afforded yellow, irregular prisms. The prisms were dissolved in water, the solution was made acid with hydrochloric acid, and the precipitate was collected. Treatment with hot benzene produced an insoluble bright yellow crop of crude **11b** or **11c**. The benzene solution afforded a crop of off-white, irregular prisms consisting of a mixture of **11a** and **11b**: ir (KBr) 3000, 1700, 1660, 1620, 1400, 1300, 710 cm^{-1}. Treatment of the mixture with chloroform, pyridine, or dimethyl sulfoxide converted it to pure **11b** or **11c**.

The yellow, irregular prisms (**11b** or **11c**) were collected: mp 244° dec; ir (KBr) 3200, 3100, 2990, 1610, 1580, 700 cm^{-1}; pmr (pyridine-d_5) δ 7.38–7.02 (m, 5, aromatic), 5.70 (s, 2, $BzCH_2$), 3.30 (s, 2, CH_2), 2.21 (s, 3, CH_3).

Anal. Calcd for $C_{18}H_{13}N_5O$: C, 61.19; H, 5.10; N, 27.44. Found: C, 60.90; H, 5.39; N, 27.47.

4-Acetamido-5-amino-1-benzyl-1,2,3-triazole (12).—A mixture of 1.0 g (0.005 mol) of **5** and 10 g of acetic anhydride was stirred at room temperature for 10 min. The precipitate that formed was collected and air dried. Two recrystallizations from water afforded 0.8 g (53%) of **12**: mp 177°; ir (KBr) 3350, 3200, 1660, 1650, 1600, 1280 cm^{-1}; pmr ($CDCl_3$) δ 7.41–7.18 (m, 5, aromatic), 5.36 (s, 2, $BzCH_2$), 2.20 (s, 3, $COCH_3$).

Anal. Calcd for $C_{11}H_{13}N_5O$: C, 57.13; H, 5.66; N, 30.28. Found: C, 57.19; H, 5.63; N, 30.66.

4-Acetamido-1-benzyl-1,2,3-triazole (13).—Compound **12** (0.5 g, 0.003 mol) was converted to 0.7 g (100%) of the corresponding diazonium fluoroborate in the usual fashion.[28] After air drying for 3 hr, the diazonium salt was dissolved in 50 ml of methanol at 0° and treated with 0.05 g of sodium borohydride. The solution was stirred for 15 min, diluted with an equal volume of water, and extracted with 4 × 50 ml of methylene chloride. After drying over magnesium sulfate, the methylene chloride extract was concentrated *in vacuo* to a viscous syrup. The syrup was chromatographed on silica gel (100 g, ethyl acetate). Concentration of the first fraction afforded **13** in the form of buff, irregular prisms. Solution in methylene chloride, decolorization with charcoal, and precipitation with hexane gave 0.12 g of pure **13**: mp 197.5–198.5°; ir (KBr) 3180, 3000, 1660, 1560, 1420, 1280, 1045, 841, 715 cm^{-1}; pmr ($CDCl_3$) δ 8.02 (s, 1, C-5 proton), 7.40–7.22 (m, 5, aromatic), 6.02 (broad s, 1, NH), 5.28 (s, 2, $BzCH_2$), 2.27 (s, 3, $COCH_3$).

Anal. Calcd for $C_{11}H_{12}N_4O$: C, 60.87; H, 5.94; N, 25.82. Found: C, 60.81; H, 5.65; N, 25.76.

5-Acetamido-1-benzyl-1,2,3-triazole (14).—A solution of 1.0 g (0.006 mol) of 5-amino-1-benzyl-1,2,3-triazole in 7.5 ml of acetic anhydride was treated with 0.5 ml of sulfuric acid. The yellow solution was stirred at room temperature for 24 hr. The crude precipitate and solution were poured onto crushed ice, and the aqueous solution was concentrated *in vacuo* to a viscous oil. Treatment of the oil with hexane produced off-white, irregular prisms of **14**. Final purification by column chromatography using 100 g of silica gel and ethyl acetate as solvent afforded pure **14**: mp 132°; ir (KBr) 3300, 3200, 3000, 1690, 1550, 1230, 980, 705 cm^{-1}; pmr ($CDCl_3$) δ 9.39 (broad s, 1, NH), 7.78 (s, 1, C-4 proton), 7.36–7.02 (m, 5, aromatic), 5.50 (s, 2, $BzCH_2$), 2.04 (s, 3, $COCH_3$).

Anal. Calcd for $C_{11}H_{12}N_4O$: C, 60.87; H, 5.94; N, 25.82. Found: C, 60.90; H, 5.82; N, 25.79.

4,5-Diacetamido-1-benzyl-1,2,3-triazole (15).—A solution of 0.1 g (0.001 mol) of **5** in 1.0 g of acetic anhydride was kept at room temperature overnight. The precipitate that formed was collected and washed with water. Three recrystallizations from water afforded 0.12 g (45%) of analytically pure **15**: mp 194°; ir (KBr), 3445, 3250, 1660, 1610, 1570, 1520, 705 cm^{-1}; pmr ($CDCl_3$) δ 8.08 (broad s, 1, NH), 7.38–7.10 (m, 5, aromatic), 5.61 (s, 2, $BzCH_2$), 2.75 (s, 3, $COCH_3$), 2.08 (s, 3, $COCH_3$).

Anal. Calcd for $C_{13}H_{15}N_5O_2 \cdot {}^1/_4H_2O$: C, 56.21; H, 5.44; N, 25.21. Found: C, 56.15; H, 5.60; N, 25.11.

(28) R. Adams, "Organic Reactions," Wiley, New York, N. Y., 1949, p 193.

Registry No.—**1**, 20271-33-4; **3**, 36540-25-7; **4**, 36540-26-8; **5**, 36540-27-9; **5** monopicrate, 36540-28-0; **5a**, 36540-29-1; **6**, 36540-30-4; **6a**, 36540-31-5; **7**, 36540-32-6; **8**, 36540-33-7; **9a**, 36540-34-8; **9b**, 36540-35-9; **10**, 36540-36-0; **11a**, 36540-37-1; **11b**, 36540-38-2; **11c**, 36540-39-3; **12**, 36540-40-6; **13**, 36540-41-7; **14**, 36540-42-8; **15**, 36540-43-9.

