$\beta = 105.8\ (10)°$, $Z = 2$, $D_{calcd} = 1.113$ g cm^{-3}. Intensities of 1280 ($F \geq 3\sigma(F)$) independent reflections with 2θ values up to 95° were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated Cu Kα radiation, using the ω–2θ scanning technique. The final R value was 0.147. The structure was resolved by direct methods by using the MULTAN 84 program.[8]

Reaction of 2 with *p*-Toluenesulfonic Acid. A solution of **2** (60 mg) and calcium chloride (60 mg) in dry benzene (10 mL) was refluxed with *p*-toluenesulfonic acid (5 drops) for 3 h. After the reaction ceased, water was added to the solution, and the product was extracted with benzene. The organic layer was washed with water. Then the extracts were dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was chromatographed on silica gel, using benzene as eluent, to give 3β-acetoxy-9,10-*seco*-5α-cycloarta-1(10),8(9)-dien-7-one (**4**, 40 mg, 69%): mp 129–130 °C; $[\alpha]_D$ −28° (*c* 0.28, $CHCl_3$); IR (KBr) ν 1735 (OAc), 1664 (C=O), 1625 cm^{-1} (C=C); UV ($CHCl_3$) 244 nm (17610); ^{1}H NMR ($CDCl_3$) δ 5.44 (1 H, m, $w/2 = 8.64$ Hz, CH=C), 4.73 (1 H, br, $w/2 = 20$ Hz, CH–OAc), 2.07 (3 H, s, $OCOCH_3$); MS m/z 482.3711, $C_{32}H_{50}O_3$, calcd 482.3747. Elution with benzene–ethyl acetate (20:1) afforded 3β-acetoxy-9,10-*seco*-cycloarta-5(10),8(9)-dien-7-one (**5**, 14 mg, 24%): amorphous; $[\alpha]_D$ +16° (*c* 0.50, $CHCl_3$); IR (KBr) ν 1735 (OAc), 1665 cm^{-1} (C=O); UV ($CHCl_3$) 242 nm (33452); ^{1}H NMR (7CDCl$_3$) δ 4.68 (1 H, br, $w/2 = 20$ Hz, CH–OAc), 3.09 (1 H, br, $w/2 = 4.2$ Hz, allylic H), 2.05 (3 H, s, $OCOCH_3$); MS m/z 482.3710, $C_{32}H_{50}O_3$, calcd 482.3747.

Acknowledgment. We thank Dr. Ken-ich Kawai, Faculty of Pharmaceutical Sciences, Hoshi University, for the X-ray crystallographic analysis of **2** and Drs. Toshio Takido and Mitsuro Aimi, Nihon University, for measurement of ^{1}H NMR and mass spectra.

Registry No. **1**, 4575-74-0; **2**, 113948-10-0; **3**, 24564-12-3; **4**, 68326-42-1; **5**, 113975-06-7.

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Photocycloadducts of Dimethylmaleic Anhydride with Unsaturated Acids and Esters

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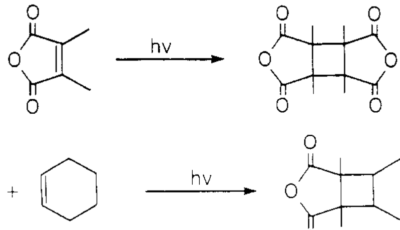
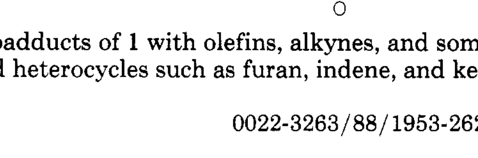
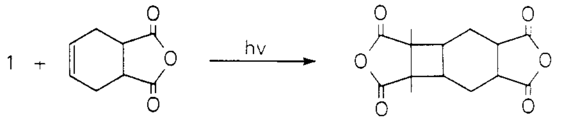
UV irradiation of dimethylmaleic anhydride (1) alone or with other unsaturated compounds yields [2 + 2] photocycloadducts as shown in eq 1 and 2. [2 + 2] photocycloadducts of 1 with olefins, alkynes, and some unsaturated heterocycles such as furan, indene, and ketene have been reported.[1] Fields and co-workers have recently reported the photocycloadducts of 1 with unsaturated anhydrides such as that shown in eq 3. Adducts of this type are monomers for polyimide engineering resins.[2]



(1)



(2)



(3)

Workers at Ciba-Geigy and elsewhere have used the ability of 1 to form [2 + 2] photocycloadducts to prepare herbicides, fungicides, and polymers useful for adhesives, coatings, photoresists, and photoimaging formulations.[3]

We now report the preparation and characterization of some novel photocycloadducts with unsaturated acids, esters, and allyl derivatives and our evaluation of some of these adducts as monomers for condensation polymers.

Experimental Section

Dimethylmaleic anhydride (1) was prepared from maleic anhydride.[4] All other reagents and materials were purchased from commercial sources and used without further purification.

Most spectroscopic and physical analyses were performed by Amoco Corp. Analytical Services. Survey ^{1}H and ^{13}C NMR spectra were obtained with a Nicolet NT-200 wide-bore, superconducting spectrometer at 200 and 50 MHz, respectively. Some ^{1}H NMR spectra were run on a Perkin-Elmer R32B (90 MHz) and will be so designated. Chloroform-*d* solutions were employed except for compounds **8** and **10** (acetone-d_6) and **9** (DMSO-d_6). We recorded the infrared spectra with a Perkin-Elmer 237B with the samples prepared as Nujol mulls between NaCl plates. Melting points were taken on a Mel-Temp heated block and are uncorrected. Gas chromatograms were obtained with a Hewlett-Packard 5710A using a 10 ft × $^1/_8$ in. stainless steel column of 3% OV-17 on 80/100 Supelcoport.

