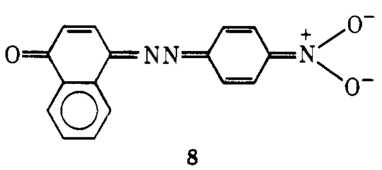
4′-nitro derivative, see Figure 9 of supplementary material), and 0.1 N NaOH (50 vol % Me$_2$SO–water) and 0.1 N NaOH–Me$_2$SO solutions (H derivative, see Figure 10 of supplementary material; 4′-nitro derivative, see Figure 11 of supplementary material). The remarkable red shift of the band of the 4′-nitro derivative can be ascribed to the lengthening of the conjugated system in the form **8**. Thus, the 4-azo dyes



8

dissolved in DMF and Me$_2$SO are converted to the phenolate ion (**7**) probably due to the high dielectric constant and high basicity of the solvent. The discussion may be supported from the absorption maximum of the electronic spectra (see Figure 12 of supplementary material) of **3** and **4** in DMF and Me$_2$SO, which are quite different from the spectra in Figure 5. The longer wavelength absorption is not due to **1** or **2**.

Registry No.—1 (X = OCH$_3$), 3009-53-8; 1 (X = CH$_3$), 5098-99-7; 1 (X = H), 3651-02-3; 1 (X = Cl), 7252-64-4; 1 (X = NO$_2$), 5290-62-0; 2 (X = OCH$_3$), 32159-06-1; 2 (X = CH$_3$), 36853-51-7; 2 (X = H), 19059-71-3; 2 (X = Cl), 36853-56-2; 2 (X = NO$_2$), 36853-60-8; **3**, 24390-69-0; **4**, 66881-37-6.

Supplementary Material Available: Figures 2, 3, and 6–12 of electronic spectra of compounds mentioned in the text (9 pages). Ordering information is given on any current masthead page.

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Photolysis and Thermolysis of Di-*n*-butylmalonyl Peroxide. Evidence for α-Lactone Intermediates[1]

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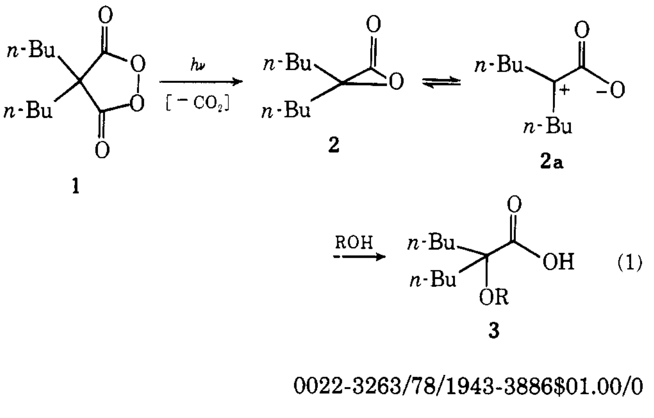
Photolysis and thermolysis of di-*n*-butylmalonyl peroxide (**1**) afford α-lactone **2** as a reaction intermediate. In a nonprotic solvent such as benzene or *n*-hexane, the α-lactone **2** polymerizes to polyester **5**, while in methanol or ethanol it is trapped nucleophilically in the form of α-alkoxy acid **3**. Some of the α-lactone decarbonylates into 5-nonanone (**4**), but only small amounts decarboxylate to give 4-nonene (**12**), presumably via its carbene. In the thermal decomposition of the malonyl peroxide **1** in methanol and ethanol, α-lactone formation is competed for by solvolytic reaction, leading to a complex product mixture of malonic half-ester **6** and its decarboxylated ester **7**, α, β-unsaturated ester **8**, α-hydroxy ester **9**, malonic acid **10**, and its decarboxylated acid **11**. This solvolytic process predominates over α-lactone formation in the thermolysis of the malonyl peroxide **1** in ethanol.

Several years ago we communicated[3] that photodecarboxylation of di-*n*-butylmalonyl peroxide (**1**) leads to α-lactones **2** as intermediates which can be trapped through their dipolar form **2a** with protic nucleophiles (eq 1). Subsequently, we showed[4] that in a matrix isolated form these elusive reaction intermediates can be preserved to enable infrared characterization. By means of bis(trifluoromethyl) substitution at the α carbon, it was possible to isolate a stable α-lactone by discouraging formation of the dipolar form **2a** through electronic destabilization.[5] Other papers on the chemistry of malonyl peroxides include their vapor phase thermolysis[6] and their solvolysis with primary and secondary alcohols.[7] In this paper, we give a full account of the photo- and thermodecarboxylation of di-*n*-butylmalonyl peroxide.



