Synthesis and Polymerization of α,α-Spirobicyclic β-Lactones

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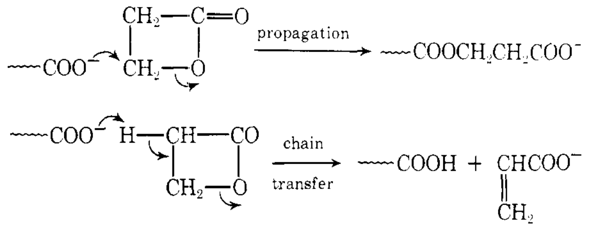
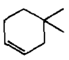
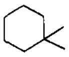
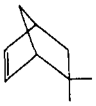
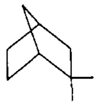
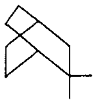
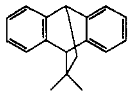
ABSTRACT: Ethyl α-hydroxymethylacrylate was converted to α-chloromethylacrylyl chloride, which readily underwent Diels–Alder reactions with butadiene, cyclopentadiene, and anthracene. The adducts **4**, **8**, and **15** were hydrolyzed to the corresponding chloro acids, which cyclized under alkaline conditions to the spiro-β-lactones **6**, **10**, and **17**. Hydrogenation of the bicycloheptene chloro acid and cyclization gave the bicycloheptane lactone **13**. When treated with a carboxylate initiator, these polymerized to high-melting polyesters. The cyclohexene and bicycloheptane monomers, perhaps because of their greater reactivity, gave higher molecular weight polymers than the bicycloheptene and anthracene compounds. The methylene protons of many of the intermediates were magnetically nonequivalent.

High molecular weight, high melting polyesters from β-lactones were sought. Although propiolactone has long been known to polymerize with nucleophiles such as sodium acetate, the polymer molecular weights are often low. The detection of olefinic bonds in most of the polymer chains[2a] suggests chain transfer as shown. This suggests that α,α-dialkyl-β-propiolactones, for which such chain transfer cannot occur, should readily give high polymer.[2b] A number of such compounds has already been prepared and polymerized to high molecular weight polymers by Fischer and his colleagues.[3,4] Second, Campbell and Foldi[5] showed that certain "spherical" bicyclospirooxetanes gave crystalline polymers with remarkably high melting points (Table I). It was of interest therefore to synthesize α,α-spiro-β-lactones and to see if they could be converted to high polymers possessing high melting points. One such compound, the cyclohexanespirolactone, had already been prepared *via* cyclohexanecarboxaldehyde and polymerized to a high-melting polymer.[4]

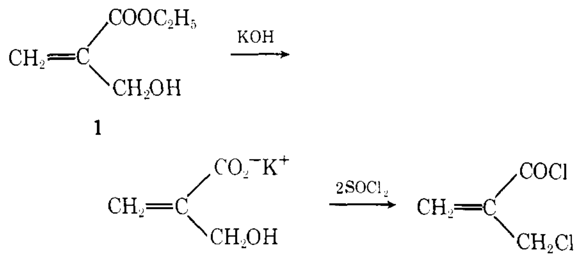


The availability[6] of ethyl α-hydroxymethylacrylate (**1**) suggested that this compound or its derivatives might undergo Diels–Alder reactions to provide useful intermediates to the β-lactones. In keeping with literature results for the Diels–Alder reaction of acrylyl chloride,[7] good results were achieved with α-chloromethylacrylyl chloride (**3**), synthesized as shown.

Table I
Melting Points of Spiro-Substituted Polymers

	Mp, °C From oxetane[a]	Mp, °C From β-lactone
	102	188
	152	260[b]
	190	243
	208	256
	290	
		305

[a] Reference 5. [b] Reference 4.



1 **2** **3**

The allylic nature of the hydroxyl group facilitated its

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(1) To whom correspondence should be addressed at the Department of Chemistry, University of Arizona, Tucson, Ariz. 85721.

(2) (a) T. Shiota, Y. Goto, and K. Hayashi, *J. Appl. Polym. Sci.*, **11**, 753 (1967); (b) Y. Yamashita, Y. Ishikawa, T. Tsuda, and S. Miura,, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **66**, 104 (1963).

(3) N. Fischer, Thesis, Paris, 1959.

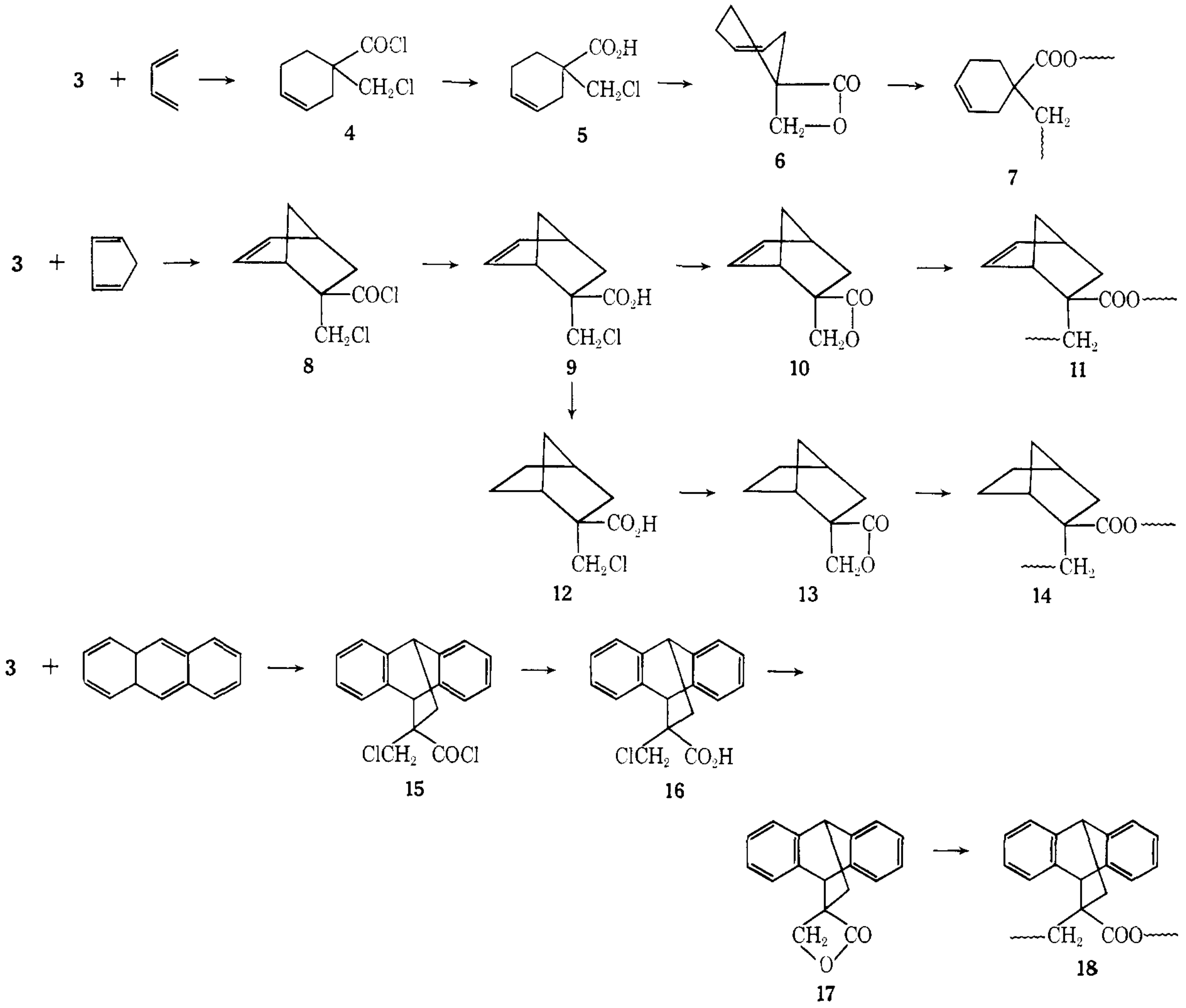
(4) (a) R. Thiebaut, N. Fischer, Y. Etienne, and J. Coste, *Ind. Plastiques Mod.* (Paris), **14** (2), 13 (1960); (b) Y. Etienne and N. Fischer, French Patent 1,231,163 (1960), to Kodak-Pathé.

(5) T. W. Campbell and V. Foldi, *J. Org. Chem.*, **26**, 4654 (1961).

(6) R. W. Rosenthal, L. H. Schwartzman, N. P. Greco, and R. Proper, *ibid.*, **28**, 2835 (1963); Koppers Monomer RDM-300.

(7) K. Alder, M. Schumacher, and O. Wolff [*Ann.*, **564**, 79 (1949)] obtained comparable yields from acrylic acid and acrylyl chloride.

Scheme I
Synthesis of β-Lactones *via* Chloro Acids



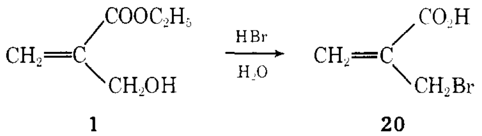
replacement by chlorine in this reaction. This chloro acid chloride added smoothly to butadiene, cyclopentadiene, and anthracene.

The chloro acid chlorides were hydrolyzed readily to the chloro acids. The bicycloheptene chloro acid **9** was hydrogenated to the corresponding bicycloheptane derivative. The four chloro acids when refluxed with alkali in water–trichloroethylene mixtures gave the corresponding β-lactones. The bicycloheptene lactone **10** formed slowly compared to α,α-dialkyl lactones, and the ethanoanthracene lactone **17** extremely so. The latter was identical with a sample prepared another way by Dr. G. Berezin of the Du Pont Co. Distillation from silver carbonate in hot dioctyl phthalate was also successful for the cyclohexene spirolactone **6**. This over-all route to β-lactones tolerates acid-sensitive or readily oxidized groups (Scheme I).

Wide melting ranges for analytically pure solid compounds, split peaks in gc traces, and split ir absorption peaks made it clear that the bicycloheptene and bicycloheptane derivatives were *endo–exo* mixtures. According to literature data[8] the carboxyl group is probably predominantly *exo*. A crystalline bicycloheptane spirolactone was isolated with large losses by crystallization, but in general the mixtures were used without separation.