Inherent viscosities of polymers were determined at a concentration of 0.4 g/dL in 40/60 trichloroethylene/phenol at 30 °C. Thermal evaluations were performed by the Polymer Physics Division of Amoco Chemicals Corp.

All ^{1}H NMR spectra for the difference nuclear Overhauser effect (DNOE) experiments were acquired at 300 MHz on a Nicolet NT-300 spectrometer. Spectra were obtained with a 90° pulse (12 μs). The spectral width and number of data points were adjusted to give a digital resolution of 0.2 Hz. Spin-lattice relaxation times were obtained by using an inversion–recovery sequence and standard Nicolet software on a Nicolet 1280 computer.

DNOE spectra were obtained by using a steady-state presaturation method.[5] The decoupler was turned on at a given resonance frequency for 12 s with the power set to give 80–90% saturation of the resonance. Then the decoupler was gated off and data were acquired. After a 10-s delay this sequence was

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(3) (a) Eur. Pat. Appl. 94913, 1983. (b) Ger. Offen. 3314951, 1983. (c) Eur. Pat. Appl. 72780, 1983. (d) Eur. Pat. Appl. 38302, 1981. (e) Jpn. Kokai Tokkyo Koho 80160010, 1980. (f) Eur. Pat. Appl. 17994, 1980. (g) Ger. Offen. 2934550, 1980. (h) Belg. 860041, 1978. (i) Ger. Offen. 2626795, 1976. (j) Ger. Offen. 2626769, 1977.

(4) (a) Baumann, M. E.; Bosshard, H. *Helv. Chim. Acta* **1978**, *61*, 2751. (b) U.S. Patent 3818050, 1974. (c) U.S. Patent 3833619, 1974.

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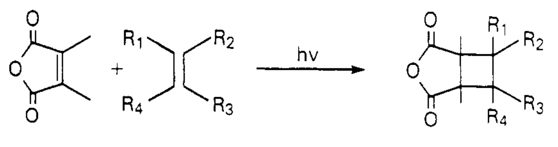
0022-3263/88/1953-2624$01.50/0

Table I. Photocycloaddition of Dimethylmaleic Anhydride (1) with Functionalized Olefins



1 2-11

substituent				product	mp, °C	yield, mol %	anal. found (calcd)	
R_1	R_2	R_3	R_4				% C	% H
H	H	H	CH_2Cl	2[a]	92–94	42	53.45 (53.53)	5.47 (5.58)
H	H	H	$CH_2O_2CCH_3$	3	102–104	33	58.40 (58.10)	6.24 (6.51)
H	H	H	$CH_2O_2CC_2H_5$	4	77–79	28	59.99 (59.95)	6.71 (6.93)
H	H	H	$CH_2O_2CC_6H_5$	5	105–106	29	66.66 (66.94)	5.59 (5.76)
H	H	H	CO_2CH_3	6	107–108	19	56.60 (56.51)	5.71 (5.70)
H	CH_3	H	CO_2CH_3	7	125–126	50	58.40 (58.37)	6.24 (6.26)
H	CH_3	H	CO_2H	8	158–160	27	56.60 (56.24)	5.70 (5.87)
H	CH_3	CH_3	CO_2H	9	248–250	59	58.40 (58.39)	6.24 (6.24)
H	H	H	CH_2CO_2H	10	183–185	46	56.60 (56.55)	5.70 (5.62)
H	H	H	$(CH_2)_8CO_2H$	11	wax	49	65.78 (65.57)	8.44 (8.51)

[a] Cl found (calcd) 17.5 (17.50).

repeated until a total of 64 scans was accumulated and stored. The decoupler frequency was offset several hundred hertz from any resonance, and the identical process was repeated to give a control spectrum that was also stored. The DNOE spectrum was obtained by subtracting the spectrum obtained with the decoupler frequency on resonance from the control spectrum. Thus in DNOE spectra a negative peak indicates a positive NOE, while an intense positive peak indicates the frequency at which the decoupler was set to obtain the spectrum.

For each molecule studied, a set of DNOE spectra were obtained for each resolved resonance in the spectrum. In some samples, different methyl resonances were too close to each other to irradiate only one of the peaks. In these cases, the decoupler was set midway between the two resonances and the power adjusted so that both resonances were equally saturated to the 80–90% level.

The chemical shifts and coupling constants for samples **5**, **6**, and **9** were obtained by spectral simulation using both iterative and noniterative software supplied by Nicolet.

Preparation of Photocycloadducts. All photochemical reactions were run similarly. Dimethylmaleic anhydride (**1**) (0.05–0.50 mol), the olefinic reagent (1–10 equiv), and benzophenone (0.05–0.50 wt % of the solution) were dissolved in toluene in a Pyrex Erlenmeyer flask. The final concentration of reagents was 20–40 wt %. The flask was fitted with a reflux condenser attached to a nitrogen supply, purged with nitrogen for 10 min, placed 4–6 in. above a G.E. sunlamp, and irradiated for about a week. Products were usually isolated in >50% crude yield and fractionally recrystallized to sharp melting points. Our results are summarized in Tables I and II.

Preparation of Poly(amide–imides). Small-scale melt polymerizations were run in 11 × 150 mm test tubes to which a ₸14/20 male joint had been attached as a side arm. The complete apparatus consisted of the test tube to which a vacuum take-off adapter and 50-mL round-bottom flask were attached.