Results and Discussion

When a 0.15 M solution of the malonyl peroxide **1** in benzene or *n*-hexane is irradiated at 350 nm in a Pyrex vessel, within 15–20 h its characteristic sharp carbonyl band at 1783 cm^{-1} is replaced by a broad carbonyl band at 1740 cm^{-1}. Removal of the solvent by distillation at reduced pressure afforded a solid residue, mp 138.5–140.5 (benzene) and 146–146.5 °C (*n*-hexane), identified as poly-3,3-di-*n*-butyloxi-

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Table I. Product Composition of the Photolysis of Malonyl Peroxide 1

	concn	$h\nu$	time[c]	volatile products (mol %)[a,b]									residue[e]
solvent	(M)	(nm)	(h)	6	7	8[d]	9	10	11	3	4	12	5
MeOH	0.280	350	27	2.7	0.3	4.1	0.6	<0.1	0.2	86.2	4.4	1.0	9.0
MeOH	0.285	310	10	2.4	0.5	4.3	0.6	<0.1	0.6	87.9	1.2	1.9	11.0
EtOH	0.116	350	24	<0.1	<0.1	6.1	0.3	0.9	0.6	88.0	4.0	0.6	
EtOH	0.282	310	12	<0.1	0.3	6.0	0.9	1.2	1.1	85.1	3.2	1.6	23.0
C_6H_6[f]	0.150	350	15								5.9	3.5	89.0
n-C_6H_{14}[f]	0.150	350	15								8.8	7.3	82.0

[a] Relative composition of distilled, volatile products after treatment with diazoalkane. The RCH_2 group stands for the alkyl group of the solvent. [b] Quantitative VPC analysis was carried out under conditions CX-2 and AZ-1. [c] Time required for peroxide carbonyl band (1783 cm^{-1}) to disappear in the IR. [d] Cis,trans mixture. [e] Polyester, determined gravimetrically (wt %). [f] Absolute product composition.

Table II. Product Composition of the Thermolysis of Malonyl Peroxide 1

	concn	temp	time	volatile products (mol %)[a,b]									residue[e]
solvent	(M)	(°C)	(h)	6	7	8[d]	9	10	11	3	4	12	5
MeOH	0.300	140	2[c]	8.3	3.6	11.0	1.5	<0.1	27.0	47.8	0.5	0.3	22.0
MeOH	0.300	140	15	2.1	17.6	9.0	0.7	<0.1	27.0	47.2	1.1	<0.1	
EtOH	0.293	140	2[c]	0.4	1.3	5.1	0.9	<0.1	71.5	18.6	2.2		12.0
EtOH	0.293	140	25	<0.1	6.6	5.4	0.7	<0.1	68.3	18.2	0.8		
EtOH	0.293	140	45	<0.1	9.7	6.4	0.6	<0.1	65.4	17.0	0.9		
EtOH	0.293	130	2[c]	0.3	1.1	4.5	0.4	4.0	70.1	18.5	1.1		
EtOH	0.293	130	25	<0.1	3.7	4.4	0.5	<0.1	72.8	17.3	1.3		
C_6H_6	0.100	140	5[c]			60.0[f]					40.0		85.0
n-C_6H_{14}	0.150	140	6[c]			35.0[f]			16.1		26.4	<0.1	91.0

[a] Relative composition of distilled, volatile products after treatment with diazoalkane. The RCH_2 group stands for the alkyl group of the solvent. [b] Quantitative VPC analysis was carried out under conditions CX-2 and AZ-1. [c] Time required for peroxide titer to drop below 0.5% (iodometry). [d] Cis,trans mixture. [e] Polyester, determined gravimetrically (wt %). [f] $RCH_2 = CH_3$ due to esterification with diazomethane.

ran-2-one (**5**), i.e., the polyester derived from the α-lactone **2**. Its structure assignment rests on the correct elemental analysis and a molecular weight of 4996 (osmometry in $CHCl_3$), corresponding to ca. 29 α-lactone units. Lithium aluminum hydride reduction of the polyester **5** gave the expected 2-*n*-butylhexane-1,2-diol[8] in 72% yield.