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Cyclic Peroxides. XVII.[1] Solvolysis of Di-*n*-butylmalonoyl Peroxide[2]

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It is postulated that in the solvolysis of di-*n*-butylmalonoyl peroxide (**1**) in methanol or ethanol initially the monoperoxy malonic acid half ester **12** is formed. Analogous to simple peroxy acids, it is proposed that in methanol this peroxy acid intermediate suffers concerted deoxygenation to produce hydrogen methyl di-*n*-butylmalonate (**6**) as the major product, but in ethanol **12** undergoes homolysis of the peroxide bond, leading to di-*n*-butylmalonic acid (**10**) as the major product. In both cases, inhibition experiments indicate that a chain process involving the hydroxyalkyl radical, derived from the solvent, contributes in a minor way. Even at relatively low temperatures, in both solvents some decarboxylation of the malonoyl peroxide **1** occurs to give α-lactone **2**.

Recently we reported[4] on the synthesis of malonoyl peroxide **1**, a novel class of cyclic diacyl peroxides, which on photolysis decarboxylates to generate α-lactones **2** (eq 1). At −196° the α-lactone **2** is perfectly stable and can be preserved indefinitely, but on further photolysis **2** decarbonylates to afford ketone **4**.[5] Warming up to −100°, α-lactone **2** rapidly polymerizes into polyester **5**,[5] which can also be obtained in high yield by photolysis of a benzene solution of malonoyl peroxide **1**.[4] On the other hand, on photolysis of **1** in alcoholic solvents such as methanol or ethanol, the α-alkoxy acid **3** is produced in high yield, as expected from the addition of R'OH to the dipolar structure of

(1) This paper is dedicated to Professor Dr. Rudolf Criegee on his 70th birthday.

(2) Part XVI: W. Adam and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 2894 (1972).

(3) Presented in part at the Cyclic Peroxide Symposium, Metrochem 71, Regional Meeting of the American Chemical Society, San Juan, Puerto Rico, April 30, 1971.

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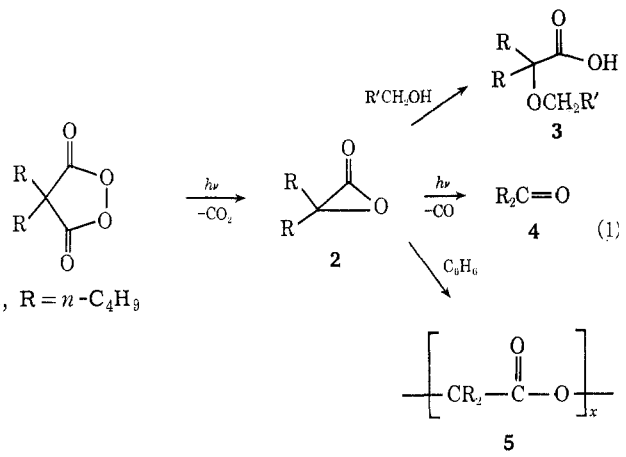

1, R = n-C_4H_9 (1)

the α-lactone.[4] However, in the latter case we observed that concurrent with the photodecarboxylation of **1** in the alcoholic solvents, a direct reaction between the solvent and the malonoyl peroxide takes place in the dark.[3] In this article we describe our results on the systematic investigation of this direct solvolysis reaction of **1** in the dark.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord 237-B using 0.1-mm sodium chloride cavity cells.

The nmr spectra were recorded on a Varian T-60 spectrometer using normal and semi-micro nmr tubes. The chemical shifts are given in δ units using TMS as internal standard.

The glpc analyses were carried out on a Varian Aerograph 202-B instrument, provided with TC detection, employing the following columns under the specified conditions: (a) 15 ft × 0.25 in. copper column, packed with 20% Carbowax 20M on 60/80 mesh Chromosorb W, operated at column, injector, and detector temperature of 175, 225, and 250°, respectively, and a helium flow of 60 ml/min (condition CX-1); and (b) 12 ft × 0.25 in. copper column, packed with 27% Apiezon M on 60/80 Chromosorb P, operated at column, injector, and detector temperatures of 214, 225, and 250°, respectively, and a helium flow of 60 ml/min (condition AZ-1). All melting points and boiling points are uncorrected.

Di-n-butylmalonoyl Peroxide.—Into four 25-ml round-bottom flasks, each provided with a spin bar and a drying tube, were placed each 2.50 g (0.0116 mol) of di-n-butylmalonic acid[6,7] and 12.5 ml of methanesulfonic acid. By means of remote control and stirring magnetically were charged into each flask a total of 4.5 ml of 98% hydrogen peroxide, 2.0 ml initially, 1.5 ml after 6 hr, and finally 1.0 ml after 10 hr of reaction time. The contents were stirred at room temperature for another 24 hr, after which time the suspended malonic acid had dissolved. The four reaction mixtures were combined and poured onto crushed ice, saturated ammonium sulfate was added, and the mixture was extracted well with n-pentane. The combined pentane extracts were washed with saturated aqueous ammonium sulfate, sodium bicarbonate, and water. After drying over magnesium sulfate and evaporation of the solvent, there was obtained 9.00 g (91%) of crude product. Fractional distillation at reduced pressure afforded 7.75 g (78%) of malonoyl peroxide, bp 49–50° (0.05 mm), $n^{22.5}$D 1.4350, 99.5% pure by iodometric titration. The spectral data are: ir (CCl_4) 1783, 1468, 1225, 1135, and 1075 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.9 (m, 3, CH_3–), 1.3 (m, 4, $-CH_2-CH_2-$), and 1.85 (m, 2, $-CH_2CC{=}O$); uv (CCl_4) λ 220 nm (ϵ 350), 250 (100), 300 (11.2), and 350 (8.4).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47; mol wt, 214.3. Found: C, 61.59; H, 8.55; mol wt, 213.2 ± 1.0 (osmometry).