A capillary glass nitrogen bubbler was inserted through a single-hole rubber stopper to the bottom of the test tube. This bubbler provided both an inert atmosphere and agitation of the melt. Acid anhydride was weighed into the test tube and liquid diamine was added. The apparatus was purged with N_2 and placed in a hot oil bath containing Dow Corning 710R silicone heat-transfer fluid. The temperature of the bath was controlled by an I^2R Thermo-watch controller (Model L7-800B). Polymerization conditions are described below. A vacuum usually was applied to the reaction mixture toward the end of the polymerization cycle. The vacuum was broken by introducing N_2 into the system. The melt was quenched in a dry ice–2-propanol bath, and the test tube was shattered to recover the polymer.

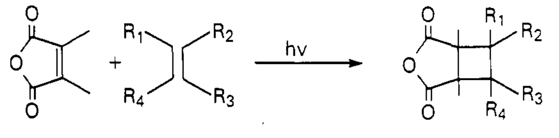
Solution polymerizations were carried out in appropriately sized standard taper laboratory glassware under an inert atmosphere. The acid anhydride (**9**) was dried at about 200 mm at 120 °C for 2 h and then maintained under vacuum at room temperature for an additional 20 h prior to use. Diamines were distilled prior to use. 1,4-Bis(aminomethyl)cyclohexane was a 40/60 mixture of the cis and trans isomers.

Poly(1,6-hexanediamine-*co*-1,2,3,4-tetramethylcyclobutane-1,2,3-tricarboxylic 1,2-anhydride). 1,2,3,4-Tetramethylcyclobutane-1,2,3-tricarboxylic 1,2-anhydride (**9**) (4.2 g, 18.75 mmol) and 1,6-hexanediamine (2.21 g, 19.00 mmol) were added in turn to the melt polymerization tube. The apparatus was heated at 100 °C to obtain a uniform melt. An exotherm resulted from the initial mixing. The polymerization temperature was increased to 160 °C after 0.5 h and to 200 °C after an additional 0.5 h. This temperature was maintained for 3.0 h, and then a vacuum was applied to the melt. Initial pressure was 0.5 mmHg, decreasing to 0.2 mmHg during an hour. The reaction temperature was increased to 225 °C while the vacuum was maintained for an additional hour. Inherent viscosity was 0.16 dL/g. Thermal analysis by DSC indicated that the polymer was amorphous with a dry T_g = 99 °C and a moist T_g = 74 °C. No other thermal transitions were detected. Thermogravimetric analysis revealed the following: onset of major weight loss at 300 °C; maximum rate of weight loss at 415 °C; and 1.7% residue at 510 °C.

Adduct **9** with 1,4-bis(aminomethyl)cyclohexane, treated similarly, gave a polymer with an inherent viscosity (IV) of 0.12 dL/g. With aromatic diamines such as 4,4′-methylenedianiline, **9** gave a tacky polymer. Adduct **10** with 4,4′-methylenedianiline yielded a polymer with an IV of 0.1 dL/g. Adduct **10** with 1,6-hexanediamine gave a polymer that was insoluble in trichloroethylene/phenol. These polymers were not investigated further.

Results and Discussion

Irradiation of **1** with unsaturated acids, esters, and allyl derivatives gives novel cyclobutanes by [2 + 2] photocycloaddition according to eq 4. The reactions were run



(4)

	R_1	R_2	R_3	R_4
2	H	H	H	CH_2Cl
3	H	H	H	$CH_2O_2CCH_3$
4	H	H	H	$CH_2O_2CC_2H_5$
5	H	H	H	$CH_2O_2CC_6H_5$
6	H	H	H	CO_2CH_3
7	H	CH_3	H	CO_2CH_3
8	H	CH_3	H	CO_2H
9	H	CH_3	CH_3	CO_2H
10	H	H	H	CH_2CO_2H
11	H	H	H	$(CH_2)_8CO_2H$

