containing perchloric acid (70%, 10 mL). After 3 h of stirring at room temperature, the precipitated thallium(I) nitrate was removed by filtration, and the filtrate was diluted with water (100 mL). The organic phase was separated, the aqueous layer was extracted with methylene chloride (50 mL), and the combined organic phases were washed with water (100 mL), dried (Na_2SO_4), and evaporated. The resulting ester was purified by chromatography on alumina with benzene eluant; collection of the blue fluorescent fraction afforded ester: 2.20 g (80%); mp 130–131 °C (methanol) (lit.[11] mp 130.6–131.8 °C); ^{1}H NMR (400 MHz, chloroform-*d*) 3.65 (s, 3 H, ester CH_3), 4.25 (s, 2 H, benzylic CH_2), 7.90–8.35 ppm (m, 9 H, aromatic H); IR (KBr) 1740 cm^{-1} (C=O).

1,2,3,6,7,8,9,10,11,12-Decahydrobenzo[*e*]pyrene (4). A mixture of ketone **3** (1.0 g, 3.62 mmol), diethylene glycol (50 mL), hydrazine monohydrate (1.0 mL), and KOH (1.0 g) was refluxed for 6 h, cooled to room temperature, and poured into an excess of water. The product was extracted into methylene chloride (2 × 50 mL), washed with water (100 mL), and dried (Na_2SO_4), and the solvent was evaporated. The product was purified by chromatography on silica with hexane as eluant to give **4**: 770 mg (81%); mp 192 °C (lit.[22] mp 192–193 °C).

4-Acetyl-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene (5). To a solution of decahydrobenzo[*e*]pyrene (**4**) (720 mg, 2.75 mmol) and acetyl chloride (0.21 mL, 2.94 mmol) in dry benzene (20 mL) was added $AlCl_3$ (463 mg, 3.45 mmol) in portions with stirring at room temperature. After stirring for 4 h, the reaction mixture was poured into ice–hydrochloride acid, the organic layer was separated, and the aqueous layer was extracted with additional benzene (100 mL). The organic phases were combined, washed with sodium bicarbonate solution (5%, 100 mL) and water (100 mL), and dried (Na_2SO_4). Following evaporation of the solvent, the product was purified by chromatography on alumina with benzene eluant to give ketone **5**: 710 mg (85%); mp 150–151 °C (hexane); ^{1}H NMR (400 MHz, CD_2Cl_2) 1.83 (m, 4 H, $H_{10,11}$), 1.96 (quintet, 2 H, J = 6.15 Hz, $H_{2\text{ or }7}$), 2.02 (quintet, 2 H, J = 6.15 Hz, $H_{7\text{ or }2}$), 2.59 (s, 3 H, $COCH_3$), 2.79 (m, 4 H, $H_{9,12}$), 2.89 (two t, 4 H, J = 6.0 Hz, $H_{1,8}$), 2.98 (t, 2 H, J = 6.15 Hz, H_6), 3.18 (t, 2 H, J = 6.15 Hz, H_3), 7.24 ppm (s, 1 H, aromatic H_5); IR (KBr) 1675 cm^{-1} (C=O); UV (CH_2Cl_2) [λ_{max}, nm ($\epsilon \times 10^{-4}$)] 360 (0.34), 319 (0.49), 309 (0.58), 299 (0.49), 269 (2.95), 265 (2.91), 233 (1.83). Anal. Calcd for $C_{22}H_{24}O$: C, 86.84; H, 7.89. Found: C, 83.96; H, 8.01.

4-Acetylbenzo[*e*]pyrene (6). A solution of **5** (684 mg, 2.25 mmol) and DDQ (2.80 g, 12.33 mmol) in dry benzene (300 mL) was refluxed under nitrogen for 12 h. Following filtration of the cooled solution, the filtrate was concentrated to 100 mL and passed through an alumina column, and the blue fluorescent fraction was collected to yield light yellow crystals of ketone **6**: 590 mg (90%); mp 214–215 °C (methanol); ^{1}H NMR (400 MHz, CD_2Cl_2) 2.90 (s, 3 H, $COCH_3$), 7.73 (m, 2 H, $H_{10,11}$), 8.05 (t, 1 H, J = 8.0 Hz, $H_{2\text{ or }7}$), 8.08 (t, 1 H, J = 8.0 Hz, $H_{7\text{ or }2}$), 8.22 (br d, 1 H, J = 7.0 Hz, H_6), 8.49 (s, 1 H, H_5), 8.82 (m, 2 H, $H_{9,12}$), 8.92–9.02 ppm (three d, 3 H, J = 8.0 Hz, $H_{1,3,8}$); IR (KBr) 1670 cm^{-1} (C=O); UV (CH_2Cl_2) [λ_{max}, nm ($\epsilon \times 10^{-4}$)] 336 (1.26), 321 (1.34), 293 (2.41), 281 (2.46), 269 (3.24), 262 (3.13). Anal. Calcd for $C_{22}H_{14}O$: C, 89.80; H, 4.76. Found: C, 89.81; H, 4.81.