Dimethyl di-n-butylmalonate was prepared in 76% yield from di-n-butylmalonic acid by treatment with ethereal diazomethane solution,[8,9] bp 113.5–114.5° (4 mm), n^{20}D 1.4350, which on standing crystallized, mp 39°. The spectral data are: ir (CCl_4) 2990–2845, 1740 (shoulder), 1725 (ester carbonyl), 1255, 1210, 1155, and 1130 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.95, 1.20, and 1.80 (m, 3:4:2, n-butyl) and 3.65 (s, 3, ester methyl).

Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 64.09; H, 9.83.

Methyl Hydrogen Di-n-butylmalonate.—To a solution of 4.32 g (20 mmol) of di-n-butylmalonic acid in 90 ml of ether, cooled to 0°, was added slowly while stirring magnetically 76 ml of a 0.131 M solution of diazomethane in ether (freshly standardized by titration with acid). The colorless reaction mixture was then extracted three times with dilute sodium hydroxide, and the combined alkaline extracts were acidified while cooling with concentrated hydrochloric acid, and extracted three times with ether. The combined ether extracts were washed with water and dried ($MgSO_4$). Evaporation of the ether at 80° (20 mm) gave 3.5 g (76%) of a residue, n^{20}D 1.4449. On distillation 2.9 g (63%) of a colorless liquid was obtained, bp 102–105° (0.04 mm), which slowly crystallized on standing, mp 39–42°. Several recrystallizations from n-hexane at −20° gave the pure material, mp 45.5–46.5°. The spectral data are: ir (CCl_4) 3400–2500 (OH of acid), 1748 (ester carbonyl), 1705 (acid carbonyl), 1274, and 1201 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.1 (m, 18, n-butyl), 3.71 (s, 3, ester $-OCH_3$), and 11.1 (s, 1, acid OH).

Anal. Calcd for $C_{12}H_{22}O_4$: acid equiv, 230.3. Found: acid equiv, 230 ± 1.

Ethyl Hydrogen Di-n-butylmalonate.—The procedure described by Büchi, *et al.*,[10] was employed, but modified as below. A solution of 10.9 g (40 mmol) of diethyl di-n-butylmalonate in 10 ml of 95% ethanol was placed into a 50-ml round-bottom flask provided with a spin bar, dropping funnel, and reflux condenser. While heating at 80°, a solution of 2.96 g (45 mmol) of KOH in 10 ml of 95% ethanol and 5 ml of water was added within 30 min, and the reaction mixture was allowed to stir for an additional 75 min at 90°. The ethanol was removed at reduced pressure [60° (20 mm)], 50 ml of water was added to the residue, and the mixture was extracted two times with n-hexane. The alkaline, aqueous solution was acidified with concentrated hydrochloric acid while cooling and extracted three times with 70-ml portions of ether. The combined ether extracts were washed with water and dried ($MgSO_4$), and the ether was evaporated [80° (20 mm)], affording 7.75 g (80%) of a viscous liquid, n^{20}D 1.4424. After distillation at reduced pressure there was obtained 5.1 g (53%) of a colorless liquid, bp 117–117.5° (0.08 mm), n^{20}D 1.4415. On standing at 20° for a day, this distillate crystallized partially, and collection of the crystals on a sintered-glass funnel gave 1.7 g (33%) of colorless crystals, mp 41–43°. The spectral data are: ir (CCl_4) 3400–2500 (acid OH), 1745 (ester carbonyl), 1705 (acid carbonyl), 1272, and 1200 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.2 (m, and overlapping t at 1.25, 21, n-butyl and CH_3 of ethoxy group), 4.15 (q, 2, J = 7 Hz, CH_2 of ethoxy group).

Anal. Calcd for $C_{13}H_{24}O_4$: acid equiv, 244.3. Found: acid equiv, 244 ± 2.

Ethyl methyl di-n-butylmalonate was prepared in 96% yield from ethyl hydrogen di-n-butylmalonate by treatment with ethereal diazomethane,[8,9] n^{20}D 1.4346, and used without further purification. The spectral data are: ir (CCl_4) 1732 with shoulder at 1745 (ester carbonyl), 1253, 1205, and 1199 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.2 (m and overlapping t at 1.25, 21, n-butyl and CH_3 of ethoxy group), 3.68 (s, 3, ester $-OCH_3$), and 4.14 (q, 2, J = 7 Hz, $-CH_2-$ of ethoxy group).

Ethyl 2-n-butylhexanoate was prepared in 73% yield from 2-n-butylhexanoic acid[11] according to the procedure of Dolique,[12] bp 110–111° (18 mm), $n^{21.5}$D 1.4220 [lit.[12] bp 110° (18 mm), $n^{22.5}$D 1.4218].

Methyl 2-n-butylhexanoate was prepared in 65% yield by treatment of 2-n-butylhexanoic acid[11] with a slight excess of ethereal diazomethane, bp 89.5–90° (9 mm), n^{23}D 1.4232 [lit.[13] bp 90° (9 mm), n^{23}D 1.4232].

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2-*n*-Butyl-2-methoxyhexanoic Acid.—A solution of 2.22 g (10.3 mmol) of methyl 2-*n*-butyl-2-methoxyhexanoate and 1.2 g (20 mmol) of KOH in 6 ml of methanol was refluxed for 7 hr. The solvent was removed at reduced pressure, and the residue was dissolved in water and extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid and extracted several times with ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent was evaporated, affording 2.1 g of slightly yellow liquid. Distillation gave 1.43 g (70%) of the acid, bp 94–95.5° (0.15 mm), $n^{20}D$ 1.4423. The spectral data are: ir (CCl_4) 3500–2500 (acid OH), 2830, 1780, and 1708 (ester carbonyl), and 1090 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.95–1.70 (m, 18, *n*-butyl), 3.25 (s, 3, $-OCH_3$), and 10.5 (s, 1, $-CO_2H$).

Anal. Calcd for $C_{11}H_{22}O_3$: acid equiv, 202.3. Found: acid equiv, 202 ± 1.