Polymerization was accomplished by heating the monomers with a thermally stable phosphobetaine initiator in γ-butyrolactone solution. High polymers formed but again the reaction was slow relative to α,α-dialkyllactones. The rate of the external S_N2 attack by the growing chain carboxylate appeared to correlate with the rate of the internal S_N2 attack during ring closure. The steric interaction of the bulky spiro ring with the carboxylate ion is responsible. As with the polymers described by Campbell and Foldi, the melting points are high (Table I).

In the cyclization step, bromo acids gave lower yields of lactone than chloro acids, in keeping with literature data.[9] α-Chloromethylacrylic acid (**19**) and α-bromomethylacrylic acid (**20**), prepared as shown,



$$CH_2{=}C\begin{matrix}\diagup COOC_2H_5\\ \diagdown CH_2OH\end{matrix} \xrightarrow[H_2O]{HBr} CH_2{=}C\begin{matrix}\diagup CO_2H\\ \diagdown CH_2Br\end{matrix}$$

1 **20**

added to cyclopentadiene and anthracene to give the

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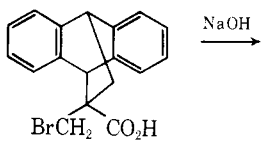
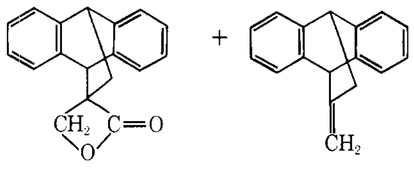
(8) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(9) H. Zaugg in "Organic Reactions," Vol. 8, R. Adams, Ed., John Wiley & Sons, New York, N. Y., 1954, p 309.

corresponding adducts **16** and **22**. The bromo acid **22** when treated with alkali gave more olefin **23** and less lactone than had been obtained from the chloro acid. Treatment of **22** with silver carbonate in acetonitrile gave almost exclusively olefin, in agreement with the idea that internal SN2 reaction gives lactone while SN1 reaction gives olefin.[9]

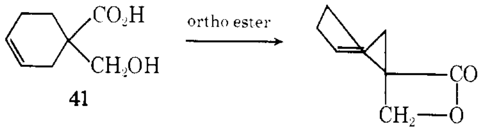


22

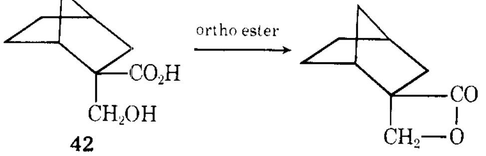


17 **23**

Adducts of ethyl α-hydroxymethylacrylate itself with dienes were of limited use in making β-lactones. Saponification gave the hydroxy acids, two of which when treated with ortho esters,[10] gave the spirolactones

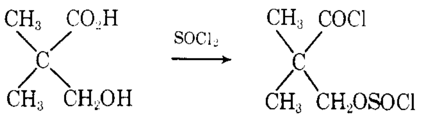


41 **6**



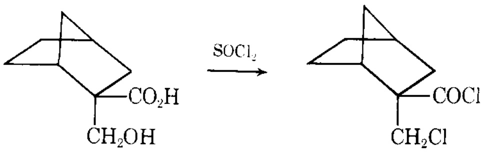
42 **13**

Also, although mild treatment of the model compound hydroxypivalic acid gave chlorosulfinyloxypivaloyl chloride **43** vigorous treatment of the bicycloheptanehydroxy acid gave the desired chloromethylbicycloheptanecarbonyl chloride **44**. Upon hydrolysis this gave the chloro acid **12**, already shown to be a useful β-lactone intermediate.



$$(CH_3)_2C(CO_2H)CH_2OH \xrightarrow{SOCl_2} (CH_3)_2C(COCl)CH_2OSOCl$$

43

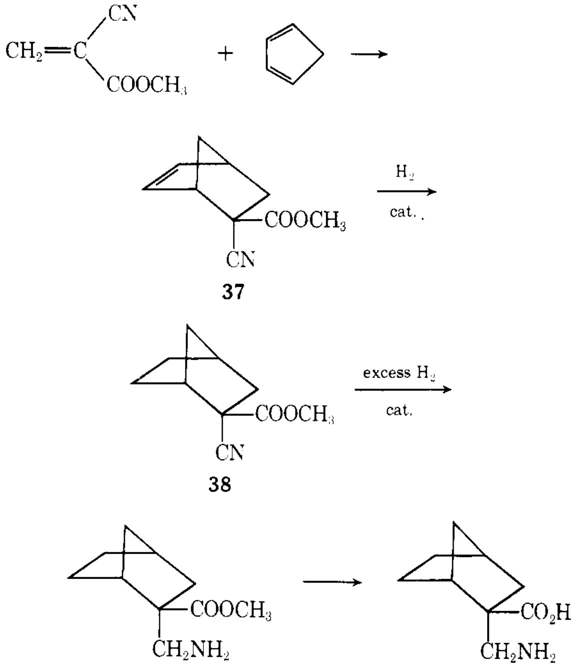


42 **44**

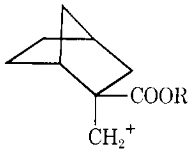
Attempts to proceed from hydroxy esters to β-lactones as follows in Scheme II succeeded only for pivalolactone.

$$\text{hydroxy ester} \xrightarrow[\text{Py}]{C_7H_7SO_2Cl} \text{tosyloxy ester} \xrightarrow[HCO_2H]{CH_3SO_3H} \text{tosyloxy acid} \xrightarrow[ClCH{=}CCl_2]{NaOH} \beta\text{-lactone}$$

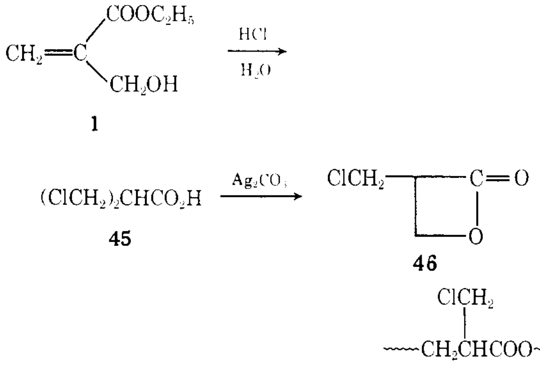
Acid-catalyzed formolysis[11] failed in the other cases because the cyclohexene and bicycloheptene derivatives gave γ-lactones, the bicycloheptane derivative underwent cleavage, and the anthracene was insoluble. Cleavage was also noted in the deamination of amino acid **40**, prepared by a route outlined by Dr. G. Berezin, and may involve a cation.



37 **38** **39** **40**



Ethyl α-hydroxymethylacrylate in the presence of excess hydrochloric acid gave β,β′-dichloroisobutyric acid **45**. This underwent cyclization upon treatment with silver carbonate in hot dioctylphthalate to give α-chloromethylpropiolactone **46**. This monomer polymerized slowly to give presumably **47**.



1 **45** **46** **47**

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(10) R. C. Blume, *Tetrahedron Lett.*, 1047 (1969).

(11) B. Loev, *Chem. Ind.* (London), 193 (1964).

SCHEME II
ATTEMPTED SYNTHESES OF β-LACTONES *via* HYDROXY ESTERS

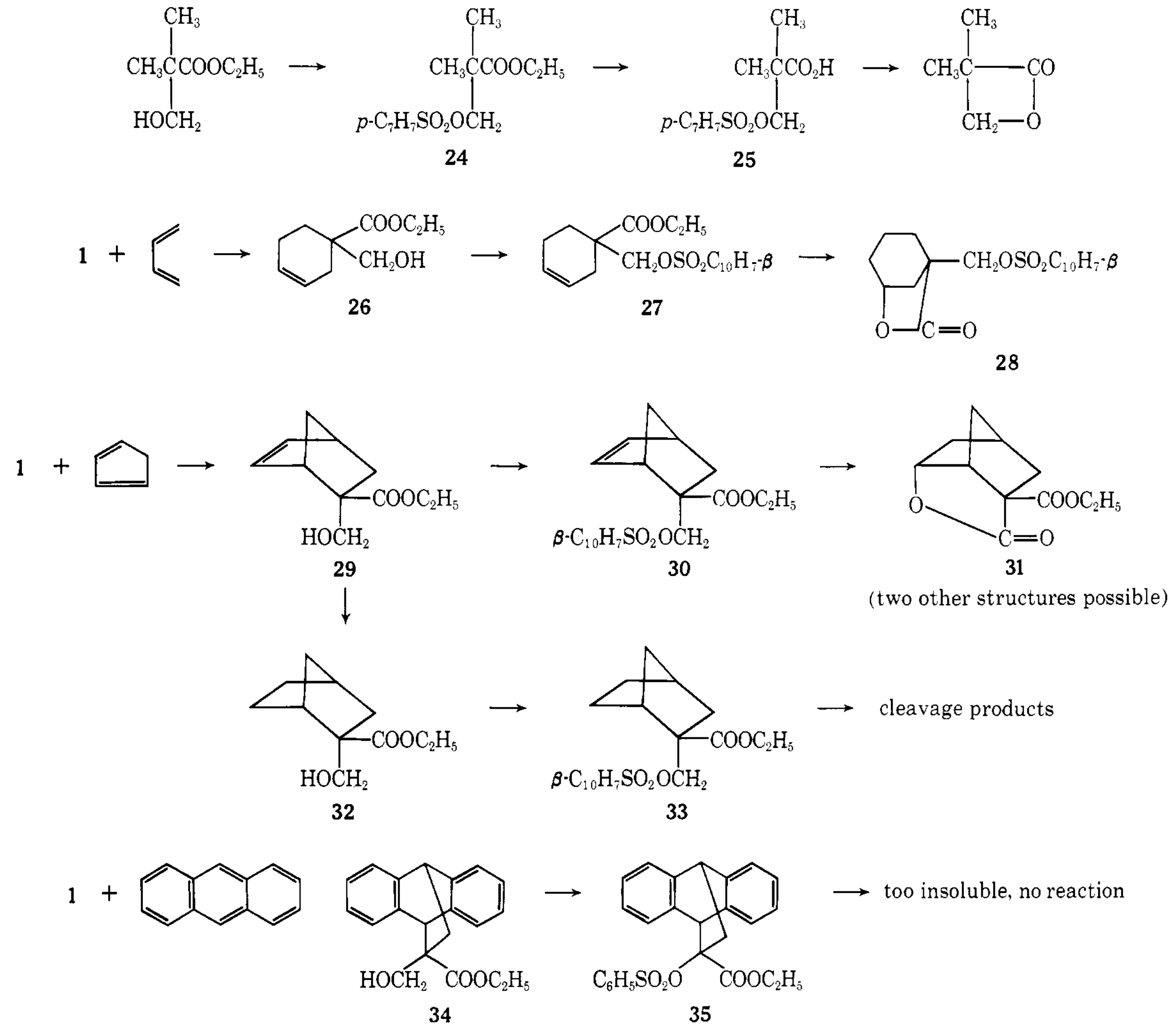

TABLE II

Compd	Solvent	Nonequivalent methylene hydrogen?
8	CCl_4	Yes (both isomers)
9	$CDCl_3$	Yes (one isomer)
12	$CDCl_3$	Yes (both isomers)
32	$CDCl_3$	Yes (one isomer)
39	$CDCl_3$	Yes (one isomer)
15	CCl_4	Yes
16	$CDCl_3$	Yes
22	THF-*d*	Yes
34	$CDCl_3$	No
34	THF-*d*	Yes
35	THF-*d*	Yes
52	THF-*d*	Tes

Nmr. The nmr spectra were routinely examined. It was of interest that the methylene hydrogens of many of the compounds were not magnetically equivalent, as described in the Experimental Section and summarized in Table II.