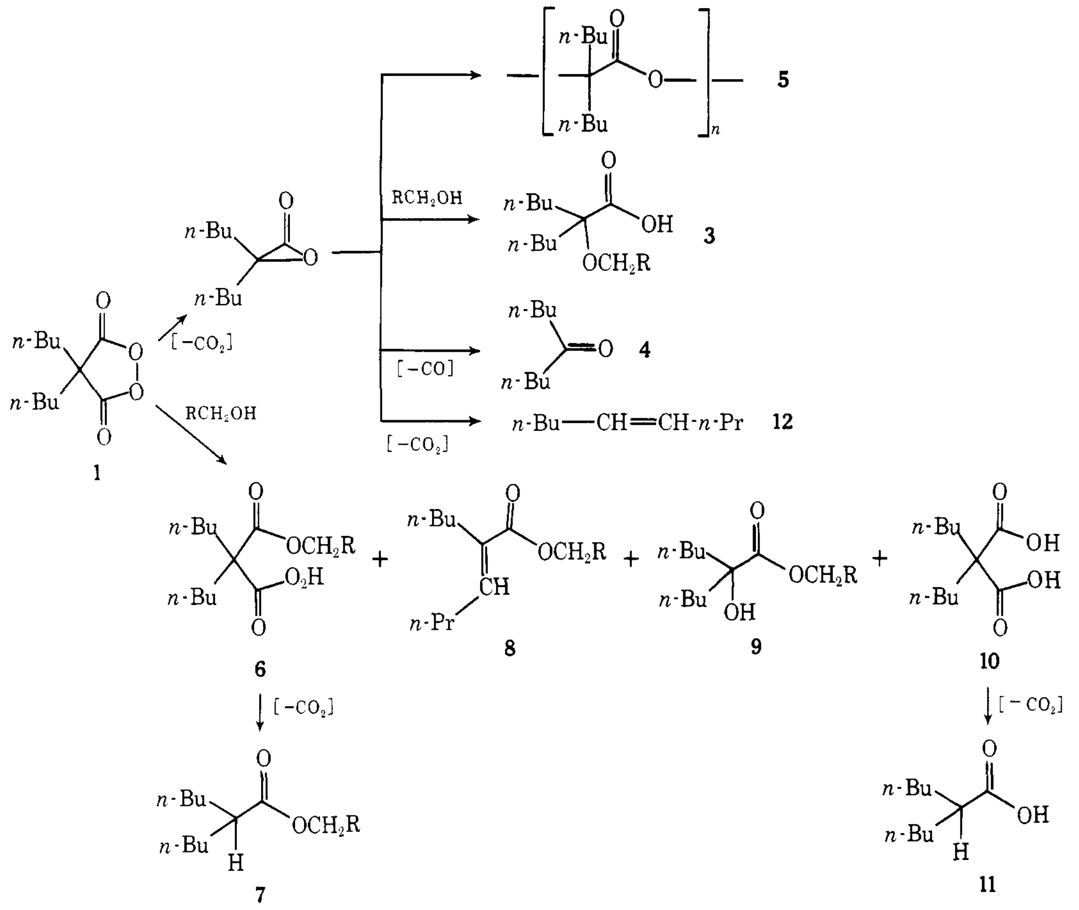
VPC analysis of the solvent distillate showed that the only volatile products were 5-nonanone (**4**) and 4-nonene (**12**). The quantitative product data of the photolysis are summarized in Table I. Control experiments revealed that the polyester **5** was stable toward irradiation at 350 nm under the reaction conditions. Thus, the 5-nonanone (**4**) and 4-nonene (**12**) are not secondary photolysis products but must arise directly on photolysis of the malonyl peroxide **1**. However, irradiation of a 0.1 M polyester solution in *n*-hexane at 254 nm for 63 h in a quartz vessel led to ca. 60% deterioration of the polyester **5** leading principally to ketone **4**, but it is important to note that under these conditions the malonyl peroxide is completely destroyed within 40 min on irradiation at 254 nm in a quartz vessel.

In contrast to the ease with which the malonyl peroxide **1** photodecarboxylates, it is thermally quite stable in inert solvents such as benzene or *n*-hexane. Thus, a 0.10–0.15 M solution of **1** in these solvents must be heated at 140 °C for 5–6 h in sealed ampules to effect complete destruction. Again, the major product is the polyester **5**, formed in 85–91% yield (Table II). The remainder are volatile products, mainly the unsaturated acid **8** (isolated as its methyl ester for convenience of VPC analysis, cf. Experimental Section) and 5-nonanone. In the case of *n*-hexane as the reaction solvent, appreciable amounts of carboxylic acid **11** were also detected (also isolated as its methyl ester for convenience of VPC analysis, cf. Experimental Section). The quantitative results of the relative composition (by VPC) of the volatile products are summarized in Table II as well as the gravimetric absolute yields of polyester **5**.