Methyl 2-*n*-butyl-2-methoxyhexanoate was prepared in 51% yield following the methoxylation procedure of Diner, *et al.*,[14] bp 52° (0.05 mm), $n^{20}D$ 1.4315. The spectral data are: ir (CCl_4) 1740, 1727, and 1205 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.9–1.6 (m, 18, *n*-butyl), 3.15 (s, 3, OCH_3), and 3.65 (s, 3, $-CO_2CH_3$).

Methyl 2-*n*-butyl-2-hydroxyhexanoate was prepared in 85% yield from 2-*n*-butyl-2-hydroxyhexanoic acid by treatment with excess diazomethane, bp 60–61° (0.1 mm), $n^{20}D$ 1.4310. The spectral data are: ir (CCl_4), 3540 (hydroxyl), 1725 (ester carbonyl), 1250, 1220, and 1165 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.9–1.55 (m, 18, *n*-butyl), 3.55 (s, 1, -OH), and 3.70 (s, 3, $-CO_2CH_3$).

Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.30; H, 10.96. Found: C, 65.21; H, 11.05.

2-*n*-Butyl-2-hydroxyhexanoic acid was prepared in 90% yield by saponification of ethyl 2-*n*-butyl-2-hydroxyhexanoate with KOH in methanol, mp 85–86° (lit.[15] mp 87.5°).

Ethyl 2-*n*-butyl-2-hydroxyhexanoate was prepared in 60% yield, bp 114–116° (10 mm), $n^{20}D$ 1.4293, according to the procedure of Stoughton[16] and of Hepworth.[17]

Ethyl 2-*n*-butyl-2-methoxyhexanoate was prepared in 88% yield by treatment of 2-*n*-butyl-2-methoxyhexanoic acid with ethereal diazoethane,[18] and after bulb-to-bulb distillation at 125° (0.05 mm), $n^{21}D$ 1.4327, used without further purification. The spectral data are: ir (CCl_4) 1735 and 1725 (ester carbonyl) and 1200 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.0 (m, 21, *n*-butyl and CH_3 of ethoxy), 3.1 (s, 3, $-OCH_3$), and 4.1 (q, 2, J = 7 Hz, $-CH_2-$ of ethoxy).

5-Nonanone was prepared in 40% yield, bp 83–84° (22 mm), $n^{21}D$ 1.4188 [lit.[19] bp 88° (22 mm), $n^{20}D$ 1.4195], from 2-*n*-butyl-2-hydroxyhexanoic acid by treatment with lead tetraacetate in dry benzene.

2-*n*-Butyl-2-ethoxyhexanoic acid was prepared by photolysis of 40 ml of a 0.116 *M* solution of di-*n*-butylmalonoyl peroxide in absolute ethanol in a 1.5-mm wall thickness Pyrex tube at 350 mm for 24 hr. Removal of the ethanol [50° (12 mm)] gave 855 mg (85%) of colorless liquid, $n^{20}D$ 1.4421, which was used without further purification. The spectral data are: ir (CCl_4) 3395 and 3500–2450 (acid OH), 1777 and 1704 (ester carbonyl), 1153, 1113, 1086, and 1043 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.0 (m, 21, *n*-butyl and CH_3- of ethoxy), 3.42 (q, 2, J = 7 Hz, $-CH_2-$ of ethoxy), and 10.0 (s, 1, -OH).

Methyl 2-*n*-butyl-2-ethoxyhexanoate was prepared in 94% yield, $n^{20}D$ 1.4346, from 2-*n*-butyl-2-ethoxyhexanoic acid with ethereal diazomethane and used without further purification. The spectral data are: ir (CCl_4) 1727 and shoulder at 1740, and 1722 (ester carbonyl), 1198, and 1130 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.5 (m, 21, *n*-butyl and CH_3 of ethoxy), 3.36 (q, 2, J = 7 Hz, $-CH_2-$ of ethoxy), and 3.61 (s, 3, $-OCH_3$).

***cis,trans*-2-Butyl-2-hexenoic Acid.**—Into a 10-ml round-bottom flask, provided with a 15-cm fractionation column with distilling head, was placed 3.76 g (20 mmol) of 2-*n*-butyl-2-hydroxyhexanoic acid, mp 84–86°, and the contents were heated for 5.5 hr at 200° to remove the water as it formed during the heating. The dark residue was fractionated at reduced pressure using a 20-cm Vigreux column, collecting a 1.60-g sample, bp 90.0–90.5° (0.3 mm), $n^{20}D$ 1.4586, which by nmr was shown to consist of a 70:30 mixture of cis(Z) and trans(E) isomers, as judged by the relative areas of the olefinic triplets at δ 6.0 and 6.9, respectively.[20] No further purification was attempted. The spectral data are: ir (CCl_4) 3400–2500 (acid OH), 1688 (acid carbonyl), and 1640 cm^{-1} (olefinic double bond); nmr (60 MHz, CCl_4) δ 0.7–2.7 (m, 16, *n*-butyl and *n*-propyl), 6.0 for cis(Z) and 6.9 for trans(E) [t, 1, J = 6.0 Hz for cis(Z) and 7.4 Hz for trans(E), olefinic =CH), and 12.1 (s, 1, acid OH).

Ethyl *cis,trans*-2-*n*-butyl-2-hexenoate was prepared in 83% yield by treatment of *cis,trans*-2-*n*-butyl-2-hexenoic acid with ethereal diazoethene, and after bulb-to-bulb distillation at 115° (7 mm), $n^{20}D$ 1.4405, used without further purification. The material was shown to be a 70:30 mixture of cis(Z) and trans(E) isomers by glpc analysis (conditions CX-1). The spectral data are: ir (CCl_4) 1710 with shoulder at 1730 (ester carbonyl), 1640 (olefinic double bond), 1205, and 1150 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.6 (m, 19, *n*-butyl, *n*-propyl, and CH_3 of ethoxy), 4.15 (q, 2, J = 7 Hz, $-CH_2$ of ethoxy), and 5.78 for cis(Z) and 6.63 for trans(E) (t, 1, J = 7 Hz, olefinic =CH).