Conclusions

Nonequivalent methylene hydrogens were recently detected in bicycloheptane esters by Wilt and Wagner.[12]

The desired spiro-β-lactones were synthesized and polymerized. High molecular weight polymers formed from the reactive cyclohexene and bicycloheptane monomers. The polymers from the less reactive bicycloheptene and ethanoanthracene monomers possessed lower molecular weight. Probably the higher temperature required for polymerization caused side reactions, such as end capping or reverse Diels-Alder reaction, to occur. The polymers were high melting as anticipated.

Experimental Section

General. Drying agent was always magnesium sulfate. Fractional distillations were carried out in spinning band columns. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were taken on a Perkin-Elmer Model 221 Instrument. A diffraction grating instrument, no. 621, was used in attempts to resolve spectra of *endo-exo* mixtures. Standard reference absorptions were taken from Bellamy's text[13] and, for the bicycloheptenes, from the work of Henbest and coworkers.[14] Nmr spectra were taken on a Varian A60 instrument using deuteriochloroform unless otherwise specified.

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[12] J. W. Wilt and W. J. Wagner, *J. Amer. Chem. Soc.*, **90**, 6135 (1968).

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1962.

[14] H. B. Henbest, G. D. Meakins, B. Nicholls, and R. A. L. Wilson, *J. Chem. Soc.*, 997 (1957).

Infrared spectra are given in microns; abbreviations are s strong, m medium, w weak. Nmr spectra are given as τ values; abbreviations are s singlet, d doublet, t triplet, q quartet, m multiplet.

Gc determinations were programmed starting at 75°, using a heating rise of 7.9° per min and a flow rate of 60 ml of helium per min. The columns were A, 2-m 20% silicone oil No. 550 on Chromosorb; B, 3-m 20% silicone grease on firebrick; and C, 2.5-m 5% XE60 nitrile silicone on diatoport S.

Acrylic and Pivalic Acid Derivatives. α-(Chloromethyl)-acrylyl Chloride (3). Ethyl α-(hydroxymethyl)acrylate **(1)**, Koppers Monomer RDM-300, was distilled, bp 92° (19 mm) (lit.[6] bp 70–71° (1 mm)), and stored in a freezer after adding a little di-*t*-butylquinone. This ester, 400 g (3.0 mol), was added with ice cooling and stirring to a solution of 186.6 g of potassium hydroxide in 1.53 l. of water. The mixture was stirred at 27° for 17 hr. Washing with 740 ml of ether, rotary evaporation of the water layer at 40° (18 mm), and pumping overnight at 1 mm gave 497.8 g of soft white potassium α-(hydroxymethyl)acrylate **(2)**. This was added with stirring during 30 min to 1.55 l. of thionyl chloride containing 10 drops of dimethylformamide and 0.5 g of di-*t*-butylquinone in a 3-l., three-necked flask fitted with reflux condenser. An inverted funnel near the addition neck leading to the aspirator removed the large amount of hydrogen chloride formed. The mixture was stirred for 30 min more and heated in an oil bath maintained at 105° for 2.4 hr. The reflux temperature rose to 78° during 1 hr and remained there. The mixture was distilled. Thionyl chloride, 470 ml, mp 78–83°, was recovered. The residue was distilled with stirring at ~150 mm to give 422 g of liquid, bp 90–96°, leaving a white caked residue of salts. Redistillation in a platinum spinning band column gave 237.9 g (55.5%) of α-(chloromethyl)acrylyl chloride **(3)**, bp 76.6–77.2° (47 mm).

Anal. Calcd for $C_4H_4OCl_2$: C, 34.57; H, 2.90; Cl, 51.02. Found: C, 35.24, 35.23; H, 3.10, 3.00; Cl, 50.2, 50.5, 51.9.

The gc purity was 97–99%; ir CH at 3.25 (vw), 3.40 (vw), C=O at 5.70 (s), C=C at 6.10 (vw); nmr =CH at 3.21 (s, 1 H) and 3.51 (sl split s, 1 H), $-CH_2Cl$ at 5.69 (sl split s, 2 H).

α-(Chloromethyl)acrylic Acid (19). To 500 ml of water was added, with vigorous stirring, 56.7 g (0.408 mol) of α-(chloromethyl)acrylyl chloride during 8 min. The temperature rose to 41° and then subsided. After 53 min, the solution was extracted with four 100-ml portions of chloroform. The organic extracts were dried over magnesium sulfate and evaporated. Hexane, 150 ml, was added, boiled down, replaced with an equal volume, and the solution was left to crystallize in the freezer. Filtration with rubber dam and pump drying gave 40.2 g (81.8%) of α-(chloromethyl)acrylic acid **(19)**, mp 61.0–62.5° (lit. mp 60.0–61.2°,[15] 62–64° [16]).

Anal. Calcd for $C_4H_5O_2Cl$: Cl, 29.42. Found: Cl, 29.38, 29.39.

Ir analyses showed CH at 3.30 (vw), 3.40 (vw), 3.42 (w), 3.49 (vw), HOOC at 3.5–4 (jagged, m), C=O at 5.85 (s), C=C at 6.14 (s); nmr HO_2C- at τ −2.36 (s, 1 H), =CH at 3.41 (s, 1 H) and 3.32 (s, 1 H), $-CH_2Cl$ at 5.70 (s, 2 H).

β,β′-Dichloroisobutyric Acid (45). Ethyl α-(hydroxymethyl)acrylate, 290 g (2.23 mol), was stirred and heated with 3.25 l. of 36% hydrochloric acid. After 3 hr, when the temperature reached 100°, gaseous hydrogen chloride was passed in for 2 hr. The mixture was cooled, again saturated with HCl, and left at 27° for 64 hr. It was continuously extracted overnight with methylene chloride. The extract was dried with magnesium sulfate and evaporated to a dark oil which crystallized. Recrystallization from 400 ml of hexane using Darco[17] and Celite and cooling to 4° gave a first crop of β,β′-dichloroisobutyric acid **(45)**, mp 65.0–66.0° (lit.[18] viscous syrup). The filtrate was concentrated to 100 ml and again allowed to crystallize giving 60.2 g (combined yield, 39.4%), mp 63.0–66.0°, mmp with α-(chloromethyl)acrylic acid 34–60°.

Anal. Calcd for $C_4H_6O_2Cl_2$: Cl, 45.17. Found: Cl, 44.93, 45.27, 45.31.

Ir analysis showed CH at 3.40 (m), 3.45 (m), 3.50 (m), HOOC at 3.5–4 (jagged, m), C=O at 5.88 (s); nmr HOOC at τ −2.08 (s, 1H), CH_2Cl at 6.08 (d, J = 6 cps, 4 H), CH at 6.83 (p, J = 6, cps, 1 H).

α-(Chloromethyl)propiolactone (46). A mixture of 15.70 g (0.10 mol) of β,β′-dichloroisobutyric acid, 32.5 g (0.118 mol) of silver carbonate, and 80 ml of dioctyl phthalate was placed in a 250-ml, three-necked flask fitted with a Nester-Faust vacuum stirrer and a Claisen head. The mixture was heated in an oil bath at 0.5 mm. At ~80°, the silver salt formed with gas evolution. When the bath temperature reached 178°, a small amount of liquid, bp 78° (1.5 mm), came over. The distillate was taken up in 60 ml of ether, stirred overnight with calcium hydride, filtered, and distilled in a small spinning-band column to give 2.31 g (19.2%) of α-(chloromethyl)propiolactone **(46)**, bp 56.5° (0.50 mm).

Anal. Calcd for $C_4H_5ClO_2$: C, 39.85; H, 4.18; Cl, 29.4. Found: C, 40.54, 40.34; H, 4.34, 4.34; Cl, 28.3, 28.4.

Ir analysis showed CH at 3.30 (vw), 3.35 (w), 3.45 (vw), C=O at 5.45 (s); nmr $ClCH_2$, CH at ~5.68 (m, 3 H), OCH_2 at 6.13 (m, 2 H).

Poly-α-(chloromethyl)propiolactone (47). When treated with a trace of phosphobetaine catalyst at room temperature, this lactone polymerized during 11 days to a gel. Precipitation in methanol gave a low yield of white polymer **47**.

α-(Bromomethyl)acrylic Acid (20). A mixture of ethyl α-(hydroxymethyl)acrylate, 510 g (3.92 mol), and 3.43 l. of 48% hydrobromic acid was stirred vigorously for 17 hr at reflux. The flask was cooled and a lower dark layer was separated. The upper layer was extracted three times with 1.5-l. portions of methylene chloride. The combined organic layers were dried with magnesium sulfate, and the methylene chloride was removed under vacuum. The residue was diluted with 500 ml of hexane and allowed to crystallize in the refrigerator. Filtration gave 256.1 g of off-white crystals. Recrystallization from 1.4 l. of hexane with generous use of Darco and Celite gave 180.8 g (28.0%) of α-(bromomethyl)acrylic acid **(20)** as white crystals, mp 73.5–76.0° (lit.[15] mp 73.5°).

Anal. Calcd for $C_4H_5O_2Br$: C, 29.12; H, 3.05; Br, 48.44; neut equiv, 165.00. Found: C, 29.48, 29.27; H, 3.08, 3.09; Br, 48.2, 48.3; neut equiv, 166.1, 164.8.