A control experiment confirmed that on heating at 230 °C for 1 h in benzene the polyester **5** is converted essentially quantitatively into the α,β-unsaturated acid **8**. Consequently, the major component of the volatile products, i.e., acid **8**, presumably arises from subsequent thermal destruction of the polyester **5**.

Clearly, both in the photolysis and the thermolysis of the malonyl peroxide **1** the α-lactone **2** intervenes as precursor to the polyester **5**. Thus, if the α-lactone intermediate is long lived enough to polymerize, it should be possible to trap it with protic solvents such as alcohol. Consequently, we examined the photolysis and thermolysis of the malonyl peroxide **1** in methanol and ethanol.

The photolysis results in methanol and ethanol are given in Table I. First of all, as expected the yield of polyester **5** is dramatically reduced; the α-alkoxy acid **3** is formed as the major product by nucleophilic trapping of the α-lactone intermediate with the alcohol solvent. Some 5-nonanone (**4**) and traces of 4-nonene (**12**) are also produced. The remainder of the products, i.e., half-ester **6**, ester **7**, α,β-unsaturated ester **8**, α-hydroxy ester **9**, malonic acid **10**, and acid **11**, all together representing less than 10% of the volatile products, are derived from competitive solvent-induced reaction of the malonyl peroxide.[7] Except for this minor side reaction, the photodecarboxylation in these alcoholic solvents is quite clean, leading to the solvent-trapped α-lactone as the final major product. As Table I reveals, the relative product composition is quite insensitive to the type of alcohol used (MeOH vs. EtOH) and wavelength (350 vs. 310 nm). Control experiments confirmed that the polyester **5** was solvolytically and photolytically stable



(2)

under the reaction conditions. Furthermore, the major product, i.e., the α-alkoxy acid **3**, was also inert to the photolysis conditions.

The thermolysis results, which are given in Table II, of the decomposition of the malonyl peroxide in the alcoholic solvents are considerably more complex than the photolysis. In methanol, considerable amounts of polyester **5** are still formed, but the major product is the α-methoxy acid **3**, resulting from methanol trapping of the α-lactone **2** intermediate. Only traces of 5-nonanone and 4-nonene are formed. The remainder of the products are derived from solvent-induced decomposition of the malonyl peroxide **1**.[7] Control experiments show that the malonic acid **10** decarboxylates to give acid **11**, and the half-ester **6** similarly decorboxylates to give ester **7** under the reaction conditions. However, the α-alkoxy acids **3** are stable to the reaction conditions and, thus, are not a source for the secondary products. Consequently, in methanol the major course of the thermolysis is α-lactone formation, but methanol-induced decomposition of the malonyl peroxide **1** competes effectively.

A contrary situation obtains in ethanol (Table II). First of all, relatively little polyester **5** is produced on thermolysis of malonyl peroxide **1** in ethanol. Furthermore, among the volatile products, the α-ethoxy acid **3** (ethanol trapping of α-lactone **2**) is formed only in ca. 18% yield. Again only traces of 5-nonanone (**4**) are produced.

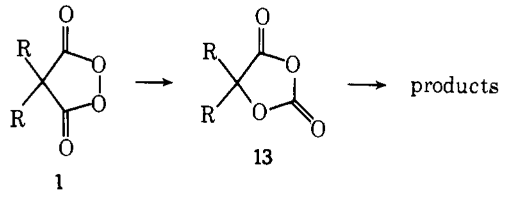
The major products are the acid **11** and ester **7**, both arising from decarboxylation of the malonic acid **10** and half-ester **6**, which in turn are derived from ethanol-induced decomposition of **1**.[7] Thus, in ethanol the major event is solvolytic destruction of the malonyl peroxide **1** rather than α-lactone formation. The greater propensity of ethanol to become engaged in radical chain reactions compared to methanol is clearly evident in these results.[9]

A unified mechanism accounting for these results is offered in eq 2. The lower branch, i.e., the solvolytic reaction by methanol or ethanol affording products **6** to **11**, has already been interpreted mechanistically[7] and shall, therefore, not be discussed here any further. For convenience, we have retained the same numbering sequence of the solvolytic products as given in reference 7 to facilitate comparison.