Methyl 4-Benzo[*e*]pyrenylacetate (7). Ketone **6** (530 mg, 1.80 mmol) was treated by the same procedure described above for 4-acetylpyrene. The crude ester was chromatographed on alumina with benzene eluant, and collection of the intense fluorescent fraction afforded ester **7**: 479 mg (82%); mp 207–208 °C (methanol); ^{1}H NMR (400 MHz, $CDCl_3$) 3.69 (s, 3 H, ester CH_3), 4.25 (s, 2 H, CH_2CO_2), 7.72 (m, 2 H, $H_{10,11}$), 7.97 (s, 1 H, H_5), 8.00 (t, 1 H, J = 7.0 Hz, $H_{2\text{ or }7}$), 8.05 (t, 1 H, J = 7.0 Hz, $H_{7\text{ or }2}$), 8.12 (br d, 1 H, J = 8.0 Hz, $H_{3\text{ or }6}$), 8.28 (br d, 1 H, J = 8.0 Hz, $H_{6\text{ or }3}$), 8.82 (m, 2 H, $H_{9,12}$), 8.86 (br d, 1 H, J = 8.0 Hz, $H_{1\text{ or }8}$), 8.92 ppm (br d, 1 H, J = 8.0 Hz, $H_{8\text{ or }1}$); IR (KBr) 1740 cm^{-1} (C=O). Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.19; H, 4.94. Found: C, 85.19; H, 4.87.

4-Benzo[*e*]pyrenylacetic Acid (8). Hydrolysis of ester **7** (450 mg, 1.39 mmol), carried out[20] in aqueous KOH (20%, 4 mL) and methanol (15 mL), gave acid **8**: 410 mg (95%); mp 231–232 °C dec (chlorobenzene); IR (KBr) 1703 cm^{-1} (C=O). Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.16; H, 4.52. Found: C, 84.99; H, 4.51.

Naphtho[1,2,3-*mno*]acephenanthrylen-3(4*H*)-one (9). Acid **8** (390 mg, 1.26 mmol) was stirred in anhydrous hydrofluoric acid for 15 h at room temperature. Following standard workup,[15] the crude product was chromatographed on alumina with chloroform eluant. Collection of the yellow band with intense blue fluorescence furnished pure cyclic ketone **9**: 294 mg (80%); mp 212–213 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) 3.86 (s, 2 H, $COCH_2$), 7.79–7.84 (m, 2 H, $H_{10,11}$), 7.82 (s, 1 H, H_5), 8.04 (t, 1 H, J = 7.76, H_7), 8.16 (br d, 1 H, J = 7.16 Hz, H_6), 8.22 (d, 1 H, J = 8.09 Hz, H_2), 8.74 (m, 2 H, $H_{9,12}$), 8.81 (br d, 1 H, J = 8.34 Hz, H_8), 8.85 ppm (d, 1 H, J = 8.09 Hz, H_1); IR (KBr) 1705 cm^{-1} (C=O); UV (CH_2Cl_2) [λ_{max}, nm ($\epsilon \times 10^{-4}$)] 405 (0.79), 382 (0.65), 358 (1.56), 342 (1.29), 322 (0.94), 296 (2.91), 275 (2.35). Anal. Calcd for $C_{22}H_{12}O$: C, 90.41; H, 4.11. Found: C, 89.92; H, 4.04.