Ir analysis showed CH at 3.40 (w), HOOC at 3.5–4 (jagged, w), C=O at 5.88 (s), C=C at 6.15 (s); nmr HO_2C at −1.92 (s, 0.5 H), =CH at 3.60 (s, 1 H) and 3.89 (s, 1H), $-CH_2Br$ at 5.82 (s, 2 H).

When ethanol and ethyl bromide were distilled as they formed, reaction appeared complete in 2.5 hr. In some preparations the bromo acid melted low and analyzed high for bromine, indicating that addition of hydrogen bromide had occurred. Such material could be purified by crystallization from hexane–ethyl acetate (2:1) at −20°. Use of larger amounts of di-*t*-butylquinone helped to give a pure product.

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[15] E. R. Buchman and D. H. Deutsch, N60nr-244-XI; N. L. Allinger and L. A. Tushans, *J. Org. Chem.*, **30**, 1945 (1966).

[16] A. F. Ferris and I. G. Marks, *J. Org. Chem.*, **19**, 1971 (1954).

[17] Trademark for Atlas Powder Co. activated carbon.

[18] A. F. Ferris, *J. Org. Chem.*, **20**, 780 (1955).

2,3-Dibromo-2-bromomethylpropionic Acid (50). To a solution of 27.1 g (0.164 mol) of α-(bromomethyl)acrylic acid in 100 ml of carbon tetrachloride was added 27.2 g (0.17 mol) of bromine over 1 hr, keeping the contents of the flask at a temperature of 5° or below. After the addition, 20 ml more of solvent was added and stirring was continued for 2.75 hr. Excess bromine and most of the carbon tetrachloride were boiled off. The resulting slurry was filtered. After washing with cold carbon tetrachloride, 40.2 g of white 2,3-dibromo-2-bromomethylpropionic acid (**50**), mp 110–111°, remained.

Anal. Calcd for $C_4H_5Br_3O_2$: C, 14.8; H, 1.55; Br, 73.8. Found: C, 14.95, 15.00; H, 1.60, 1.61; Br, 74.1, 74.3.

Ir analysis showed CH at 3.43 (s), 3.50 (w), HOOC at 3.5–4 (jagged, w), C=O at 5.80 (s).

With sodium carbonate in a stirred chloroform–water mixture, this tribromo acid gave a dibromohydroxy acid **51**, mp 135.0–138.0° after recrystallization from methanol.

Anal. Calcd for $C_4H_6O_3Br_2$: C, 18.3; H, 2.3. Found: C, 18.20, 18.21; H, 1.77, 1.84.

Ir analysis showed HO at 2.85 (w), CH at 3.40 (s), 3.48 (w), HOOC at 3.5–4 (jagged, w), C=O at 5.71 (s), 5.82 (m).

α-(Hydroxymethyl)acrylic Acid (48). In a 500-ml erlenmeyer flask was mixed a solution of 52 g (0.4 mol) of ethyl (α-hydroxymethyl)acrylate in 60 ml of absolute ethanol and 100 ml of an aqueous solution containing 16 g (0.4 mol) of NaOH. This was warmed and stirred under N_2 for 3 hr, after which time the ethanol was removed and the aqueous phase was transferred to an ion-exchange column containing one pound of moist Amberlite[19] IRH-50. The column was eluted with water and the appearance and disappearance of **48** was followed by the nitrochromic acid reagent. After removal of water, about 10 g of α-(hydroxymethyl)acrylic acid (**48**) remained as a thick oil, as found earlier.[6,18]

Anal. Calcd for $C_4H_6O_3$: C, 47.0; H, 5.9. Found: C, 47.4, 47.6; H, 6.6, 6.7.

Ir analysis showed HO at 3.1 (m, broad), CH at 3.38 (m), HOOC at 3.85 (jagged, w), C=O at 5.88 (s), C=C at 6.10 (m).

Ethyl α-(Chloromethyl)acrylate (49). Ethyl α-(hydroxymethyl)acrylate, 604 g (4.64 mol), was added during 1 hr with stirring to 1.0 kg of thionyl chloride containing 10 small drops of dimethylformamide. During 1.5 hr, the inner temperature was brought to 107° and refluxing was continued for 2 hr. The excess thionyl chloride was distilled, bp up to 90° (150 mm). Then the pressure was reduced and 550.8 g (80.0%) of ethyl α-(chloromethyl)acrylate **49**, bp 64–74° (9 mm) (lit.[15] bp 70–75° (16 mm), 45° (3.4 mm) distilled.

Anal. Calcd for $C_6H_9O_2Cl$: C, 23.86. Found: Cl, 23.3, 23.4.

The purity by gc was 97+%, and less than 1% of the starting ester was present.

Ir analysis showed CH at 3.35 (m), 3.45 (vw), C=O at 5.80 (s), C=C at 6.10 (m); nmr HC= at 3.70 (s, 1 H), 4.05 (s, 1 H), $ClCH_2$ at 5.70 (s) and OCH_2 at 5.78 (q, J = 7 cps, total 4 H), CH_3 at 8.72 (t, J = 7 cps, 3 H).

This compound was *TOXIC* and should be handled in a good hood. (Not all compounds synthesized in this research were tested, so others may also be toxic.)

Reaction of Hydroxypivalic Acid with Thionyl Chloride. To 55.4 g (0.30 mol) of hydroxypivalic acid at 5° was added with stirring 89.2 g (0.75 mol) of thionyl chloride. No reaction was visible. N,N-Dimethylformamide, 12 drops, and 100 cc more thionyl chloride were added and the mixture was stirred overnight. The thick suspension changed to an orange liquid. The excess thionyl chloride was removed under aspirator vacuum and the residue was distilled under vacuum pump pressure. As the pot temperature increased from 64 to 89°, the pressure rose to 10 mm and then decreased at which time 60.2 g of liquid distilled over. This was redistilled in a spinning band column to give 43.6 g (71.5%) of chlorosulfinyloxypivaloyl chloride (**43**), bp 48–54° (0.29–0.44 mm).

Anal. Calcd for $C_5H_8O_3SCl_2$: C, 27.41; H, 3.67; Cl, 32.36. Found: C, 27.79, 27.73; H, 3.73, 3.82; Cl, 33.06, 33.18.

Ethyl-*p*-Toluenesulfonyloxypivalate (24). Reaction of 80.0 g (0.547 mol) of ethyl hydroxypivalate with 109.8 g (0.577 mol) of *p*-toluenesulfonyl chloride in 450 g of pyridine was carried out at 4° for 18 hr. The mixture was poured into 1 l. of ice add water and stirred awhile. Concentrated hydrochloric acid, 350 ml, and 2.5 l. of hexane were added and the mixture was shaken well. The organic layer was washed with 300 ml of water, dried, and evaporated. The oily residue crystallized in the refrigerator. It was broken up, rinsed with 100 ml of hexane, and dried to give 138.4 g of white crystals. Recrystallization from 200 ml of hexane–14 ml of ethyl acetate gave 121.2 g (74.7%) of hard white crystals of the toluenesulfonyloxy ester **24**, mp 62.0–63.0°.

Anal. Calcd for $C_{14}H_{20}O_5S$: C, 55.98; H, 6.71; S, 10.67. Found: C, 56.17, 56.14, 56.15; H, 6.1, 6.8, 6.5; S, 10.2, 10.4.

The infrared spectrum was consistent with the assigned structure and resembled that of the methyl ester (see below).

***p*-Toluenesulfonyloxypivalic Acid (25).** Ethyl *p*-toluenesulfonyloxypivalate, 82.7 g (0.275 mol), was subjected to methanesulfonic acid catalyzed formolysis.[11] The solvents were evaporated under reduced pressure and the resulting white solid was stirred vigorously with 300-ml portions of water, the final filtrate being almost neutral. Drying gave 72.6 g of white solid, hot bar mp 166°. Recrystallization from 500 ml of ethyl acetate with use of $MgSO_4$ and Celite[20] gave 56.8 g (75.8%) of white crystals of *p*-toluenesulfonyloxypivalic acid (**25**), mp 165.0–166.5°.

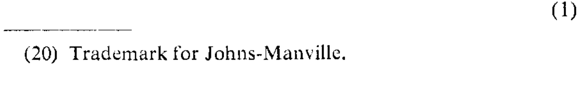
Anal. Calcd for $C_{12}H_{16}O_5S$: C, 52.92; H, 5.92; S, 11.77. Found: C, 52.96, 52.87; H, 5.81, 5.76; S, 11.3, 11.4.

Ir analysis showed CH at 2.9–3.3 μ (m, broad), CO_2H at 3.6–4.1 μ (m, broad), C=O at 5.89 μ (s), sulfonate at 7.36 μ (s), 8.43 μ (s); nmr (DMSO-*d*) ArH at τ 1.9–2.7 (wssw), CH_2 at 5.95 (s), CH_3Ar at 7.55 (s), and two CH_3 at 8.88 (s), relative intensities 4:2:3:6 (no CO_2H was visible in this solvent).

Pivalolactone, in various concentrations and solvents, reacted with sulfonic acids to form only low molecular weight polymers rather than arenesulfonyloxypivalic acids.

Cyclization of *p*-Toluenesulfonyloxypivalic Acid to Pivalolactone. *p*-Toluenesulfonyloxypivalic acid, 27.23 g (0.100 mol), was stirred at room temperature with 96.0 ml of 1.000 *N* sodium hydroxide solution, 50 ml of water, and 150 ml of methylene chloride for 15 min. The lower layer was separated and 150 ml of fresh methylene chloride was added and stirred for 30 min. Longer reaction time gave no additional product. The organic layers were dried with $MgSO_4$ and CaH_2, filtered, and distilled to give 7.61 g (79.2% yield) of pivalolactone, bp 52° (13 mm), pure by infrared spectrum.

Reaction of Pivalolactone with Methyl *p*-Toluenesulfonate. It was of incidental interest that pivalolactone could be reconverted to β-toxyloxypivalic ester by an ionic chain reaction with methyl toxylate



$$CH_3C(CH_3)(CH_2\text{–}O\text{–})C{=}O + Bu_4N^+\ {}^-O_3SC_7H_7 \rightarrow CH_3C(CH_3)(CH_2OSO_2C_7H_7)COO^-NBu_4^+ \tag{1}$$

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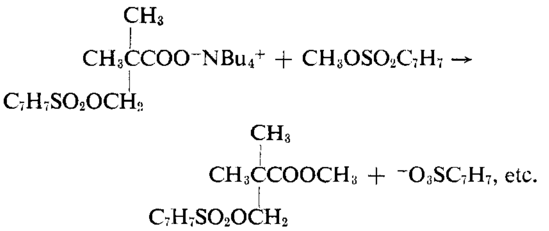
(19) Trademark for Rohm and Haas synthetic resin catalyst.