Table II. Infrared and NMR Spectra of Photocycloadducts

product	IR,[a] ν(CO)	^{1}H NMR[b]	^{13}C NMR[c]
2	1850 (m), 1775 (s)	3.7 (m, 2 H, CH_2Cl), 1.9–3.1 (m, 3 H, C-4 ring), 1.41 (s, 6 H, (CH_3)	174.4 (s), 173.3 (s), 48.1 (s), 43.7 (s), 41.9 (t), 37.8 (d), 32.1 (t), 14.9 (q), 7.6 (q)
3	1835 (m), 1770 (s), 1725 (s)	4.19 (m, 2 H, OCH_2), 2.1–2.4 (m, 3 H, C-4 ring), 2.09 (s, 3 H, C(O)CH_3), 1.38 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3)	176.1 (s)8 175.6 (s), 170.7 (s), 63.0 (t), 49.2 (s), 45.5 (s), 36.2 (d), 31.7 (t), 20.9 (q), 16.3 (q), 9.9 (q)
4	1840 (m), 1775 (s), 1725 (s)	4.20 (m, 2 H, OCH_2), 2.7 (m, 2 H, C-4 ring), 2.40 (q, J = 8 Hz, 2 H, CH_2), 2.0 (m, 1 H, C-4 ring), 1.38 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.20 (t, J = 8 Hz, 3 H, CH_3)	176.5 (s), 176.1 (s), 174.0 (s), 62.8 (t), 49.2 (s), 45.1 (s), 36.3 (d), 31.6 (t), 27.5 (t), 16.2 (q), 9.8 (q), 9.0 (q)
5	1850 (m), 1780 (s), 1715 (s)	7.8 (m, 5 H, phenyl), 4.43 (d, J = 6.8 Hz, 2 H, OCH_2), 3.04 (m, 1 H, $\mathrm{C}H_\mathrm{M}\mathrm{CH_2O}$), 2.64 (dd, J_{BM} = 8.8 Hz, J_{BA} = 12.8 Hz, 1 H, $\mathrm{C}H_\mathrm{B}\mathrm{H_ACH_M}$), 2.07 (dd, J_{AM} = 8.0 Hz, 1 H, $\mathrm{CH_B}H_\mathrm{A}\mathrm{CH_M}$), 1.40 (s, 6 H, CH_3)	176.2 (s), 175.5 (s), 166.3 (s), 133.6 (d), 129.8 (d), 129.6 (s), 116.1 (d), 63.5 (t), 49.4 (s), 45.7 (s), 36.7 (d), 31.7 (t), 16.8 (q), 10.0 (q)
6	1835 (m), 1780 (s), 1720 (s)	3.78 (s, 3 H, OCH_3), 3.38 (dd, J_{BX} = 7.4 Hz, J_{AX} = 8.8 Hz, 1 H, $\mathrm{C}H_\mathrm{X}\mathrm{CH_BH_A}$), 2.70 (dd, J_{AB} = 13.3 Hz, 1 H, $\mathrm{CH_XC}H_\mathrm{B}\mathrm{H_A}$), 2.55 (dd, 1 H, $\mathrm{CH_XCH_B}H_\mathrm{A}$), 1.40 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3)	175.4 (s), 174.4 (s), 170.8 (s), 52.4 (q), 49.5 (s), 45.7 (s), 41.2 (d), 30.3 (t), 15.8 (q), 11.4 (q)
7	1840 (m), 1780 (s), 1725 (s)	3.77 (s, 4 H, OCH_3), 2.8–3.0 (m, 2 H, C-4 ring), 1.38 (s, 3 H, CH), 1.28 (s, 3 H, CH_3), 1.15 (d, J = 5.8 Hz, 3 H, CH_3)	174.2 (s), 173.5 (s), 170.2 (s), 52.3 (q), 49.9 (s), 49.0 (d), 47.3 (s), 37.7 (d), 16.1 (q), 15.9 (q), 10.6 (q)
8	1835 (m), 1775 (s), 1700 (s)	2.8–3.0 (m, 2 H, C-4 ring), 1.35 (s, 6 H, CH_3), 1.17 (d, J = 6.8 Hz, 3 H, CH_3)	175.0 (s), 174.3 (s), 173.7 (s), 50.4 (s), 49.2 (d), 47.7 (s), 38.3 (d), 16.7 (q), 16.4 (q), 11.2 (q)
9	1840 (m), 1775 (s), 1680 (s)	9.38 (br s, 1 H, OH), 3.19 (q, J = 7.5 Hz, 1 H, CH), 1.36 (s, 6 H, CH_3), 1.07 (d, J = 7.5 Hz, 3 H, CH_3)	174.1 (s), 172.8 (s), 52.6 (s), 49.0 (s), 48.8 (s), 40.2 (d), 16.5 (q), 15.6 (q), 12.7 (q), 11.0 (q)
10	1845 (m), 1790 (s), 1685 (s)	3.0 (m, 1 H, C-4 ring), 2.66 (d, J = 6.8 Hz, CH_2), 2.6 (m, 2 H, C-4 ring), 1.39 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3)	175.4 (s), 174.1 (s), 170.8 (s), 47.2 (s) 43.5 (s), 33.6 (t), 33.0 (t), 32.2 (d), 14.6 (q), 7.8 (q)
11	1835 (m), 1775 (s), 1700 (s)		180.3 (s), 177.0 (s), 174.3 (s), 49.6 (s), 45.6 (s), 38.6 (t), 35.9 (d), 31.0 (t), 26–29 (overlapping signals), 16.9 (q), 9.1 (q)

[a] Nujol mulls between NaCl plates. [b] 200-MHz (**4**–**7** and **10**) or 90-MHz (**2**, **3**, **8**, and **11**) spectra in chloroform-*d* solution, acetone-d_6 (**8** and **10**), or DMSO-d_6 (**9**). [c] 50- or 20-MHz spectra in the same solvents noted in *b*.

as toluene solutions in Pyrex flasks using G.E. sunlamps as the UV source and benzophenone as a sensitizer. This equipment is less costly and more amenable to larger scale reactions than the more widely used Hannovia reactors and Hg-arc sources. The Pyrex flask filters out UV light of <300-nm wavelength that we find leads to formation of colored byproducts. The sunlamp warms the toluene solutions to about 70 °C. Acetone was tested as a solvent but we found that substantial amounts of the photodimer of **1** formed also. Without benzophenone, only very small amounts of product were isolated. No attempt was made to optimize yields of crude photocycloadduct, usually >50% after 1 week. Some experiments with 15-W fluorescent black lights indicate a substantial saving in electrical costs can be made in these and other sensitized photochemical reactions.

Most of the photocycloaddition reactions proceed cleanly, albeit slowly. In the reaction with allyl chloride, 84% of **1** was converted in 77.3 h. The only detectable competing reaction is the formation of the photodimer of **1**. The mechanism of these reactions was not studied in detail. Most likely it proceeds via a triplet of **1** in a manner similar to that proposed for enone reactions.[6]

Cycloadducts **2**–**11** initially form as a mixture of stereoisomers. This was especially obvious for the reactions with the allyl esters and with 11-undecenoic acid. All compounds were isolated in >90% stereoisomeric purity by fractional recrystallization. The configuration of these isomers could not be determined completely from the normal NMR spectra. The ^{1}H NMR spectra are consistent with retention of the stereochemistry of the original reactants and with cis addition to each other. Trans fusion is considered unlikely on the grounds of ring strain. We could not distinguish between anti and syn isomeric possibilities using chemical shifts or coupling constants. Rather we elected to use difference nuclear Overhauser effect (DNOE) spectra to determine the stereochemistry of these cycloadducts.[8] Three samples (**5**, **6**, and **9**) were selected for study using DNOE data. The structural designations used in the discussion of DNOE data are shown in Table III, which also contains the chemical shifts, coupling constants and T_1's for samples **5**, **6**, and **9**.