The upper branch proceeding through the α-lactone intermediate is the exclusive path in the photolysis and thermolysis of the malonyl peroxide **1** in nonprotic solvents such as benzene and *n*-hexane. Most of the α-lactone **2** polymerizes to afford the polyester **5**, some decarbonylates into 5-nonanone, and presumably a little decarboxylates to give 4-nonene via the corresponding carbene.[4-6]

Also photolysis in methanol or ethanol affords principally the α-lactone **2**, which now, however, is trapped by the protic solvent through its dipolar form **2a** as the α-alkoxy acid **3**. Even then some of the α-lactone manages to polymerize and decarbonylate but very little decarboxylates, since only traces of 4-nonene are formed. The solvolytic pathway (lower branch in eq 2) occurs to a minor extent (less than 10%) in these photolyses. However, in the thermolysis reaction of malonyl peroxide **1** in these alcoholic solvents the solvolytic process competes effectively. For methanol, the major path is still α-lactone formation, but for ethanol the major path is solvolysis.

The possibility, although quite improbable, that the malonyl peroxide **1** carboxy inverts[10] to give the isomeric 1,3-dioxolane-2,4-dione (**13**) (eq 3) and the latter then serves as a precursor to the α-lactone products was discounted by the



(3)

following control experiment. Authentic 5,5-dimethyl-1,3-dioxolane-2,4-dione (**13a**) was prepared[11] and shown to be stable to the photodecarboxylation conditions of the malonyl peroxide **1**. The anhydrocarbonate **13a** could be destroyed by irradiating with a full mercury arc of a 200-W Hanovia lamp in acetonitrile using a quartz reaction vessel (Corex filter). Acetone and ca. 10% tarry residue were the only products. Thermolysis in benzene, as reported previously,[11] leads to polyester, presumably via an α-lactone intermediate.

Experimental Section

Instruments. Infrared spectra were recorded on a Perkin-Elmer Infracord 237-B using 0.1-mm sodium chloride cavity cells, and the absorptions are given in reciprocal centimeters. The NMR spectra were recorded on a Varian T-60 spectrometer using normal and semimicro NMR tubes. The chemical shifts are given in δ (ppm) using Me_4Si as an internal standard. The VPC analyses were carried out on a Varian Aerograph 202-B instrument, provided with TC detection, employing the following columns under the conditions specified below.

Condition CX-1: 5 ft × 0.25 in. copper column, packed with 15% Carbowax 20 M on 60–80 mesh Chromosorb W, operated at column, injector, and detector temperatures of 155, 200, and 250 °C, respectively, and a helium flow of 60 mL/min.

Condition CX-2: 15 ft × 0.25 in. copper column, packed with 20% Carbowax 20 M on 60–80 mesh Chromosorb W, operated at column, injector, and detector temperatures of 175, 225, and 250 °C, respectively, and a helium flow of 60 mL/min.

Conditions AZ-1: 12 ft × 0.25 in. copper column, packed with 27% Apiezon M on 60–80 mesh Chromosorb P, operated at column, injector, and detector temperatures of 210, 225, and 250 °C, respectively, and a helium flow of 60 mL/min.

Conditions AZ-2: 12 ft × 0.25 in. copper column, packed with 18% Apiezon M on 60–80 mesh Chromosorb P, operated at column, injector, and detector temperatures of 205, 225, and 250 °C, respectively, and a helium flow of 60 mL/min.

Chemicals. All commercial solvents and reagents were purified according to literature methods to match reported physical constants. All the starting materials and products were prepared according to published literature procedures and purified to match the reported physical constants. The details will not be reproduced here, since the substances 2-*n*-butyl-2-ethoxyhexanoic acid, 2-*n*-butylhexanoic acid, 2-*n*-butyl-2-methoxyhexanoic acid, di-*n*-butylmalonic acid, di-*n*-butylmalonyl peroxide, diethyl di-*n*-butylmalonate, dimethyl di-*n*-butylmalonate, ethyl 2-*n*-butylhexanoate, ethyl *cis,trans*-2-*n*-butyl-2-hexenoate, ethyl 2-*n*-butyl-2-hydroxyhexanoate, ethyl 2-*n*-butyl-2-methoxyhexanoate, ethyl hydrogen di-*n*-butylmalonate, ethyl methyl di-*n*-butylmalonate, hydrogen methyl di-*n*-butylmalonate, methyl 2-*n*-butyl-2-ethoxyhexanoate, methyl 2-*n*-butylhexanoate, methyl *cis,trans*-2-*n*-butyl-2-hexenoate, methyl 2-*n*-butyl-2-hydroxyhexenoate, methyl 2-*n*-butyl-2-methoxyhexanoate, and 5-nonanone are described in reference 7, 2-*n*-butyl-1,2-hexanediol in reference 8, and 5,5-dimethyl-1,3-dioxolane-2,4-dione in reference 11.