(20) Trademark for Johns-Manville.



$$\mathrm{CH_3C(CH_3)(CH_2OSO_2C_7H_7)COO^-NBu_4^+ + CH_3OSO_2C_7H_7 \rightarrow CH_3C(CH_3)(CH_2OSO_2C_7H_7)COOCH_3 + {}^-O_3SC_7H_7,\ etc.} \quad (2)$$

A mixture of 10.02 g (0.100 mol) of pivalolactone, 18.63 g (0.100 mol) of methyl *p*-toluenesulfonate, and 0.0572 g of tetrabutylammonium *p*-toluenesulfonate was held at reflux under nitrogen in an oil bath at 180° for 21.5 hr. The infrared spectrum showed that no pivalolactone was present. The material was taken up in 100 ml of ether and stirred with 100 ml of water while a little solid sodium bicarbonate was added to neutralize it. The water layer was separated, extracted with ether, and discarded. The ether layers were dried with magnesium sulfate, evaporated, and distilled to give 17.36 g, bp 115–210° (0.8–0.5 mm). Fractionation in a spinning band column gave 7.62 g of recovered methyl *p*-toluenesulfonate, bp 94–102° (0.15 mm), and 5.94 g of methyl tosyloxypivalate, bp 144–148° (0.15 mm), which crystallized on keeping. Recrystallization from a mixture of 20 ml of hexane–3 ml of ethyl acetate gave 3.95 g (13.8%) of white crystals, mp 68.5–69.0°.

Anal. Calcd for $C_{13}H_{18}O_5S$: C, 54.53; H, 6.34; S, 11.2. Found: C, 54.55, 54.58; H, 6.32, 6.39; S, 10.8, 10.8.

Ir analysis showed no OH at 2.7–3.1 μ, ester at 5.80 μ (s), sulfonate at 7.39 μ (s), 8.50 μ (s); nmr (deuteriochloroform) aromatic H at τ 1.9–2.7 (wssw), CH_2 at 5.88 (s), OCH_3 at 6.34 (s), CH_2Ar at 7.52 (s), and two CH_3 at 8.80 (s), relative intensities, 4:2:3:3:6.

Analogous reactions did not take place with benzenesulfonyl chloride (no reaction) or benzenesulfonyl fluoride (polymerization).

Cyclohexene Derivatives. 1-Chloromethyl-3-cyclohexene-1-carbonyl Chloride (4). A mixture of 69.5 g (0.50 mol) of α-(chloromethyl)acrylyl chloride, 38 g (0.70 mol) of butadiene, 0.2 g of 2,5-di-*t*-butylquinone, and 150 ml of benzene was maintained in a glass-lined bomb at 150° for 8 hr. The mixture was cooled and distilled twice in a spinning-band column to give 70.4 g (72.9%) of 1-chloromethyl-3-cyclohexene-1-carbonyl chloride (**4**), bp 53.8–54.8° (0.24 mm), 99+% pure by vpc.

Anal. Calcd for $C_8H_{10}OCl_2$: C, 49.76; H, 5.22; Cl, 36.73. Found: C, 50.01, 50.31, 50.28; H, 5.03, 5.29, 5.04; Cl, 37.6, 36.9.

Ir analysis showed CH at 3.30 (w), 3.45 (w), 3.55 (w), C=O at 5.55 (s), C=C at 6.05 (w); nmr =CH at τ 4.38 (m, 2 H), $-CH_2Cl$ at 6.28 (sl split s, 2 H), CH at 7.90 (m, 6 H).

1-Chloromethyl-3-cyclohexene-1-carboxylic Acid (5). To a solution of 50.0 g (0.259 mol) of 1-chloromethyl-3-cyclohexene-1-carbonyl chloride in 500 ml of acetone was added with stirring and ice cooling 200 ml of water containing 2 ml of 12 *N* hydrochloric acid. The solution was left at 28° for 3.5 hr. The acetone was boiled out through an air condenser. The oil was extracted with two 200-ml portions of benzene, which were dried with magnesium sulfate and evaporated. The residue was taken up in 100 ml of hot hexane and left to crystallize in the freezer. Filtration with dam and pump drying gave 38.5 g of 1-chloromethyl-3-cyclohexene-1-carboxylic acid (**5**), mp 49.0–51.0°. A second crop of 2.5 g, mp 41–49°, was obtained. Sublimation of crop 1 at 90–110° (0.10 mm) gave 31.4 g (69.5%) of pure chloro acid, mp 49.0–50.5°.

Anal. Calcd for $C_8H_{11}O_2Cl$: C, 55.01; H, 6.35; Cl, 20.30. Found: C, 55.07, 54.98; H, 6.39, 6.30; Cl, 19.6, 19.9.

Ir analysis showed CH at 3.30 (w), 3.45 (w), 3.55 (w), HOOC at 3.6–4 (jagged, w), C=O at 5.90 (s), C=C at 6.05 (w); nmr HOOC at −2.41 (s, 0.4 H), =CH at 4.32 (broad s, 2 H), $-CH_2Cl$ at 6.33 (s, 2 H), –CH at 7.52 (m, 1 H), and 7.92 (m, 5 H).

Cyclohexenespirolactone (6) *via* Reaction of Chloro Acid with Silver Carbonate in Dioctyl Phthalate. Stirring and heating a mixture of 9.20 g (0.0527 mol) of 1-chloromethyl-3-cyclohexene-1-carboxylic acid, 10.91 g (0.080 equiv) of silver carbonate, and 60 ml of dioctyl phthalate as before led to smooth distillation at 82.5° (0.3 mm) of 6.39 g of cyclohexenespirolactone. It crystallized immediately in the receiver, mp 59.5–61.5°, mmp with the material below, 59.5–61.5°. Sublimation of 50–70° (0.10 mm) gave 6.06 g (83.3%), mp 60.0–62.0°.

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30; mol wt., 138. Found: C, 69.54, 69.50; H, 7.30, 7.24; mol wt., 140.

Ir analysis showed CH at 3.30 (w), 3.41 (m), 3.49 (w), C=O at 5.43 (s), C=C at 6.05 (vw); nmr =CH at 4.27 (sl split s, 2 H), OCH_2 at 5.98 (sl split s, 2 H), HC at 7.89 (m, 6 H).

1-Carbethoxy-1-hydroxymethyl-3-cyclohexene (26). Butadiene, 108 g, was condensed with 228 g of ethyl α-(hydroxymethyl)acrylate during 12 hr in a bomb at 150°. The product was distilled once to give 283.8 g, bp 79–115° (2 mm). Fractionation in a spinning-band column with pot temperature below 120° gave 231.6 g, bp 68° (0.10 mm).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.95, 64.92; H, 8.63, 8.68.

Vpc and tlc data showed an 85:15 mixture to be present. A high-resolution ir spectrum showed two peaks, that at 1737 cm^{-1} having lower intensity than that at 1712 cm^{-1}. To obtain a purer compound, the Diels–Alder reaction was repeated with 54 g of butadiene, 101.4 g of ethyl α-(hydroxymethyl)acrylate, and 10 ml of 2,4,6-collidine to maintain basic conditions.[21] Distillation gave 22.5 g, bp 60.5–63.5° (0.12 mm), 93% pure by vpc; and 64.4 g, bp 63.5° (0.12 mm), 96% pure by vpc: ir HO at 2.85 (m), CH at 3.31 (w), 3.35 (w), 3.42 (m), 3.55 (vw), C=O at 5.80 (s), C=C at 6.05 (w), 6.15 (w).

1-(Hydroxymethyl)-3-cyclohexenecarboxylic Acid (41). The hydroxy ester **26** (310 g) was stirred overnight with 3 l. of 2 *N* sodium hydroxide solution. The basic solution was neutralized with cold 8 *N* sulfuric acid solution and was extracted twice with ether. The ether extracts were combined and washed with a saturated sodium chloride solution. Benzene was added to the ether extract and the ether was distilled. The hot benzene solution was filtered and upon cooling gave 140 g of product, mp 82–83°. The product was recrystallized from benzene to give 136 g (50%) of material, mp 84–85°. A mixture melting point experiment with the compound *via* the aldehyde showed no melting point depression.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75; O, 30.73; neut equiv, 156. Found: C, 61.73, 61.59; H, 7.90, 7.79; O, 30.54, 30.56, 30.78; neut equiv, 153, 151.

Ir analysis showed HO at 3.01 (m), CH at 3.35 (vw), 3.45 (m), HOOC at 3.5–4 (jagged, m), C=O at 5.95 (s), C=C at 6.10 (m, sh).

Cyclohexenespirolactone (6) *via* Reaction of Hydroxy Acid with Methyl Orthoisophthalate. A mixture of 15.62 g (0.100 mol) of hydroxy acid **41** and 14.08 g (0.0492 mol) of methyl orthoisophthalate[22] was heated at 50 mm in an oil bath at 115–180° during 50 min. The pressure was reduced to 13 mm, and 4.38 g (31.7%) of cyclohexenespirolactone (**6**), bp 106–113° (13 mm), distilled and crystallized immediately in the receiver, mp 61.0–62.5°.

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(21) A. F. Bickel, J. Knotnerus, E. C. Kooyman, and J. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

(22) S. J. Lapporte, *J. Org. Chem.*, **27**, 3100 (1962).

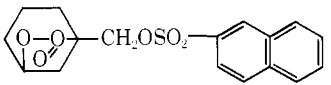
1-Carbethoxy-1-naphthalenesulfonyloxymethyl-3-cyclohexene (27). The hydroxy ester **26**, 96% pure, 33.3 g, was treated with 43.0 g of recrystallized 2-naphthalenesulfonyl chloride in 133 ml of pyridine at 0° overnight and was worked up as before. The mixture was poured into water, acidified, extracted with methylene chloride, and dried. The methylene chloride was evaporated gently and the residue pumped overnight to leave 60.4 g (89.9%) of **27** as a pale oil which did not crystallize. The analytical sample was filtered through Celite using a vacuum pump and pumped overnight over P_2O_5 and paraffin wax.