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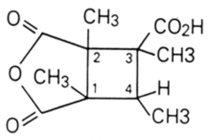
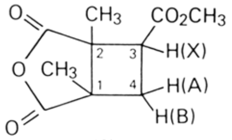
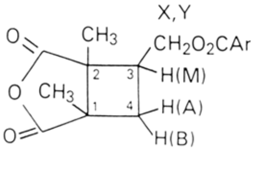
[6] DeMayo, P. *Acc. Chem. Res.* **1971**, *4*, 41.

[7] Johnson, C. K. ORTEP, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

[8] Noggle, J. H.; Schirmer, R. H. *The Nuclear Overhauser Effect*; Academic: New York, 1971.

Table III. Chemical Shifts (ppm) and T_1 Values (s) for Various Protons in 5, 6, and 9

structure	proton	δ	T_1	coupling constants, Hz
 (9)	C-1 CH_3	1.39[a]	1.1	
	C-2 CH_3	1.38[a]	0.9	
	C-3 CH_3	1.32	0.7	
	C-4 CH_3	1.05	1.1	
	C-4 CH	3.25	3.1	$J_{H(CH_3)}$ = 7.5
 (6)	C-1 CH_3	1.40	1.7	J_{AB} = 13.28
	C-2 CH_3	1.28	1.5	J_{AX} = 8.79
	C-3 H_X	3.37	9.7	J_{BX} = 7.36
	C-4 H_A	2.54	2.5	
	C-4 H_B	2.67	2.5	
	CO_2 CH_3	3.78	3.40	
 (5)	C-1 CH_3	1.40[a]	1.2	J_{AB} = 13.02
	C-2 CH_3	1.41[a]	1.1	J_{AM} = 8.13
	C-3 H_M	3.05	3.6	J_{BM} = 9.02
	C-4 H_A	2.08	1.3	J_{MX} = 8.66
	C-4 H_B	2.65	1.5	J_{MY} = 5.38
	OCH_2 H_X	4.41	1.2	J_{XY} = 11.86
	OCH_2 H_Y	4.45	1.2	

[a] Assignments may be interchanged.

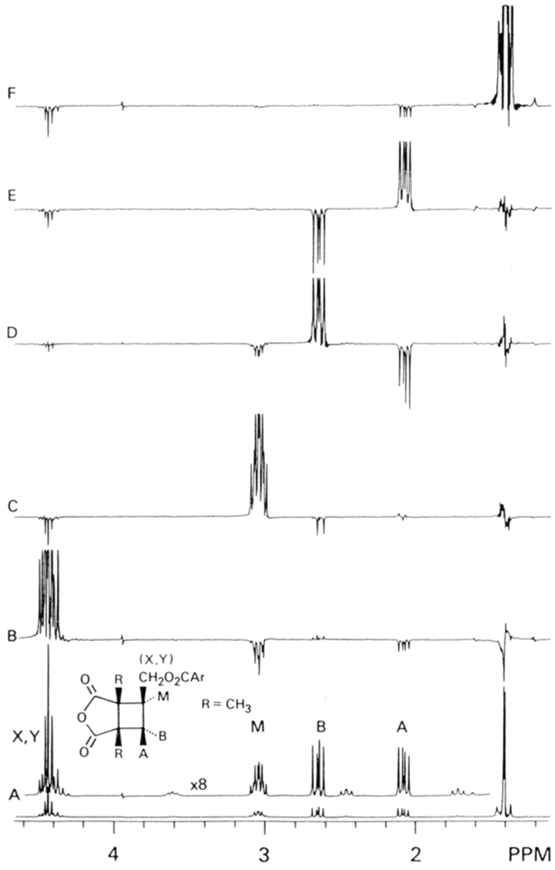


Figure 1. ^1H and DNOE spectra of **5**.

Throughout the discussion of spectral assignments we assume that the methyls on C-1 and C-2 are cis because of models of a trans anhydride on a cyclobutane ring cannot be made. The normal ^1H and DNOE spectra of **5** are shown in Figure 1. The ^1H spectrum shows small peaks near 4.35, 3.60, and 2.45 ppm whose intensities increased with time as the sample was kept in solution. These peaks were found to be due to free acid that resulted from the hydrolysis of the anhydride but did not interfere with the analysis.