Methyl *cis,trans*-2-*n*-butyl-2-hexenoate was prepared in 95% yield by treatment of *cis,trans*-2-*n*-butyl-2-hexenoic acid with ethereal diazomethane and after bulb-to-bulb distillation at 115° (10 mm), $n^{20}D$ 1.4435, used without further purification. It was shown to be at 70:30 mixture of cis(Z) and trans(E) isomers by glpc (conditions CX-1). The spectral data are: ir (CCl_4) 1717 with shoulder at 1735 (ester carbonyl), 1643 (olefinic double bond), 1212, and 1150 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.7–2.6 (m, 16, *n*-butyl and *n*-propyl), 3.67 (s, 3, $-CO_2CH_3$), and 5.79 for cis(Z) and 6.64 for trans(E) (t, 1, J = 7 Hz, olefinic =CH).

General Solvolysis Procedure of Di-*n*-butylmalonoyl Peroxide.—A stock solution of di-*n*-butylmalonoyl peroxide was prepared in the desired anhydrous alcohol (methanol or ethanol) at the appropriate concentration (0.25–0.30 *M*), distributed into constricted Pyrex test tubes, and sealed. These ampoules were placed into an oil bath, regulated within ±1° of the specified temperature, and aliquots of the reaction mixture were analyzed for peroxide titer. After the titer dropped below 0.5%, the remaining ampoules were opened and the contents were combined and treated with ethereal diazoalkane (in the case of methanol as solvent diazoethane was utilized, while in the case of ethanol as solvent diazomethane was used) until persistence of the yellow color. The solvent was removed at reduced pressure, the distillate was collected in a Dry Ice cooled vacuum trap, and the resulting oily product was submitted to bulb-to-bulb distillation, flushing several times with solvent distillate. The involatile residue, identified by ir as polyester,[4] was weighed to account for product balance. The molecular distillate and the solvent distillate were combined, adjusted to the appropriate volume, and submitted to glpc analysis, using conditions CX-1 and AZ-1. Each product formed in amounts greater than 0.1 mol % was collected and its structure was confirmed by comparison of glpc retention times and ir spectra with those of the authentic materials. The quantitative glpc results are collected in Table I, and reported as relative composition (mol %) of the volatile products. In all cases nearly 100% product balance, *i.e.*, volatile products and involatile residue, was achieved.

Solvolytic Stability of Di-*n*-butylmalonic Acid.—A solution of the malonic acid in the anhydrous alcohol was heated in an ampoule under identical conditions with the solvolysis of the malonoyl peroxide. The resulting reaction mixture was treated with the appropriate ethereal diazoalkane and submitted to glpc analysis (conditions AZ-1 and CX-1). At 80° after 60-hr reaction time 31% decarboxylation took place, while after 100 hr 48% took place, as evidenced by the formation of 2-*n*-butylhexanoic acid.

Solvolytic Stability of Hydrogen Alkyl Di-*n*-butylmalonate.—A solution of the appropriate malonate (alkyl as methyl or ethyl) in the anhydrous alcohol was heated in an ampoule under identical conditions with the solvolysis of the malonoyl peroxide. The resulting reaction mixture was treated with an ethereal solution of the appropriate diazoalkane and submitted to glpc analysis (conditions AZ-1 and CX-1). Small amounts of decarboxylation was observed at 80° within 100 hr, but at 140° for 2 hr 34 mol % of decarboxylation was established.

Rates.—Stock solutions (0.20–0.30 *M*) of the di-*n*-butylmalonoyl peroxide (1) in the anhydrous solvent were placed into

(14) U. E. Diner, F. Sweet, and R. K. Brown, *Can. J. Chem.*, **44**, 1591 (1966).

(15) C. W. Stacy and R. M. McCurdy, *J. Amer. Chem. Soc.*, **76**, 1915 (1954).

(16) R. W. Stoughton, *ibid.*, **63**, 2376 (1941).

(17) H. Hepworth, *J. Chem. Soc.*, **115**, 1206 (1919).

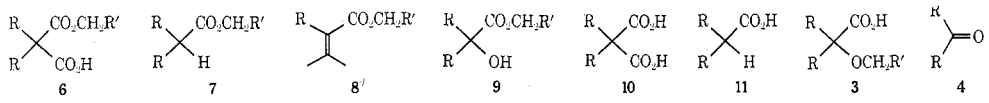
(18) A. L. Wilds and A. L. Maeder, Jr., *J. Org. Chem.*, **13**, 770 (1948).

(19) J. A. King and F. H. McMillan, *J. Amer. Chem. Soc.*, **68**, 1371 (1946).

(20) M. D. Nair and R. Adams, *ibid.*, **82**, 3786 (1960); **83**, 922 (1961); R. R. Frazer and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961).

TABLE I

PRODUCT COMPOSITION OF THE SOLVOLYSIS OF MALONOYL PEROXIDE 1



6 7 8 9 10 11 3 4

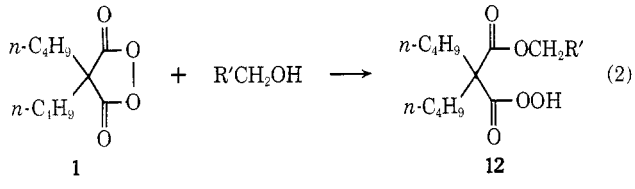
Solvent	Concn, M	Temp, °C	Time,[c] hr	Volatile products, mol %[a,b] 6	7	8[d]	9	10	11	3	4	Residue[e] 5
MeOH	0.302	22	2500	94	0.2	0.2	1.8	2.5	0.2	0.1	1.4	4
MeOH	0.300	50	566	93	1.1	0.1	1.0	3.4	0.7	0.1	0.7	15
MeOH	0.300	80	100	82	0.6	0.2	0.5	6.4	5.2	2.3	0.5	29
MeOH	0.276	80[f]	108	81	0.6	0.6	0.6	5.6	5.2	1.0	0.1	
EtOH	0.293	50	233	21.1	0.2	0.1	0.5	73.4	3.3	0.3	1.2	
EtOH	0.293	80	60	7.7	2.2	0.3	0.1	58.9	28.8	0.8	1.2	15
EtOH	0.270	80[g]	100	6.2	2.8	3.0	1.1	37.7	41.4	6.3	6.5	
EtOH	0.270	80	100	7.6	3.8	1.2	0.1	39.1	44.0	2.6	2.2	