Anal. Calcd for $C_{20}H_{22}O_5S$: C, 64.16; H, 5.92; S, 8.56. Found: C, 63.72, 63.52; H, 5.85, 6.01; S, 8.05, 7.94.

Thin layer chromatography on silica gel showed only faint traces of two impurities.

Ir analysis showed CH at 3.31 (w), 3.40 (m), 3.45 (m), 3.55 (w), C=O at 5.80 (s), C=C at 6.06 (w), 6.19 (w), 6.30 (w), SO_2 at 7.40 (s), 8.55 (s); nmr (for the methyl ester) ArH at 2.41 (s, 1 H) and 3.01 (m, 6 H), =CH at 5.33 (broad s, 2 H), OCH_2 at 6.69 (s, 2 H), OCH_3 at 7.36 (s, 3 H), CH at 8.90 (m, 6 H).

Formolysis of 1-Carbethoxy-1-naphthalenesulfonyloxymethyl-3-cyclohexene (27). The ester sulfonate **27**, 112.3 g (0.300 mol), and methanesulfonic acid, 28.8 g (0.300 mol), were refluxed in 300 ml of 90% formic acid for 5 hr.[11] The solvents were evaporated under vacuum to leave a taffylike solid. This was taken up in 800 ml of methylene chloride, washed three times with 500-ml portions of water, and dried with magnesium sulfate. Evaporation of the methylene chloride left a residue which slowly crystallized. Recrystallization from 2 l. of ethyl acetate–hexane (1:1) with hot filtration through Celite led to 41.4 g of white crystals. Recrystallization from 250 ml of ethyl acetate–375 ml of hexane gave 29.4 g (28.3%) of 1,3-lactone **28**, mp 132.5–134.0°.



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Anal. Calcd for $C_{18}H_{18}O_5S$: C, 62.41; H, 5.24; S, 9.26. Found: C, 62.40, 62.28; H, 5.05, 5.08; S, 9.77, 9.75.

The ir spectrum of this compound was that of an ester, not an acid. It was insoluble in saturated sodium bicarbonate solution. Under high resolution, the carbonyl group absorption lay at 1772 cm^{-1} in carbon tetrachloride or at 1780 cm^{-1} in chloroform. This corresponds to a five-membered lactone:[23] nmr ArH at 2.31 (s, 1 H) and 2.98 (m, 6 H), OCH at 6.20 (m, 1 H), OCH_2 at 6.82 (sl split s, 2 H), CH at 9.30 (m, 8 H). The aliphatic C–H nmr pattern was quite unsymmetrical, also favoring 1,3 structure.

Reaction of Hydroxy Acid 41 with Silver Carbonate and 2-Naphthalenesulfonyl Chloride. A mixture of 15.62 g (0.100 mol) of hydroxy acid **41**, 22.67 g (0.100 mol) of 2-naphthalenesulfonyl chloride, and 27.58 g (0.200 equiv) of silver carbonate in 200 ml of anhydrous acetonitrile was stirred magnetically for 5.3 hr at 27°. The soft yellow insoluble silver carbonate quickly gave way to a thin white slurry. The mixture was filtered with Celite and rinsed with acetonitrile. The solid, about 18 g, appeared to be silver naphthalenesulfonate from its ir spectrum. The filtrate was evaporated and the semisolid residue was taken up in 400 ml of water and 200 ml of benzene–hexane (1:1). A little insoluble material was filtered. The aqueous layer (pH 4) was discarded. The organic layer was dried and evaporated to give 8.5 g of semicrystalline solid. Recrystallization from 20 ml of hexane–2 ml of ethyl acetate at −20° gave 5.02 g, mp 51–57°. Another crystallization gave 1.42 g (10.3%) of cyclohexenespirolactone (**6**), mp 57.0–61.5°, mmp 61.0–63.0°. The ir spectrum agreed with that of the authentic sample.

Carboxysulfonate 36 *via* Reaction of Silver 1-Hydroxymethyl-3-cyclohexene-1-carboxylate with 2-Naphthalenesulfonyl Chloride. A mixture of 15.62 g (0.100 mol) of hydroxy acid **41** and 15.0 g (0.109 equiv) of silver carbonate in 150 ml of water was taken to the boiling point with stirring and filtered while hot. The filtrate was evaporated and dried at 50° (0.5 mm) to leave the silver carboxylate. This salt was stirred vigorously for 16 hr at 27° with 12.00 g of silver carbonate, 150 ml of acetonitrile, and 22.7 g (0.100 mol) of 2-naphthalenesulfonyl chloride. The mixture was filtered, rinsed with acetonitrile, and evaporated. The residue was taken up in 500 ml of water and 1.5 l. of hexane–ether (1:1), shaken, and filtered. The strongly acidic aqueous layer was discarded. The organic layer was washed twice with 500-ml portions of water, the last wash being neutral, dried, and evaporated to give 12.1 g of semicrystalline solid. Recrystallization from 60 ml of hexane–ethyl acetate (1:1) at −20° gave 3.84 g (11.1%) of 1-(2-naphthalenesulfonyloxymethyl-3-cyclohexene-1-carboxylic acid (**36**), mp 147.0–148.5°.

Anal. Calcd for $C_{18}H_{18}O_5S$: C, 62.42; H, 5.24; S, 9.25. Found: C, 62.54, 62.33; H, 5.38, 5.20; S, 8.52, 8.74, 8.76.

Ir analysis showed CH at 3.35 (vw), 3.40 (w), 3.45 (w), 3.52 (vw), HOOC at 3.5–4 (jagged, vw), C=O at 5.85 (s,) C=C at 6.15 (w) and 6.29 (w), SO_2 at 7.35 (s) and 8.50 (s).

Polycyclohexenespirolactone (7). To a solution of 0.70 g of cyclohexenespirolactone in 5 ml of purified tetrahydrofuran with stirring and refluxing was added 2 drops of a 10% solution of tetraethylammonium pivalate in acetonitrile. After 30 min, an additional 3 drops was added. After a reaction period of 3 hr the polymer had separated as a thick white slush. This was cooled, precipitated into methanol in a blender, filtered, and dried at 80°. The yield of white polymer, η_{inh} 1.06 in trifluoroacetic acid, was quantitative. (This viscosity determination was done at 0.1% concentration; other values recorded were at 0.5%.)

Bicycloheptene Derivatives. 2-Chloromethyl-5-bicycloheptene-2-carbonyl Chloride (8). To a solution of 69.5 g (0.50 mol) of α-chloromethylacrylyl chloride and 0.1 g of di-*t*-butylquinone in 150 ml of dry benzene was added with stirring most of 56.5 g (0.86 mol) of freshly distilled cyclopentadiene. The mixture became warm enough to boil momentarily. It was cooled and the remainder of the cyclopentadiene was added. After 4 days, the mixture was distilled twice in a spinning-band column to give 62.8 g (71.0%) of 2-chloromethyl-5-bicycloheptene-2-carbonyl chloride **8**, bp 63.8–58.9° (0.34–0.25 mm).

Anal. Calcd for $C_9H_{10}OCl_2$: C, 52.71; H, 4.92; Cl, 34.58. Found: C, 53.16, 53.08; H, 4.93, 4.90; Cl, 34.6, 34.8.

For this bicycloheptene and for others described below, reverse Diels–Alder reaction occurred during attempted gc determinations: ir CH at 3.29 (w), 3.39 (m), 3.50 (w), C=O 5.56 (s), bicycloheptene at 13.80 (m, sh), 13.95 (s). The nmr spectrum (CCl_4) was consistent with the chemical structure and of a roughly equal *endo–exo* isomer mixture. The most striking feature was the occurrence of both chloromethyl groups as AB quartets (isomer I at 6.28 and 6.43, J = 11 cps; isomer II at 5.84 and 6.31, J = 11 cps; ratio I:II ~1.4). Bridgeheads occurred as broad single peaks at 6.67 and 6.99, and the 3 positions at 8.11 and 8.41 as irregular triplets. *anti-* and *syn-*7 protons lay as multiplets in the region of 7.5 and 8.8.

A second experiment in which ice cooling was used to maintain the reaction temperature at 25–30° gave a 95.7% yield of chloro acid chloride **8**, bp 72.5–77.5° (0.75 mm).

2-Chloromethyl-5-bicycloheptene-2-carboxylic Acid (9). Hydrolysis of 50.0 g of the acyl chloride **8** exactly as for the

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[23] H. K. Hall, Jr., and R. Zbinden, *J. Amer. Chem. Soc.*, **80**, 6428 (1958).

cyclohexene derivative gave 40.6 g of 2-chloromethyl-5-bicycloheptene-2-carboxylic acid (**9**), mp 70.0–76.0°. Sublimation at 90–110° (0.1 mm) gave 38.4 g (84.3%), mp 68.0–70.5°, mmp 68.0–72.5° with the compound prepared below by direct addition of α-(chloromethyl)acrylic acid.

Anal. Calcd for $C_9H_{11}O_2Cl$: C, 57.91; H, 5.94; Cl, 19.00. Found: C, 58.02, 57.91; H, 5.86, 5.85; Cl, 18.8, 19.1, 19.3.

Ir analysis showed CH at 3.25 (w), 3.35 (w), 3.42 (m), 3.50 (w), HOOC at 3.5–4 (jagged, w), C=O at 5.85 (s), bicycloheptene at 13.83 (s) and 14.05 (s).

The nmr spectrum was similar to that of the corresponding acid chloride but with a carboxyl group evident. The isomers appeared present in roughly equal amounts as judged from chloromethyl intensities. Now $ClCH_2$ of isomer I appeared at 5.9 and 6.31, J = 10 cps, but $ClCH_2$ of isomer II appeared as a singlet at 6.43, perhaps owing to the change in solvent to $CDCl_3$.

The second experiment, where the original Diels–Alder reaction had been cooled, gave chloro acid which did not crystallize well. Short-path distillation gave chloro acid **9**, bp 120–122° (0.7 mm), which crystallized readily.

Chloro Acid 9 ***via*** **Reaction of α-(Chloromethyl)acrylic Acid with Cyclopentadiene.** A solution of 24.5 g (0.203 mol) of α-(chloromethyl)acrylic acid and 15.0 g (0.227 mol) of freshly distilled cyclopentadiene in 100 ml of anhydrous ether was made up without visible heat effect. After 72 hr at 27°, a little flocculent material was filtered and the filtrate was evaporated and set aside at −20°, whereupon it crystallized almost completely. Filtration with rubber and recrystallization of the crystalline product from 25 ml of hexane at −20° gave, after drying, 18.6 g of white solid, mp 68.0–75.0°. Sublimation at 90–110° (0.1 mm) gave 16.0 g (42.2%), mp 69.0–74.0°.