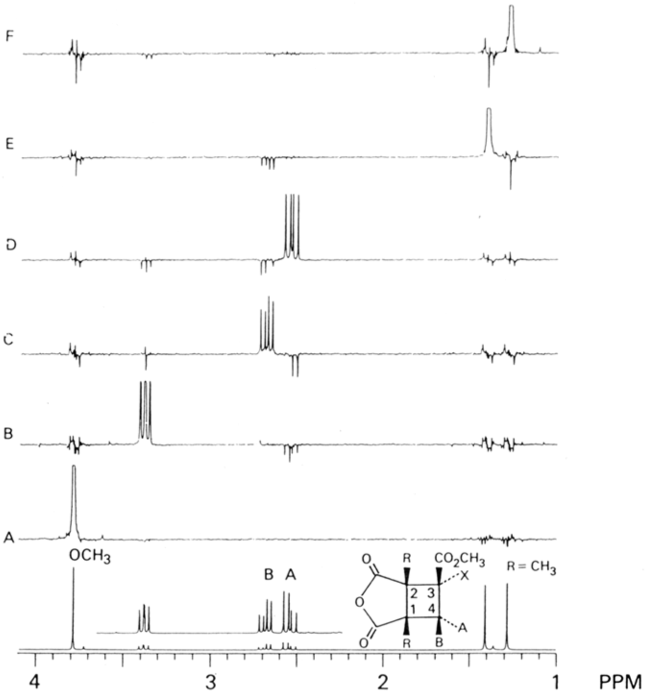


Figure 2. ^1H and DNOE spectra of **6**.

The ^1H spectrum of **5** consists of four well-resolved multiplets and two closely spaced singlets. The multiplets near 4.4 ppm is assigned to the two ester methylene protons, which are nonequivalent due to the chiral center at C-3 in the cyclobutane ring. These protons are labeled X and Y for purposes of this discussion. The three cyclobutane ring proton resonances at 3.05, 2.65, and 2.08 ppm are labeled M, B, and A, respectively. The chemical shift of 3.05 ppm indicates that resonance M is assignable to the methine proton on C-3, which will be referred to as H_M. The B and A resonances are due to the two protons on C-4—H_A and H_B—and their exact assignments are made from the NOE data. The singlets at 1.40 and 1.31 ppm are due to the C-1 and C-2 methyl groups but they could not be assigned unambiguously to specific methyl groups.

Simultaneous irradiation of X and Y results in an NOE at resonances M and A. Irradiation of M leads to an NOE at X, Y, and B. Irradiation of B leads to a small NOE at X and Y and larger NOE's at M and A. Irradiation at A leads to an NOE at X, Y, and B. These data are consistent with the structure in which H_M is cis to H_B and trans to H_A while H_X and H_Y are on a carbon cis to H_A and trans to H_B. No NOE was observed at the ring methyl resonances on irradiation of the ring protons presumably because relaxation of a methyl proton is dominated by interactions with its geminal neighbors.[8] Selective irradiation of individual methyl peaks was not experimentally possible due to the proximity of these peaks. When both methyl peaks are simultaneously irradiated NOE's were observed at resonances X, Y, and A. This confirms that the methyl groups are cis to the ester methylene protons and H_A. Thus, **5** has the cis–anti–cis configuration.

The ^1H and DNOE spectra of **6** and **9** are shown in Figures 2 and 3, respectively, and lead to cis–anti–cis configurations for both materials.

To determine unequivocally the molecular geometry of **9** we used X-ray diffraction. An ORTEP[7] perspective drawing of **9** and the labeling scheme utilized are presented in Figure 4. Compound **9** crystallizes with one molecule in the asymmetric unit. The cyclobutane ring in **9** is

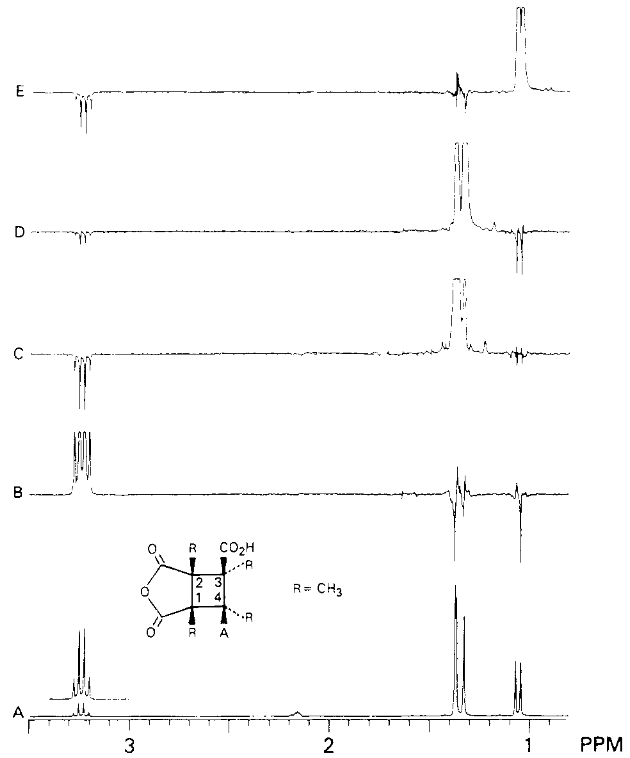


Figure 3. ^1H and DNOE spectra of **9**.

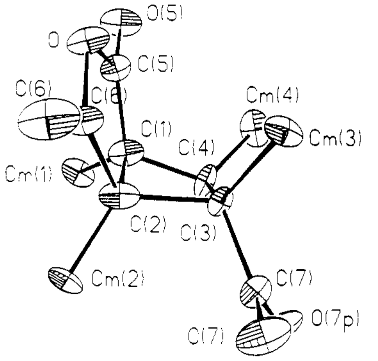
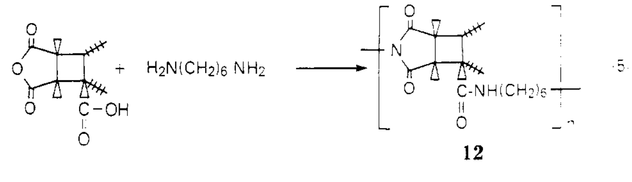


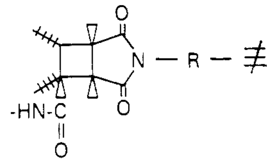
Figure 4. Molecular structure of **9**.

presumably distorted to minimize steric interactions among the four methyl groups. The nonplanarity of the ring can be easily measured by examining some torsional angles of the ring carbons. For example, the torsional angle for C(3)–C(1)–C(2)–C(4) is 17.3° and the three remaining torsional angles are all about 17°. The structure of **9** is clearly shown to be the cis–anti–cis isomer. A crystallographic summary, tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen final atomic coordinates are available as Supplementary Material.