[a] Relative composition of distilled, volatile products after treatment with diazoalkane. The $R'CH_2$– group stands for the alkyl group of the solvent. [b] Quantitative glpc analysis was carried out under conditions CX-1 and AZ-1. [c] Time required for peroxide titer (iodometry) to reach less than 0.5%. [d] Cis and trans mixture. [e] Per cent by weight, determined gravimetrically. [f] Run in open vessel by allowing solvent to reflux. [g] In the presence of 0.03 *M* inhibitor.

volumetric flasks, sealed with a serum cap, and placed into a constant-temperature bath. By means of a calibrated syringe, periodic samples were removed and analyzed for total peroxide content by iodometric titration and for the 1783-cm^{-1} carbonyl band of the malonoyl peroxide 1 by infrared. In the latter analysis the samples were appropriately diluted with carbon tetrachloride. The rates were reproducible within 10%. No efforts were made to improve on these preliminary solvolysis results, since the detailed kinetic study of the thermolysis of 1 in a variety of solvents shall be reported separately.

Results and Discussion

Preliminary kinetics in the alcoholic solvents methanol and ethanol reveals that the disappearance of the malonoyl peroxide 1783-cm^{-1} carbonyl band and the reduction of the peroxide titer proceed at the same rate within the experimental error (*ca.* 10%). However, under the same conditions the rate of thermal decomposition is negligible (*ca.* 2–3%) in hydrocarbon solvents such as benzene or hexane.[21] Thus, we postulate that the initial reaction involves solvolysis of **1** by $R'CH_2OH$ (R′ = H, Me) leading to the peracid half ester **12** (eq 2).



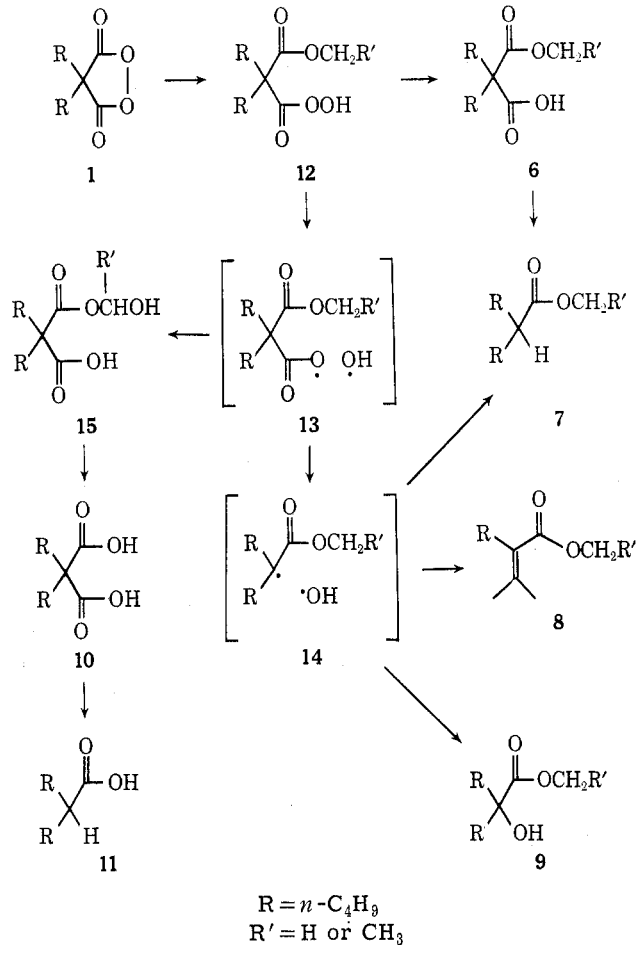
1 12 (2)

In the alcoholic solvent the peroxy half ester **12** is decomposing at least as fast as it is forming, since otherwise it should have built up and the peroxide titer should have diminished at a slower rate than the malonoyl peroxide carbonyl bond.

The complex product mixture (see Table I) obtained in the solvolysis of the malonoyl peroxide **1** in methanol or ethanol hints to the fact that the postulated initial solvolysis product, peroxy half ester **12**, undergoes a number of competitive decomposition modes (see Scheme I). However, before entering into detailed mechanistic interpretations, it is convenient to review

(21) A full account of the thermal decomposition of malonoyl peroxides is in preparation.

SCHEME I



R = *n*-C_4H_9
R′ = H or CH_3

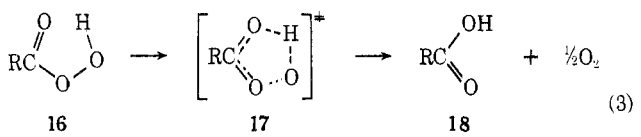
the behavior of simpler peracids, since they should reflect to a considerable degree on the fate of our intermediary peracid **12** in alcoholic solvents.

Detailed studies on the thermal decomposition of peroxylauric acid (**16**)[22,23] indicate two major competi-

(22) D. Lefort, C. Paquot, and Y. Sorba, *Bull. Soc. Chim. Fr.*, 1385 (1959); D. Lefort, Y. Sorba, and D. Rouillard, *ibid.*, 2219 (1961); V. Vorobiev, D. Lefort, S. Sorba, and D. Rouillard, *ibid.*, 1577 (1962).