3-Hydroxy-3,4-dihydronaphtho[1,2,3-*mno*]acephenanthrylene (10). Sodium borohydride (100 mg) was added in portions to a solution of ketone **9** (263 mg, 0.90 mmol) in THF (30 mL) and methanol (15 mL) and stirred at ambient temperature for 1 h. Following addition of distilled water (25 mL), the organic solvents were removed on a rotary evaporator. The precipitated colorless alcohol **10** (256 mg, 97%) was filtered, dried in vacuo, and used directly in the next step.

Naphtho[1,2,3-*mno*]acephenanthrylene (2). After dehydration[20] of alcohol **10** (240 mg, 0.82 mmol) by 2.5 g of alumina (neutral activity I) in dry benzene (150 mL), the crude PAH was chromatographed on alumina with elution by 1:2 benzene–hexane. Collection of the yellow-orange, nonfluorescent band afforded **2**: 191 mg (85%); mp 190–191 °C; ^{1}H NMR (400 MHz, acetone-d_6) 7.26 (d, 1 H, J = 5.13 Hz, etheno H_4), 7.42 (d, 1 H, J = 5.13 Hz, etheno H_3), 7.76 (m, 2 H, $H_{10,11}$), 8.06 (t, 1 H, J = 7.80 Hz, H_7), 8.12 (d, 1 H, J = 7.76 Hz, H_2), 8.36 (s, 1 H, H_5), 8.38 (br d, 1 H, J = 7.71 Hz, H_6), 8.74 (d, 1 H, J = 7.81 Hz, H_1), 8.80 (m, 1 H, $H_{9\text{ or }12}$), 8.88 (m, 1 H, $H_{12\text{ or }9}$), 8.95 ppm (br d, 1 H, J = 7.84 Hz, H_8); IR (KBr) 3030, 1615, 1535, 1475, 1360, 1337, 1235, 1110, 915, 885, 860, 825, 750, 710 cm^{-1}; UV (heptane) [λ_{max}, nm ($\epsilon \times 10^{-4}$)] 397 (0.81), 376 (0.78), 365 (1.21), 358 (1.16), 349 (1.52), 336 (1.11), 324 (1.82), 307 (sh, 1.97), 298 (2.30), 286 (2.27), 269 (sh, 2.05), 256 (4.04), 247 (4.17), 225 (3.99); accurate mass molecular ion 276.0932, calcd for $C_{22}H_{12}$ 276.0937; mass spectrum, m/e (relative intensity) 276 (100, M^+), 274 (17, M – H_2), 138 (22, M^{2+}), 137 (9, (M – H_2)$^{2+}$); HPLC retention time 33.45 min. Anal. Calcd for $C_{22}H_{12}$: C, 95.65; H, 4.35. Found: C, 95.46; H, 4.40.

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Registry No. **2**, 113779-16-1; **3**, 68151-08-6; **4**, 92387-50-3; **5**, 113779-17-2; **6**, 113779-18-3; **7**, 113779-19-4; **8**, 113779-20-7; **9**, 113779-21-8; **10**, 113779-22-9; 4-acetylpyrene, 22245-47-2; acetyl chloride, 75-36-5.

Transformation of Cycloartanyl Acetate into B-Homo Triterpenoids

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About 15 years ago, Lawrie et al.[1] reported that oxidation of cycloartanyl acetate (**1**) with ozone yielded 7-oxocycloartanyl acetate (**3**) as the major product. On the basis

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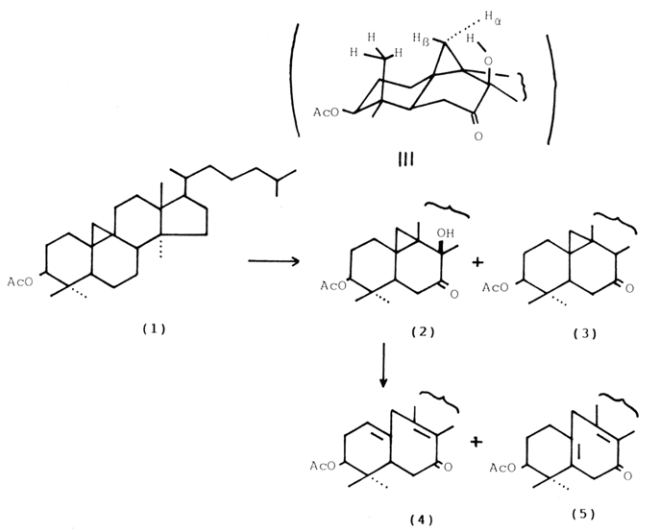
Scheme I



of the results of ozonolysis on alicyclic hydrocarbons such as decahydronaphthalenes and perhydrophenanthrenes,[2] it was considered likely that an α-hydroxy ketone would be obtained as a minor product in the above reaction. Thus the ozone oxidation of **1** was reexamined.