12

Amide–imide polymers are a commercially important class of engineering resins and also find use as wire enamels and adhesives. We attempted the polymerization of cycloadducts **8–11** with diamines as illustrated by the example in eq 5. Very similar polyimides, useful as engineering resins, have been reported from the reaction of cyclobutane dianhydrides and diamines.[2] To date, high molecular weight polymers have not been obtained from anhydride–acids **8–11**. It was anticipated that the poly(amide–imides) of these cycloadducts would be amorphous due to the dissymmetry of the anhydride–acids. Because diastereomeric chain segments are possible, head-to-tail orientation would not result in sufficient order to develop crystallinity. That is, the two enantiomers of **9** (for example) would result in diastereomeric chain segments **16** and **17** being present in the polymer:



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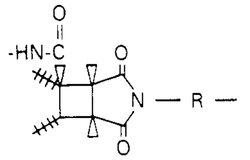

17

The fact that these poly(amide–imides) could be amorphous would not preclude their use as engineering polymers. For example, polyarylates are amorphous. However, to realize adequate thermal and mechanical properties rigid aromatic diamines would be required. All attempts to produce high molecular weight polymers from cycloadducts **8–11** and aromatic amines (4,4′-oxybis(aniline) or 4,4′-methylenedianiline) were unsuccessful. Only tacky, low molecular weight materials formed. For example, melt polymerization of cycloadduct **10** and 4,4′-methylenedianiline gave a material with an inherent viscosity of 0.1 dL/g. These materials were not characterized further.

Poly(amide–imides) with aliphatic diamines have been used as adhesives and electrically insulating lacquers. The reactions of **9** or **10** with more reactive aliphatic diamines also gave low molecular weight materials. Melt polymerization of cycloadduct **9** with 1,6-hexanediamine gave poly(amide–imide) **12**. Early in the reaction the viscosity of the melt increased rapidly but soon stopped. the isolated polymer was amorphous with T_g = 74 °C and an inherent viscosity of 0.16 dL/g. Similar melt polymerization of **9** and 1,4-bis(aminomethyl)cyclohexane gave a polymer with an inherent viscosity of 0.12 dL/g. These polymers are inferior to the randomly oriented trimellitic anhydride polymer with 1,6-hexanediamine that has T_g = 115 °C. Melt polymerization of **10** with 1,6-hexanediamine produced a gel, suggesting that **10** is trifunctional. Only water-dispersible oils were obtained from the solution polymerization of **9** or **10** with 1,6-hexanediamine. We previously observed that cycloadducts **8** and **11** were less reactive than **9** and **10** so they were not tested with aliphatic diamines.

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Registry No. 1, 766-39-2; 2, 114058-05-8; 3, 114058-06-9; 4, 114058-07-0; 5, 114058-08-1; 6, 114094-29-0; 7, 114058-09-2; 8, 114058-10-5; 9, 114058-11-6; 10, 114058-12-7; 11, 114058-13-8; $H_2C{=}CCH_2Cl$, 107-05-1; $H_2C{=}CHCH_2OCOCH_3$, 591-87-7; $H_2C{=}CHCH_2OCOCH_2CH_3$, 2408-20-0; $H_2C{=}CHCH_2OCOPh$, 583-04-0; $H_2C{=}CHCO_2CH_3$, 96-33-3; (*E*)-$H_3CCH{=}CHCO_2CH_3$, 623-43-8; (*E*)-$H_3CCH{=}CHCO_2H$, 107-93-7; (*E*)-$H_3CCH{=}C(CH_3)CO_2H$, 80-59-1; $H_2C{=}CHCH_2CO_2H$, 625-38-7; $H_2C{=}CH(CH_2)_8CO_2H$, 112-38-9; $H_2N(CH_2)_6NH_2$, 124-09-4; 1,4-bis(aminomethyl)cyclohexane, 2549-93-1; 4,4′-methylenedianiline, 101-77-9.

Supplementary Material Available: Listings of final atomic coordinates, anisotropic thermal parameters, and bond lengths and bond angles together with complete details of the structure determination for **9** (10 pages). Ordering information is given on any current masthead page.

Dichlorofluoromethane-*d*: A Versatile Solvent for VT-NMR Experiments

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VT-NMR experiments are often hindered or complicated by problems associated with the physical properties of the solvent being used. The most critical of these properties can be identified as follows: (1) the liquid range of the solvent (mp, bp); (2) the viscosity of the solvent at low temperatures; (3) the ability of the solvent to solvate a wide range of solutes; (4) the chemical and signal purity (spectral window); (5) the ease and expense of the solvent preparation. The solvents most commonly used today falter in a least one or more of these areas. For example, chloroform, though a good solvent for many solutes, has a relatively high melting point (–60 °C) and is rather viscous below –50 °C. Dichloromethane-d_2 and dichloromethane-d_2/pyridine-d_5 have greater liquid ranges but are expensive with the latter having additional problems, associated with the lack of chemical inertness. Dimethyl ether-d_6 has been proposed[1] because of its low melting point, but it too is very expensive.