(23) W. E. Parker L. P. Witnauer, and D. Swern, *J. Amer. Chem. Soc.*, **80**, 323 (1958).

tive modes. On one hand, we have the molecular pathway (eq 3) *via* the concerted transition state **17**,



16 **17** **18** (3)

affording lauric acid (**18**) and molecular oxygen. On the other hand, we have a free-radical chain pathway (eq 4)

$$\begin{aligned} RCO_2OH &\longrightarrow RCO_2\cdot + HO\cdot \\ RCO_2\cdot &\longrightarrow R\cdot + CO_2 \\ R\cdot + RCO_2OH &\longrightarrow ROH + RCO_2\cdot \end{aligned} \quad (4)$$

in which an alkyl radical R·, formed after decarboxylation of the acyloxy radical $RCO_2\cdot$, serves as chain carrier. Depending on the reaction conditions, the molecular path (eq 3) or the radical chain path (eq 4) prevails, but usually both take place concurrently. Since the activation enthalpy is lower for the molecular process in which molecular oxygen is extruded, it is observed that at moderate temperature (below 80°) the concerted decomposition predominates. Similarly, in the presence of inhibitors such as molecular oxygen or hydroquinone the radical chain process is suppressed in favor of the concerted path. Finally, in alcoholic solvents peracids decompose faster because a new radical chain process is initiated (eq 5)[23,24] in which the

$$\begin{aligned} RCO_2OH &\longrightarrow RCO_2\cdot + \cdot OH \\ RCO_2\cdot + R'CH_2OH &\longrightarrow RCO_2H + R'\dot{C}HOH \\ RCO_2OH + R'\dot{C}HOH &\longrightarrow RCO_2\cdot + R'CHOH \\ &\qquad\qquad\qquad\qquad\quad | \\ &\qquad\qquad\qquad\qquad\quad OH \end{aligned} \quad (5)$$

hydroxyalkyl radical R'CHOH becomes the chain carrier.

With these facts in mind on the thermal behavior of peracids, a class of peroxides for which it is difficult to obtain reproducible and reliable data in view of their propensity to catalytic decomposition by trace impurities,[22,24] we now return to our results on the solvolysis of di-*n*-butylmalonoyl peroxide (**1**). In the case of the methanolysis of **1** at 22° (first entry in Table I), the major product is hydrogen methyl di-*n*-butylmalonate (**6**, RCH_2 = Me), formed in 94% yield. As in the case of peroxylauric acid,[22,23] at relatively low reaction temperatues the intermediary peroxy half ester **12** prefers concerted deoxygenation affording half ester **6** (see Scheme I). At 50° (second entry in Table I) relatively little change in the product composition is provoked, since half ester **6** is the major product (93% yield) by far. However, at 80° (third entry in Table I) we note that, although **6** is still the major product (82% yield), the yields of di-*n*-butylmalonic acid (**10**), 2-*n*-butylhexanoic acid (**11**), and 2-methoxy-2-*n*-butylhexanoic acid (**3**) are significantly increased.

The latter product **3** is most likely formed by trapping of the α-lactone intermediate **2** (eq 1) by methanol,[4] and it is expected that this thermal decarboxylation of the malonoyl peroxide **1** should be enhanced at the higher temperature. Also, as expected, the homolytic decomposition of peroxy acid **12** is enhanced at the higher temperature, as evidenced in the products **10** and **11**. Here it is important to mention that a control experiment revealed that malonic acid **10** undergoes about 50% decarboxylation at 80° for 100 hr in methanol to give **11**. Consequently, practically all of the 2-*n*-butylhexanoic acid (**11**) is a secondary product, derived from the malonic acid **10**, and not directly from peroxy acid **12**.

The formation of the malonic acid **10** (see Scheme I) is conveniently explained, analogous to peroxylauric acid (**16**),[22,23] by homolytic fission of the peroxide bond in **12** to give the radical pair **13**. Internal hydrogen abstraction from the methoxy group by the carboxylate radical and coupling leads to acid **15**, which on loss of formaldehyde (on work-up the stench of formaldehyde was clearly noticeable) produces malonic acid **10**.

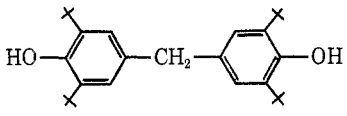
The minor products **8** and **9** probably are formed by decarboxylation of radical pair **13** to give **14**, which on coupling gives hydroxy ester **9** and by hydrogen abstraction a mixture of methyl *cis*(*Z*)- and *trans*(*E*)-2-*n*-butyl-2-hexenoate (**8**). No doubt, alternative radical chain processes (eq 4 and 5) can be written to account for the formation of **8** and **9**. However, we observed no significant differences in the product composition when the solvolysis in methanol was carried out in a sealed ampoule (third entry in Table I) *vs.* refluxing of the solvent in an open vessel (fourth entry), which would allow effusion of the molecular oxygen formed during the decomposition of **12**. In regard to peroxylauric acid (**16**), for which the radical chain process (eq 4) is inhibited by molecular oxygen that is generated in the concerted decomposition (eq 5)[22,23] the above result speaks in favor of our interpretation that in the radical pair **13** internal hydrogen abstraction prevails over external abstraction from the solvent.

To substantiate our hypothesis, we examined the reaction of the malonoyl peroxide **1** in ethanol. We argued that, if the initial step entails solvolysis of **1** by ethanol to give peroxy half ester **12** and if this step be rate determining, the rate of consumption of **1** should be about that in methanol, but more of the intermediary peracid **12** should be diverted into malonic acid **10** rather than half ester **6** because internal hydrogen abstraction should be more efficient in the ethyl (R′ = Me) than in the methyl (R′ = H) peroxy half ester **12**. Indeed, while the rate of solvolysis at 50° was only doubled in ethanol, the major product (73.4% yield) was now malonic acid **10**, while only 21.1% of the half ester **6** (R′ = Me) was obtained (fifth entry in Table I). At 80° the results are still more dramatic (sixth entry in Table I), since *ca.* 88% malonic acid **10** and only *ca.* 10% half ester **6** (R′ = Me) are formed. Into these figures the yield of acid **11** (decarboxylated **10**) and ester **7** (decarboxylated **6**), respectively, are incorporated because control experiments showed that under these solvolysis conditions extensive decarboxylation of **11** → **10** and **6** → **7** takes place.