Anal. Found: C, 57.89, 57.80; H, 5.96, 5.85; Cl, 18.8, 19.0, 19.2.

Bicycloheptenespirolactone (10). A mixture of 75.8 g (0.406 mol) of 2-chloromethyl-5-bicycloheptene-2-carboxylic acid, 180 ml (0.360 mol) of 2.00 N sodium hydroxide solution, 1.1 l. of trichloroethylene, and 0.8 l. of water was held at reflux with vigorous stirring for 18.5 hr.[24] The mixture was cooled and the layers were separated. The water layer was extracted with 100 ml of trichloroethylene. It had pH 6 and gave only a faint turbidity when strongly acidified. The trichloroethylene layers were dried with magnesium sulfate and evaporated. The residue was crystallized from 50 ml of hexane in the freezer, filtered with a rubber dam, and pumped dry to give 18.6 g of white solid, mp 46.5–57.0°. Two sublimations at 60–80° (0.08 mm) gave 16.0 g (26.2%) of colorless lactone **10**, mp 53.0–57.0°, mmp 53.0–57.0° with material from bromo acid.

Treatment of the filtrate with calcium hydride and distillation in a small spinning-band column gave 6.6 g of waxy lactones, bp 63–76° (0.50 mm), and, oddly, 4.71 g of recovered chloro acid, bp 109–115° (0.55 mm). Recrystallization of the chloro acid from 20 ml of hexane at 4° gave 2.93 g, mp 76.0–84.0°.

Further crystallization led to crystalline bicycloheptenespirolactone (**10**), mp 58.0–59.5°.

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.02, 71.92; H, 6.73, 6.66.

Ir analysis showed CH at 3.35 (w), C=O at 5.45 (s), bicycloheptene at 14.05 (m) and 14.20 (m).

Polybicycloheptenespirolactone (11). A polymerization experiment using 6.12 g of lactone **10** and 0.1 ml of catalyst solution (monomer/catalyst = 4×10^4) (see below) carried out for 48 hr at 154° gave a clear glass. The ampoule was under slight internal pressure when broken at room temperature. The polymer oiled out when precipitation experiments were attempted from various solvents, so it was recovered and dried overnight in a vacuum oven at 80°. Polymer **11** weighed 2.60 g and had an inherent viscosity of 0.17 in tetrahydrofuran. By DTA it melted at 243° and decomposed exothermically with maximum at 339°. A TGA determination showed weight loss beginning at 194°, an inflection at 327° (28% weight loss), and final levelling off at 511° (85% weight loss).

2-Bromomethyl-5-bicycloheptene-2-carboxylic Acid (21). In 20 ml of ethyl ether was dissolved 7.5 g (0.045 mol) of α-(bromomethyl)acrylic acid, and to this was added with swirling 5.0 g (0.076 mol) of freshly distilled cyclopentadiene. The flask was stored in the freezer overnight. Evaporation of the ether and excess cyclopentadiene yielded 11.1 g of crystals, which after recrystallization from hexane–heptane gave 6.15 g (59.0%) of **21**, mp 87–88.5°.

Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.7; H, 4.8. Found: C, 46.8, 46.6; H, 4.58, 4.58.

Ir analysis showed CH at 3.29 (w), 3.45 (m), 3.55 (w), HOOC at 3.5–4 (jagged, w), C=O at 5.80 (s), bicycloheptene at 13.65 (sh, m) and 13.85 (s).

2-Hydroxymethyl-2-carboethoxy-5-bicycloheptene (29). A mixture of 132 g of dicyclopentadiene, 260 g of ethyl α-(hydroxymethyl)acrylate, and 2 g of hydroquinone was heated in a bomb for 10 hr at 180°. The mixture was cooled and distilled at 70–93° (0.3 mm) to give 315 g of liquid. Redistillation in a spinning-band column gave 262.2 g (68.5%) of hydroxy ester **29**, bp 78.5–83.5° (0.32–0.21 mm).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.67, 67.47; H, 8.05, 8.02.

Ir analysis showed OH at 2.90 (m), CH at 3.29 (w), 3.39 (m), 3.50 (w), C=O at 5.80 (s), bicycloheptene at 13.90 (sh, m) and 14.10 (m).

High-resolution ir spectroscopy using $CHCl_3$ showed a shoulder on the C=O peaks but could not resolve them. Repetition of this experiment in the presence of 2,4,6-collidine[21] gave a 66.2% yield of the same adduct. In one preparation some polymer formed, so it may be advisable to use more dicyclopentadiene and inhibitor.

2-Naphthalenesulfonyloxymethyl-2-carbethoxy-5-bicycloheptene (30). The sulfonylation was carried out as usual, using 32.4 g (0.165 mol) of hydroxy ester **29**, 41.6 g (0.184 mol) of recrystallized 2-naphthalenesulfonyl chloride, and 120 ml of pyridine at 4° overnight. The mixture was poured into 1 l. of water, stirred for 30 min, acidified with 110 ml of concentrated hydrochloric acid, and extracted twice with 200-ml portions of methylene chloride. The organic layer was washed twice with 400-ml portions of water, dried with $MgSO_4$, evaporated gently, and pumped overnight at 0.5 mm to give 58.3 g (91.5%) of **30** as a pale oil. The last solvent was removed by filtration through Celite using full pump vacuum and pumping overnight over paraffin wax and P_2O_5.

Anal. Calcd for $C_{21}H_{22}O_5S$: C, 65.27; H, 5.74; S, 8.29. Found: C, 64.98, 64.89; H, 5.75, 5.78; S, 7.79, 7.71.

Ir analysis showed CH at 3.29 (w), 3.39 (m), 3.50 (w), C=O at 5.80 (s), C=C at 6.15 (w) and 6.30 (w), SO_2 at 7.40 (s) and 8.55 (s), bicycloheptene at 13.83 (broad, m) and 14.05 (sh, m).

γ-Lactone Sulfonate 31. Formolysis[11] of 178.5 g (0.462 mol) of ester sulfonate **30** was carried out with 44.4 g (0.462 mol) of methanesulfonic acid and 460 ml of 90% formic acid for 5 hr at reflux. The solvents were evaporated to leave a viscous liquid. This was dissolved in 1200 ml of ether and washed rapidly with 500 ml of water. A heavy precipitate which formed in the organic layer was filtered, rinsed with 200 ml of ether, and pumped dry to give 20.1 g of white solid. The ether extracts were washed several times with 500-ml portions of water until the water layer was only faintly acidic. The ether layer was dried with

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(24) C. E. Lorenz, U. S. Patent 3,291,810 (1966).

TABLE III
POLYMERIZATION OF BICYCLOHEPTANESPEROLACTONE

Lactone sample	Catalyst soln, ml	Reaction time, hr	Temp, °C	Polymer yield, g (%)	Mp by DTA, °C	η_{inh} (TFA)
Cryst	0.3	8	100	4.36 (99.1)	211	0.54
					225	
Cryst	0.1	40	100	6.93 (92.4)	265	1.99
		4	154			
Mixed	0.4	25	100	32 (100)	233	0.69
		4	154			

magnesium sulfate, filtered through Darco and Celite, and evaporated to a dark syrup. The insoluble solid was recrystallized from 220 ml of ethyl acetate with use of Darco and Celite to give 13.7 g (8.3%) of white crystals of γ-lactone sulfonate **31**, mp 156.0–157.0°.

Anal. Calcd for $C_{19}H_{18}O_5S$: C, 63.67; H, 5.06; S, 8.95. Found: C, 63.76, 63.54; H, 4.97, 4.93; S, 8.69, 8.64.

The ir spectrum under high resolution showed a single C═O absorption at 1780 cm^{-1}, characteristic of a five-membered lactone.[23,25] No carboxyl group could be seen. The compound was insoluble in saturated sodium bicarbonate solution or in aqueous ammonium hydroxide.

Nmr analysis showed ArH at 2.57 (sl split s, 1 H) and 3.68 (m, 6 H), OCH at 6.40 (broad t, 1 H), OCH_2 at 5.64 and 5.83, J_{gem} = 11 cps, bridgeheads at 7.98 (broad d, 1 H) and 8.76 (broad s, 1 H), CH at 9.61 (broad s, 6 H). The remainder of the product was also neutral and was obtained as a viscous material which did not crystallize.

2-Hydroxymethyl-5-bicycloheptene-2-carboxylic Acid. To 375 ml of 2 *N* sodium hydroxide in 1:1 aqueous methanol was added 100.0 g (0.510 mol) of 2-carbethoxy-2-hydroxymethyl-5-bicycloheptene (**29**) with magnetic stirring. After 80 hr at room temperature, masses of crystals had formed in the flask. Filtration with rubber dam gave 79 g of wet crystals (crop 1). The filtrate deposited crystals when cooled in ice. Filtration gave 38 g of wet crystals (crop 2). Crop 1 was taken up in 125 ml of water and 125 ml of ether and acidified with 30 ml of 12 *N* hydrochloric acid. The water layer was separated and extracted with 125 ml of ether. The combined ether layers were dried with magnesium sulfate, filtered, and evaporated to give 48.8 g of crude hydroxy acid, mp 133–139°. Recrystallization from 375 ml of hexane-ethyl acetate (1:1) gave 40.1 g of white crystals of hydroxy acid, mp 135.0–138.0°. Similar work-up of crop 2 gave 12.0 g (14.0%) of hydroxy acid, mp 134.0–138.0°, mmp 135.0–139.0°, combined yield 60.7%. A sample of crop 1 of hydroxy acid was sublimed at 90–115° (0.3 mm), mp 141.0–144.0°.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.65, 64.50; H, 7.21, 7.14.

Ir analysis showed HO at 2.96 (m), CH at 3.28 (w), 3.42 (m), 3.50 (w), HOOC at 3.5–4 (jagged, w), C═O at 5.88 (s), bicycloheptene at 14.10 (m).