To address this problem, we present here a simple one-step procedure for the synthesis of dichlorofluoromethane-*d* (DCFM). The solvent physical properties of DCFM are well-suited for variable temperature work: mp –135 °C, bp 10 °C;[2] low viscosity at low temperatures; solvates solutes analogously to chloroform; chemically inert; synthesized readily from commercially available chloroform-*d*.

Previously, DCFM has been reported in the literature to have been made by the action of NaOD/D_2O on chlorofluoromethane,[3] by mercuric salt catalyzed fluorination of chloroform,[4] and by a manner similar to what we report herein using antimony trifluoride to fluorinate chloroform-*d*.[5] Our method uses a stoichiometric amount of antimony trifluoride and chloroform-*d* with a catalytic amount of antimony pentachloride. It is performed at 30–35 °C in an all-glass one-pot set-up from which the product distills as it is formed and is collected in a dry ice/acetone cooled trap. The procedure is accomplished in high yield (80%) and can be run on large scale (100 mL of $CDCl_3$) conveniently.

The purity of this material has been checked by ^1H and ^{13}C NMR (Figure 1). Some chloroform-*d* and a small amount of chlorodifluoromethane-*d* (CDFM) distills over with the product.[6] These secondary components typically do not interfere with the solvent's utility but they can be removed and the product can be purified by simple distillation.

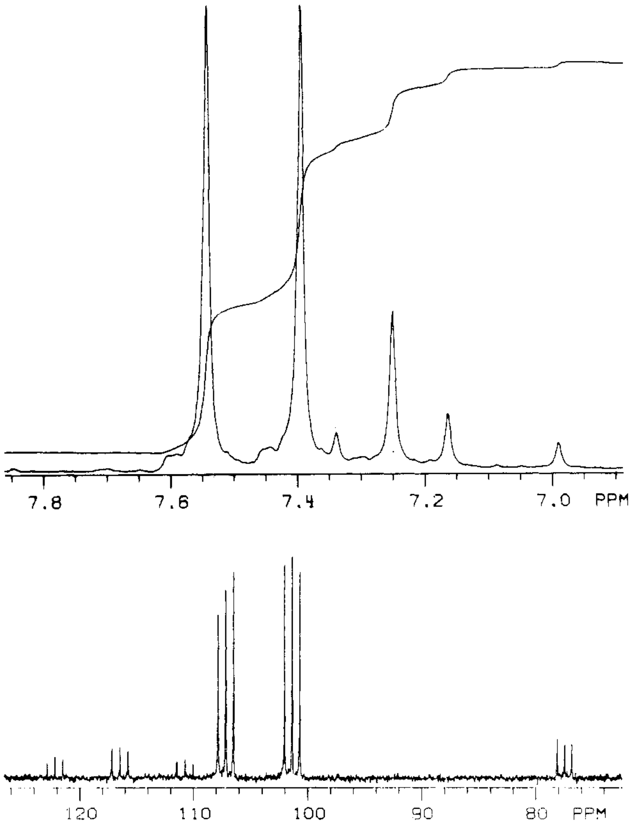

Figure 1. ^1H and ^{13}C NMR spectra of crude distillate from the halogen exchange reaction. ^1H NMR spectrum shows integration which indicated a product mixture of 80% DCFM, 13% $CDCl_3$, and 7% CDFM.

We have used this solvent successfully in a number of variable temperature studies,[7] and we anticipate its wide spread utility to many other problems of general interest.

Experimental Section

General Data. Proton NMR spectra were recorded on a ^1H NMR spectrometer equipped with a Nicolet 1180E computer interfaced with an Oxford magnet operating at 360 MHz. Carbon NMR spectra were recorded on a Nicolet NT200 spectrometer. All chemicals were used in their commercially available form (Aldrich).

Dichlorofluoromethane-*d*. A 100-mL single-neck Kjeldahl flask is charged with 50 g (0.28 mol) of antimony trifluoride from a freshly opened bottle which has been hand ground in a mortar and pestle.[8] Chloroform-*d* (100 g, 0.84 mol) plus 3 mL (6.9 g, 0.023 mol) of antimony pentachloride are added to the reaction flask. The flask is then immediately fitted to the all-glass apparatus. The reaction begins almost at once with bubbles appearing within a few minutes. The reaction is run under a static blanket of argon and is vented via the curved adaptor through the mercury bubbler which is attached to the argon manifold. A dry ice/acetone bath is brought up around the airless flask, thus submerging the greater portion of the flask. The product distills

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[1] Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

[2] DCFM can be supercooled easily to –150 °C for an hour.

[3] Hine, J.; Burske, N. W. *J. Am. Chem. Soc.* **1956**, *78*, 3337.

[4] (a) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1979**, *101*, 3500. (b) Squillacote, M. E.; Neth, J. E. *Magn. Reson. Chem.* **1987**, *25*, 53.

[5] Andrews, L.; Willner, H.; Prochaska, F. T. *J. Fluorine Chem.* **1979**, *13*, 273.

[6] From the integration of the residual ^1H NMR signals one can estimate the solvent composition as 80% DCFM, 13% chloroform, and 7% CDFM.

[7] (a) Anet, F. A. L.; Bacon, B.; Kofelevich, M., Unpublished results. (b) Kilway, K. V.; Siegel, J. S., manuscript in preparation. (c) Anet, F. A. L.; Chmurny, G. N.; Kane, J. *J. Am. Chem. Soc.* **1973**, *95*, 4423.

[8] (a) This step does not require the use of a drybox or special atmosphere but the transfer of the freshly ground material to the reaction apparatus must be expedient so as to avoid collecting too much moisture.