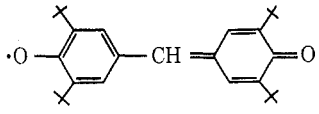
Consequently, as anticipated, in ethanol homolytic fission of **12** to give the radical pair **13** outweighs concerted deoxygenation into half ester **6**, while the reverse is the case in methanol. Further confirmation of our mechanistic interpretation was achieved through attempts at suppressing possible radical chain processes between **1** and ethanol by running the ethanolysis in the presence of trihydrogalvinoxyl (**19**), an excellent inhibitor.[25] The reaction rate was only reduced by *ca.*

(24) K. Tokumaru, O. Simamura, and M. Fukuyama, *Bull. Chem. Soc. Jap.*, **35**, 1673 (1962); K. Tokumaru and O. Simamura, *ibid.*, **36**, 72 (1963); K. Tokumaru and O. Simamura, *ibid.*, **36**, 333 (1963).

(25) W. Adam and W. T. Chiu, *J. Amer. Chem. Soc.*, **93**, 3687 (1971).



19



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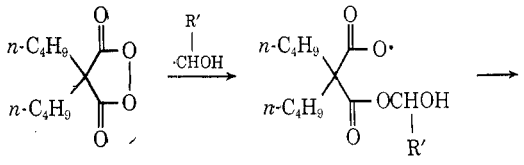
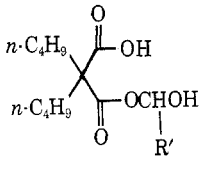
50% with **19** present. More important, no significant alteration in the yields of products **6** and **10** was observed (compare seventh and eighth entry in Table I). Therefore, chain propagation as shown in eq 6 to



1



15

(6)

produce malonic acid **10** *via* loss of RCHO from **15** cannot be a major process, unless very short chain lengths are involved. To be more definite on this point, we would have liked to use galvinoxyl (**20**) as a radical counter, but unfortunately **20** is unstable in ethanol.[25]

Registry No.—**1**, 30842-78-5; dimethyl di-*n*-butylmalonate, 36602-11-6; methyl hydrogen di-*n*-butylmalonate, 36602-12-7; ethyl hydrogen di-*n*-butylmalonate, 36602-13-8; ethyl methyl di-*n*-butylmalonate, 36602-14-9; 2-*n*-butyl-2-methoxyhexanoic acid, 36602-15-0; methyl 2-*n*-butyl-2-methoxyhexanoate, 36602-16-1; methyl 2-*n*-butyl-2-hydroxyhexanoate, 36602-17-2; ethyl 2-*n*-butyl-2-methoxyhexanoate, 36622-57-8; 2-*n*-butyl-2-ethoxyhexanoic acid, 36602-18-3; methyl 2-*n*-butyl-2-ethoxyhexanoate, 36602-19-4; *cis*-2-butyl-2-hexanoic acid, 36602-20-7; *trans*-2-butyl-2-hexenoic acid, 36602-21-8; ethyl *cis*-2-*n*-butyl-2-hexenoate, 36602-22-9; ethyl *trans*-2-*n*-butyl-2-hexenoate, 36602-23-0; methyl *cis*-2-*n*-butyl-2-hexenoate, 36602-24-1; methyl *trans*-2-*n*-butyl-2-hexenoate, 36602-25-2.

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Hydrogen Cyanide Chemistry. III. Synthesis of Diiminosuccinonitrile and Its Conversion to Diaminomaleonitrile[1]

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Received August 9, 1972

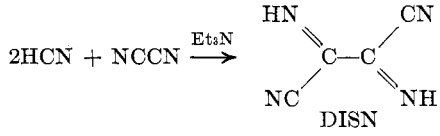
Diiminosuccinonitrile (DISN) is produced by base-catalyzed addition of hydrogen cyanide to cyanogen. Reduction of DISN yields diaminomaleonitrile (DAMN). Chlorination of DISN produces *N*-chlorodiiminosuccinonitrile or *N,N'*-dichlorodiiminosuccinonitrile.

Hydrogen cyanide has considerable synthetic potential that has not been fully utilized because it is toxic and explosive, and thus many research workers are reluctant to use it. We believe that hydrogen cyanide will eventually become a major building block for heterocyclic synthesis and are thus engaged in research to exploit its chemistry. Indeed, hydrogen cyanide has been suggested as the basic material from which purines, present in all living matter as components of nucleic acids, arose in prebiotic times.[2] Adenine (HCN pentamer) is commercially produced by heating HCN to 120° in liquid ammonia[3] and caffeine is readily accessible from diaminomaleonitrile (HCN tetramer).[4]

Some notable examples of other heterocyclic systems available by combination of HCN with other reagents are hydantoins,[5] imidazoles,[2] and *s*-triazines.[6]

Results and Discussion

Diiminosuccinonitrile (DISN) is formed quantitatively by base-catalyzed addition of hydrogen cyanide to cyanogen at −40°. DISN can also be prepared by passing chlorine into a toluene solution of HCN and trimethylamine at −15°.



DISN

$$4HCN + 2Me_3N + Cl_2 \longrightarrow DISN + 2Me_3NHCl$$

The first step in the formation of DISN is no doubt attack by cyanide ion on cyanogen. The resulting

(1) Paper I: R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.*, **93**, 4953 (1971), reported this work in part in a preliminary communication. Presented at 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 16, 1971, Abstract ORGN 126.

(2) R. A. Sanchez, J. P. Ferris, and L. E. Orgel *J. Mol. Biol.*, **30**, 223 (1967); *Science*, **153**, 72 (1966), and references cited therein.

(3) H. Wakamatsu, Y. Yamada, T. Saito, I. Kumashiro, and T. Takenishi, *J. Org. Chem.*, **31**, 2035 (1966).

(4) D. W. Woodward, U. S. Patent 2,534,331 (1950); *Chem. Abstr.*, **45**, 5191 (1951).

(5) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold, New York, N. Y., 1947.

(6) C. Grundmann, *Angew. Chem., Int. Ed., Engl.*, **2**, 309 (1963).