General Photolysis and Thermolysis Procedures. A stock solution of the malonyl peroxide was prepared in the desired anhydrous solvent at the appropriate concentration (~0.3 M), distributed into constricted Pyrex test tubes, and sealed under vacuum. In the case of photolyses, these ampules were placed into the RP-100 Rayonet Photoreactor, equipped with a merry-go-round and the appropriate lamps, and photolyzed at 35–40 °C. In the case of thermolyses, these ampules were placed into a constant-temperature bath, which was regulated at the desired temperature within ±1.0 °C. When the peroxide titer had dropped below 0.5%, as determined by iodometric titration of samples taken periodically, the remaining ampules were opened, and the contents were combined and treated with an ethereal solution of diazoalkane (diazomethane in the case of ethanol, benzene and *n*-hexane and diazoethane in the case of methanol as solvent) until persistence of the yellow color. The solvent was removed at reduced pressure, collecting the distillate in a dry ice cooled vacuum trap, concentrating the reaction mixture to 2–3 mL volume. The residual oily product was bulb-to-bulb distilled at reduced pressure (130–140 °C at 0.05 mm), flushing several times with 3–5 mL of solvent distillate. The yield of involatile residue, identified as polyester as described below, was determined gravimetrically. The molecular distillate and the solvent distillate were combined, adjusted to the appropriate volume, and submitted to VPC analysis using conditions CX-2 and AZ-1. Each product formed in amounts greater than 0.1 mol % was collected, and its structure was confirmed by comparison of VPC retention times and IR and ^1H NMR spectra with authentic materials. The quantitative VPC results are reported in Table I for the photolyses and Table II for the thermolyses as relative compositions (mol %) of the volatile products and absolute yields (wt %) of involatile residue; nearly 100% product balance was achieved in most runs.

Characterization of Polyester 5. The involatile residue, obtained after removal of the solvent and the volatile products, consisted of a partly crystalline, colorless powder, mp 138.5–140.5 (benzene) and 146.0–146.5 °C (*n*-hexane). This residue was identified as polyester **5** [poly(3,3-di-*n*-butyloxiran-2-one)] on the basis of its elemental analysis, its molecular weight of 4996 (osmometry in $CHCl_3$), corresponding to 29.2 α-lactone units, its C=O band at 1740, and lithium aluminum hydride reduction to 2-*n*-butylhexane-1,2-diol in 72% yield after distillation, bp 110 °C at 0.3 mm, $n^{20}{}_D$ 1.4527 (lit.[8] bp 140 °C at 13 mm, $n^{20}{}_D$ 1.4538).

Solvolytic Stability of Polyester 5 in Methanol. A 0.1 M solution of the polyester in benzene and methanol (5:1) was irradiated at 350 nm in a Pyrex test tube for 17 h. By means of IR analysis it was established that no 2-*n*-butyl-2-methoxyhexanoic acid (**3**, RCH_2 = methyl) was formed.

Photolytic Stability of Polyester 5 in Hexane. A 0.1 M solution of **5** in hexane was irradiated at 350 nm for 45 h in a Pyrex test tube. By IR analysis, not even traces of ketone **4** or olefin **12** were formed. However, irradiation of a 0.1 M hexane solution of **5** in a quartz vessel at 254 nm for 63 h indicated that 60% deterioration of the polyester had taken place to give principally ketone **4**.

Thermal Stability of Polyester 5. A 0.1 M solution of polyester **5** in benzene which was heated in an ampule at 230 °C for 1 h was converted quantitatively into the α,β-unsaturated acid **8**, as confirmed by IR analysis.

Photolysis of Malonyl Peroxide 1 at 254 nm in Hexane. When a 0.1 M hexane solution of **1** was irradiated at 254 nm in a quartz vessel at −78 °C, within 40 min all peroxide was consumed, as confirmed by monitoring the reaction mixture by IR. Polyester **5** was formed essentially quantitatively.