Treatment of **1** with oxygen containing ca. 1.2% ozone in chloroform at −60 °C for 1 h followed by chromatography over silica gel gave **3** in 34% yield, the melting point and spectral data of which are in agreement with Lawrie's report[1] (Scheme I). However, a new product (**2**) (mp 200–201 °C, M^+ m/z 500 ($C_{32}H_{52}O_4$), $[\alpha]_D$ +47° (c 0.20, $CHCl_3$)) was also isolated in 14% yield.

Compound **2** has bands at 3400 (OH), 1729 (OAc), and 1682 cm^{-1} (C=O) in its IR spectrum. The ^{13}C NMR spectrum of **1**[3] has a signal (triplet) at 28.0 ppm arising from C-7. This signal is absent from the spectrum of **2**, and an additional signal (singlet) appears at 215.2 ppm. These spectral changes indicate that the carbonyl group of **2** is located at C-7. In the ^1H NMR spectrum of **2**, the signal of 8-H, which appears at 2.76 ppm in ^1H NMR spectrum of **3**, is not observed, and a signal is found at 3.29 ppm, which disappeared on treatment with deuterium oxide. These spectral data suggest introduction of a hydroxyl group at C-8 of **2**. Nuclear Overhauser enhancement (NOE) in the ^1H NMR spectrum of **2** was observed between 8-OH and 19β-H and between 19β-H and 30-H. The NOE revealed a β-configuration of the hydroxyl group at C-8. Attempted acetylation of the hydroxyl group of compound **2** was unsuccessful. However, from the above evidence compound **2** might be either 3β-acetoxy-8β-hydroxy-cycloartan-7-one or 3β-acetoxy-5β-hydroxycycloartan-6-one. Therefore, the structure and stereochemistry of **2** were established by X-ray crystallographic analysis. The crystal structure was determined as shown in Figure 1. Accordingly, it is concluded that **2** is 3β-acetoxy-8β-hydroxycycloartan-7-one. Although the mechanism of ozonation of cyclic alkanes is discussed in some papers,[4a,b] the sequence leading to α-hydroxy ketone is still obscure.

In order to examine ring expansion of the B ring, we refluxed **2** with a catalytic amount of p-toluenesulfonic acid–$CaCl_2$[5] in benzene for 3 h. Product (**4**) was obtained

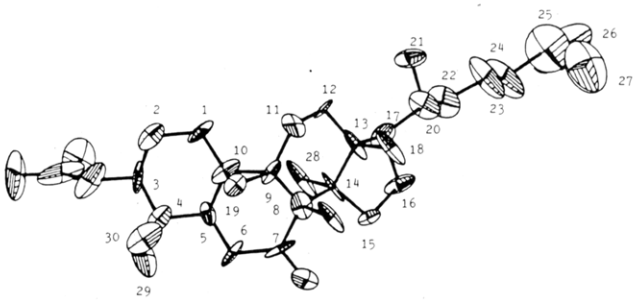


Figure 1. Perspective view of **2**.

in 69% yield: mp 129–130 °C; M^+ m/z 428 ($C_{32}H_{50}O_3$); $[\alpha]_D$ −28° (c 0.28, $CHCl_3$); IR ν 1735 (OAc), 1664 (C=O), 1625 cm^{-1} (C=C); ^1H NMR 5.44 ppm (m, $w/2$ = 8.64 Hz, olefinic H). The IR and ^1H NMR spectra indicate that **4** contains an α,β-unsaturated carbonyl system in the molecule. Furthermore, the signals centered at 0.35 and 0.65 ppm (dd, J = 5.9 Hz) in the ^1H NMR spectrum of **2** due to cyclopropane methylene protons are not observed in the spectrum of **4**. In the UV and ^1H NMR spectra of **4**, the existence of an $\alpha\beta,\gamma\delta$-conjugated dienone system was not observed. On the basis of these spectral data, compound **4** is considered to be 3β-acetoxy-9,10-*seco*-5α-cycloarta-1(10),8(9)-dien-7-one. In addition, 3β-acetoxy-9,10-*seco*-cycloarta-5(10),8(9)-dien-7-one (**5**) (amorphous; M^+ m/z 482 ($C_{32}H_{50}O_3$); IR ν 1735 (OAc), 1665 cm^{-1} (C=O); ^1H NMR 3.09 ppm (br s, $w/2$ = 4.2 Hz, allylic H)) was obtained in 24% yield as a minor product. The transformation **2** → **4** results from acid-catalyzed cleavage of the cyclopropane ring of **2** and formation of two olefinic bonds. This reaction is the first conversion of a cycloartane into a B-homo triterpenoid although there are reports on the conversion of cycloartanes to lanostanes[6] and cucurbitanes (19(10→9β)-abeolanostanes).[7]