Photolysis of Malonyl Peroxide 1 in the Absence and Presence of Molecular Oxygen. A 0.1 M stock solution of **1** in benzene was divided into two equal portions and placed into consticted Pyrex test tubes by means of a syringe. One sample was rigorously deaerated with helium gas using five freeze–pump–thaw cycles and sealed under vacuum; the other sample was saturated with molecular oxygen using five freeze–pump–thaw cycles and sealed at atmospheric pressure. Both ampules were irradiated at 350 nm in the RP-100 Rayonett photoreactor until complete consumption of peroxide (no 1783 band in the IR). Each ampule was opened, and the solvent was removed at reduced pressure, collecting it in a dry ice vacuum trap, and analyzed for 5-nonanone by IR and VPC. No significant differences in yield could be discerned between the two samples.

Photolysis of 5,5-Dimethyl-1,3-dioxolane-2,4-dione (13). A 0.1 M solution of the 1,3-dioxolane **13** in benzene was irradiated in a Pyrex ampule at 310 nm. Even after 75 h no consumption of 1,3-dioxolane **13** was observed. However, irradiation of a 0.1 M solution in acetonitrile with a 200-W Hanovia lamp, filtering with a Corex filter, gave acetone as the only product after 21.5 h of irradiation.

Photolytic Stability of 2-*n*-Butyl-2-methoxyhexanoic Acid (3). A 0.1 M methanolic solution of the α-methoxy acid **3** in a Pyrex test tube was irradiated at 350 nm for 24 h. Treatment of the resulting solution with excess diazomethane and submission to VPC analysis (conditions CX-1) confirmed that not even traces of ketone **4** or α,β-unsaturated ester **8** were formed. The exclusive product was the α-methoxy acid **3** in the form of its methyl ester.

Thermal Stability of 2-Alkoxy-2-*n*-butylhexanoic Acid (3). A 0.30 M solution of the α-alkoxy acid **3** (RCH_2 methyl or ethyl) in the appropriate alcohol (methanol or ethanol) was heated in an ampule for 2 h at 140 °C, esterified with the appropriate diazoalkane, and analyzed by VPC (conditions AZ-1 and CX-2). The α-alkoxy acid was stable under these thermolysis conditions.

Thermal Stability of Di-*n*-butylmalonic Acid (10). A 0.30 M solution of the malonic acid **10** in the alcohol (methanol or ethanol) was heated in an ampule at 130 °C for 2 h. The mixture was then esterified with the appropriate diazoalkane (diazoethane in the case of methanol and diazomethane in the case of ethanol) and analyzed by VPC (conditions CX-2). In both solvents a total of 92–92.5% decarboxylation took place to give 2-*n*-butylhexanoic acid (**11**), while the remainder 7.5–8.0% was converted to the dialkyl malonate (dimethyl in the case of methanol and diethyl in the case of ethanol).

Thermal Stability of Alkyl Hydrogen Di-*n*-butylmalonate (6). A 0.3 M solution of the half ester **6** (RCH_2 methyl or ethanol) in alcohol (methanol or ethanol) was heated in an ampule at 140 °C for 2 h. The mixture was then esterified with the appropriate diazoalkane (diazoethane in the case of methanol and diazomethane in the case of ethanol) and analyzed by VPC (conditions AZ-1). In both solvents about 33–34% of decarboxylation took place to give alkyl 2-*n*-butylhexanoate (**7**).

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Registry No.—**1**, 30842-78-5; **3** (R = H), 36602-15-0; **3** (R = Me), 36602-18-3; **4**, 502-56-7; **5**, 67315-53-1; *cis*-**8** ($RCH_2 = CH_3$), 36602-24-1; *trans*-**8** ($RCH_2 = CH_3$), 36602-25-2; **11**, 3115-28-4; **13** (R = Me), 22713-42-4; di-*n*-butylmalonic acid, 2283-16-1.

References and Notes

(1) Paper No. 71 in the Cyclic Peroxide Series.
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Rearrangement of Allyl Alcohols to Aldehydes with Superacids[1]

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The superacid-catalyzed rearrangement of allyl alcohols into aldehydes was studied in superacid solutions under stable ion conditions followed by ^1H NMR spectroscopy, as well as in the gas phase over a solid perfluorinated resinsulfonic acid catalyst (Nafion-H).