Experimental Section

All melting points are uncorrected. IR spectra were obtained in KBr on a JASCO IR-G instrument. UV spectra were recorded in $CHCl_3$ on a Shimadzu UV-2100 spectrometer. ^1H NMR and ^{13}C NMR spectra were measured at 100 and 400 MHz, with deuteriochloroform as solvent. Chemical shifts are given in ppm, with tetramethylsilane (TMS) as an internal standard (JNM-FX100 and GX-400 instruments). Mass spectra were recorded on a Hitachi M-80B system at 70 eV. X-ray diffraction data were obtained on a Rigaku AFC-5 single-crystal diffractometer, using Cu Kα radiation. Optical rotations were measured in $CHCl_3$ on a Horiba SEPA-200 polarimeter.

Ozonation of 1. A solution of cycloartanyl acetate (**1**, 300 mg) in chloroform (150 mL) was treated with ozonized oxygen (ca. 1.2%) at −60 °C until the solution turned blue (1 h). The reaction mixture was treated with aqueous ferrous sulfate and washed with water. The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was chromatographed on silica gel, using benzene–ethyl acetate (20:1) as the eluent, to give 7-oxocycloartanyl acetate[1] (**3**, 118 mg, 34%). Elution with benzene–ethyl acetate (10:1) afforded 3β-acetoxy-8β-hydroxycycloartan-7-one (**2**, 49 mg, 14%): mp 200–201 °C; $[\alpha]_D$ +47° (c 0.20, $CHCl_3$); IR (KBr) ν 3400 (OH), 1729 (OAc), 1682 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 4.60 (1 H, br, $w/2$ = 20 Hz, CH–OAc), 3.29 (1 H, s, OH), 2.08 (3 H, s, $OCOCH_3$), 0.65 and 0.35 (2 H, dd, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$) δ 215.2 (s, C-7), 81.8 (s, C-8), 79.3 (d, C-3); MS m/z 500.3837, $C_{32}H_{52}O_4$, calcd 500.3852.

X-ray Diffraction. Crystal data: $C_{32}H_{52}O_4$, monoclinic, space group $P2_1$, a = 17.217 (21) Å, b = 6.666 (7) Å, c = 13.537 (21) Å,

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β = 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 (17 610); ^{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 (33 452); ^{1}H NMR (7$CDCl_3$) 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.

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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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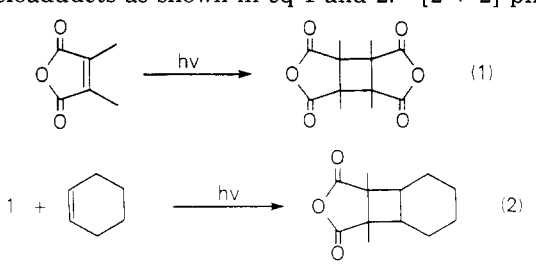
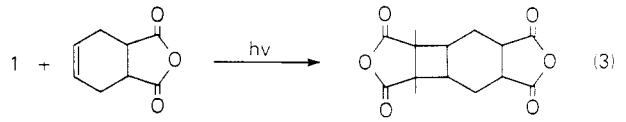
UV irradiation of dimethylmaleic anhydride (1) alone or with other unsaturated compounds yields [2 + 2] photocycloadducts as shown in eq 1 and 2. [2 + 2] photocycloadducts of 1 with olefins, alkynes, and some unsaturated heterocycles such as furan, indene, and ketene have been reported.[1] Fields and 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]





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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