The catalytic rearrangement of allyl alcohol to propionaldehyde, brought about by H_2SO_4,[2] $Fe(CO)_4$,[3] $Fe(CO)_5$,[4] $Co_2(CO)_8$,[5] and acid-catalyzed electrolysis,[6] as well as in the gas phase, over Al_2O_3, ZnO, or pumice at elevated temperatures[7] has been studied. We wish to report now a study of the mechanism of the superacid-catalyzed isomerization of allyl alcohols in superacid solutions under stable ion conditions using ^1H NMR spectroscopy and directly observing the intermediate(s) responsible for such transformations. We also report that similar superacid-catalyzed isomerization takes place by catalysis over Nafion-H, a solid perfluorinated resinsulfonic acid in the gas phase at relatively mild conditions. Allyl alcohol is effectively isomerized to propionaldehyde. 2-Methylallyl alcohol, crotyl alcohol, and 3-methyl-2-buten-2-ol are also isomerized, under the same condition, to isobutyraldehyde, butyraldehyde and methyl isopropyl ketone, respectively.

Study of Allyl Alcohols in Superacid Solutions

When a solution of allyl alcohol **1** in SO_2ClF at −78 °C (dry ice–acetone bath) is slowly introduced into a well-stirred solution of $FSO_3H–SbF_5–SO_2ClF$ kept below −100 °C (ethanol–dry ice bath), protonated allyl alcohol **2** is observed.

$$\underset{\substack{\textbf{1a},\ R = H\\ \textbf{b},\ R = CH_3}}{RCH{=}CHCH_2OH} \xrightarrow[<-100\ ^\circ C]{FSO_3H–SbF_5–SO_2ClF} \underset{\substack{\textbf{2a},\ R = H\\ \textbf{b},\ R = CH_3}}{RCH{=}CHCH_2OH_2{}^+} \qquad (1)$$

The structure of **2** is identified by its 60-MHz ^1H NMR spectrum (Figure 1) obtained at −90 °C, which shows four proton resonances (Table I). The two-proton signal at δ 9.75 assigned to the protonated hydroxyl group confirms the formation of **2**. Protonated alcohols are known to show strong absorptions at about δ 10–11 in superacids.[8]

When raising the temperature of protonated allyl alcohol **2** in $FSO_3H–SbF_5–SO_2ClF$ above −80 °C, **2** slowly undergoes addition of FSO_3H to the double bond, giving protonated 2-fluorosulfonyl-1-propanol (**3**). The structure of **3** is confirmed by its proton and fluorine-19 NMR spectra (Table I). The process of slow transformation from **2** (−90 °C) to **3** (−40 °C) is clearly seen in Figure 1. When the solution of **2** is allowed to stand at −40 °C, the original ^1H NMR spectrum of

Table I. Proton and Fluorine-19 NMR Parameters of Protonated Allyl Alcohol and Its FSO_3H and HF Addition Products

ion	registry no.	acid (temp, °C)[b]	CH_3	$CH_2–OH_2^+$	CH	=CH	$=CH_2$	$-CH_2-$	OH_2^+	ϕ_{19F}	J_{H-F}, Hz
2	67315-77-9	A, B, (−90)		5.28 (d, 6.0)		6.58 (m)	6.17 (m)		9.75 (b)		
3a	67315-78-0	A (−50)	185 (d, 6.6)	5.12 (b)	5.78 (m)				11.05 (b)	−40.0 (s)	
3b	67315-79-1	A (−50)	1.94 (t)	5.24 (b)	5.75 (b)			3.88 (m)	10.3		
4	67315-80-4	B (−50)	1.60 (dd, 6.6)	5.10 (dt)	5.75 (dqm)				11.0 (t, 4.0)	+185.3 (dq)	$J_{CH_3-F} = 24.0$; $J_{CH_2-F} = 22.0$; $J_{CH-F} = 50.0$

[a] Proton and fluorine-19 chemical shifts are in ppm from external Me_4Si and CCl_3F, respectively. Multiplicities and coupling constants (in Hz) are given in parentheses: b = broad, d = doublet, m = multiplet, s = singlet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, dqm = doublet of quartet of multiplets, tt = triplet of triplets, td = triplet of doublets, qt = quartet of triplets. [b] A = $FSO_3H–SbF_5–SO_2ClF$; B = $HF–SbF_5–SO_2ClF$.

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