Bicycloheptane Derivatives. 2-Chloromethylbicycloheptane-2-carboxylic Acid (12) *via* Hydrogenation. The unsaturated chloro acid **9**, 14.0 g (0.075 mol), in 140 ml of tetrahydrofuran, absorbed 65% of the theoretical amount when hydrogenated at 25° over 1.5 g of 5% platinum on charcoal. The catalyst was filtered. Evaporation and recrystallization from 100 ml of hexane, using Darco and Celite, gave 12.3 g of white crystals, mp 107.0–116.0°. Sublimation at 90–110° (0.1 mm) gave 11.6 g (81.7%) of **12**, mp 96.5–118.0°, mmp 95.0–105.0°.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.94; Cl, 18.8. Found: C, 57.45, 57.31; H, 6.84, 6.84; Cl, 18.8, 18.8.

Ir analysis showed CH at 3.25 (w), 3.40 (m), 3.45 (m), and 3.51 (w), HOOC at 3.7–4 (jagged, w), C═O at 5.90 (s); nmr HO_2C at −2.40 (s, 1 H), $ClCH_2$ of isomer I at 6.18 and 6.42 (J = 11 cps) and $ClCH_2$ of isomer II at 6.00 and 6.69 (J = 11 cps), ratio 1:2∼5, total 2 H, CH at τ 7.28 (m, 1 H), 7.71 (m, 2 H) and 8.57 (m, 7 H).

Bicycloheptanespirolactone (13) *via* Chloro Acid with Alkali. A mixture of 147.0 g (0.779 mol) of chloro acid **12**, 422 ml (0.844 mol) of 2.00 *N* sodium hydroxide, 2.2 l. of trichloroethylene, and 1.5 l. of water was stirred vigorously at reflux for 16 hr and cooled.[24] The aqueous layer was extracted with 150 ml of trichloroethylene. Acidification gave only a faint turbidity. The organic layers were dried and evaporated at 40° on a rotary evaporator. Distillation of the residue from calcium hydride gave 66.1 g (55.8%) of waxy semisolid bicycloheptanespirolactone (**13**), bp 68–52° (0.7–0.18 mm). Two crystallizations from 70-ml portions of ether gave 12.4 g of highly crystalline lactone **13**, mp 67.0–69.0°. Further crystallization raised the melting point to 71.0–72.5°.

Anal. Calcd for $C_9H_{10}O_2$: C, 71.02; H, 7.95. Found: C, 71.15, 70.88, 70.95; H, 7.88, 7.76, 7.63.

Ir analysis showed CH at 3.39 (m) and 3.49 (w), C═O at 5.49 (s).

As before, the lactone mixture recovered by distilling the filtrates could not be separated by tlc and showed only a single sharp β-lactone ir absorption under high resolution. On gc column C two equal peaks at nearly equal retention times were detected.

Anal. Found: C, 71.04, 70.70, 70.78; H, 7.91, 7.84, 7.92.

Polybicycloheptanespirolactone (14). Bicycloheptanespirolactone (**13**) was polymerized in sealed ampoules under nitrogen. The polymer was broken up using liquid nitrogen. The results are given in Table III.

Polymerization was extensive even in 1 hr at 100°, so this lactone is fairly reactive. DTA showed a small endothermic peak at 243° and a large one at 256° (melting); endothermic decomposition peaked at 423°. TGA showed weight loss beginning at 350°.

2-Carbethoxy-2-hydroxymethylbicycloheptane (32). The unsaturated hydroxy ester **29**, 100 g (0.51 mol), in 175 ml of ethanol was hydrogenated over 1 g of palladium on charcoal at room temperature with absorption of 72% of the calculated amount of hydrogen. The mixture was filtered with Celite, which was rinsed with ethanol. The filtrate was evaporated on a rotary evaporator and distilled in a spinning band column. 2-Carbethoxy-2-hydroxymethylbicycloheptane (**32**), bp 71–72° (0.07 mm), weighed 80.3 g (79.4%).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.55, 66.29; H, 9.00, 9.09.

Ir analysis showed OH at 2.85 (w), CH at 3.38 (s), 3.48 (w), C═O at 5.75 (s); nmr ethyl ester was present, as was HO at 6.82 (1 H), OCH_2 lay as a singlet at 6.28 and as an AB quartet at 5.69 and 5.91, J = 7 cps, ratio ∼0.8, total 2 H.

Under high resolution, using CCl_4 as solvent, two C═O absorptions, that at 1735 cm^{-1} being about twice as intense

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(25) S. Beckmann and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).

as that at 1700 cm^{-1}, were seen while gc using column A showed a 32× peak and a 4× peak.

2-Hydroxymethylbicycloheptane-2-carboxylic Acid (42). To 75 ml of 2 *N* sodium hydroxide in methanol–water (1:1) was added at room temperature with magnetic stirring 17.8 g (0.090 mol) of hydroxy ester **32**. After 4 days, a white solid had formed in the flask. Crop 1, 12.4 g, was isolated by filtration at room temperature. It was taken up in 100 ml of water and 100 ml of ether and acidified with 15 ml of 12 *N* hydrochloric acid. The aqueous layer was separated and extracted with 100 ml of ether. The ether layers were dried with magnesium sulfate and evaporated to give 10.6 g of white solid, mp 100–102°. Recrystallization from 100 ml of heptane–ethyl acetate (8:1) gave 10.6 g (69.2%) of hydroxy acid **42**, mp 103.0–107.0° (contains bubbles clearing at 114°). Crop 2, 3.6 g, isolated by chilling and filtering, was worked up similarly to give 1.2 g, mp 97–100°. Recrystallized from 100 ml of heptane–ethyl acetate (30:1), it weighed 0.68 g (4.4%, combined yield 73.6%) and melted at 100.0–107.0° with bubbled clearing at 116°. A mixture with the bicycloheptenehydroxy acid melted at 126–133°.

A sample of crop 1 of hydroxy acid **42** was sublimed at 93–115° (0.3 mm), mp 98.0–102.0°.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.99, 63.77; H, 8.12, 8.01.

Ir analysis showed OH at 2.95 (w), CH at 3.42 (s), 3.50 (w), HOOC at 3.5–4 (jagged, w), C=O at 5.90 (s).

Bicycloheptanespirolactone (13) *via* Hydroxy Acid. Reaction of 53.2 g (0.313 mol) of hydroxy acid **42** with 50.5 g (0.476 mol) of methyl orthoformate[10] in 150 ml of benzene with slow distillation in a spinning band column led to distillation of crude lactone at 128–133° (13 mm). A higher boiling viscous contaminant was present. Redistillation in a small spinning band column gave 12.20 g (25.7%) of semisolid lactone **13**, bp 51.8–53.7° (0.075 mm). Recrystallizations from hexane in the freezer failed to give a crystalline lactone. Only a single sharp β-lactone peak could be seen in the infrared spectrum, but the compound was undoubtedly an *endo–exo* mixture; however, vpc did not separate it into two clean peaks.

2-Chloromethylbicycloheptane-2-carbonyl Chloride (44). Hydroxy acid **42**, 248 g (1.46 mol), was added with stirring during 25 min to a mixture of 1430 g (12.1 mol) of thionyl chloride and 1.0 ml of dimethylformamide. Excess thionyl chloride was distilled at atmospheric pressure and then the residue was distilled, bp 130–148° (13 mm), bath temperature 145–180°, 307 g. Careful refractionation in a spinning band column gave a main fraction of 2-chloromethylbicycloheptane-2-carbonyl chloride (**44**), bp 77.7–92.5° (1.0–2.9 mm), 212.7 g (70.3%). The slight decomposition of traces of chlorosulfite occurred in the boiler during the distillation.

Anal. Calcd for $C_9H_{12}OCl_2$: C, 52.19; H, 5.84; Cl, 34.23. Found: C, 53.12, 53.06; H, 6.05, 5.76; Cl, 33.4, 33.5.

Ir analysis showed CH at 3.39 (m) and 3.49 (w), C=O at 5.55 (s).

2-Chloromethylbicycloheptane-2-carboxylic Acid 42 *via* Acid Chloride. The acid chloride **44**, 31.2 g (0.151 mol), was hydrolyzed exactly as before to give 24.7 g (86.6%) of sublimed 2-chloromethylbicycloheptane-2-carboxylic acid (**12**), mp 92.0–111.0°.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.94; Cl, 18.8. Found: C, 57.46, 57.37; H, 6.99, 6.80; Cl, 19.0, 19.3, 19.6.

2-Carbethoxy-2-naphthalenesulfonyloxymethylbicycloheptane (33). The ester sulfonate **33** was prepared as usual by adding 58.7 g (0.259 mol) of recrystallized 2-naphthalenesulfonyl chloride with stirring at 0–5° to 49.3 g (0.249 mol) of hydroxy ester **32** in 200 ml of pyridine. After 4 days at 4°, the mixture was poured into 1 l. of water, stirred for 2 hr, and neutralized with 225 ml of concentrated hydrochloric acid with cooling. The mixture was extracted with 200 ml and with 150 ml of methylene chloride. The extracts were washed with 500-ml portions of water (once) containing a few drops of hydrochloric acid, saturated sodium bicarbonate solution (twice), and water (once) containing potassium chloride, dried over $MgSO_4$, and evaporated to give 79.4 g (82.1%) of **33** as a pale oil. This was filtered through Celite using full pump vacuum and pumped further overnight over paraffin wax and P_2O_5.

Anal. Calcd for $C_{21}H_{24}O_5S$: C, 64.93; H, 6.23; S, 8.25. Found: C, 64.72, 64.34; H, 5.98, 6.18; S, 8.45, 7.81, 8.10.

The ir spectrum supported the assigned structure. Thin layer chromatography showed the material to be quite pure, only one faint impurity spot being detectable. Formolysis[11] gave only a gross mixture of low-boiling products containing ester and carbonyl groups.

2-Cyano-2-carbomethoxy-5-bicycloheptene (37). Methyl α-cyanoacrylate (Eastman 910 adhesive, used as received), 389.0 g (3.50 mol) was added with cooling and stirring to 231.6 g (3.50 mol) of freshly distilled cyclopentadiene. Temperature was kept below 20°, and the addition required 2.5 hr. Near the end, the addition caused no further heat evolution, so 22.2 g of cyclopentadiene was added and the solution was left at room temperature for 3 days. The thick solution was poured into excess hexane in a large blender with vigorous stirring and the precipitated polymer was filtered, rinsed with hexane, and discarded. Hexane was evaporated and the residue was vacuum distilled with magnetic stirring. A forerun was discarded and the pressure slowly dropped to 0.18 mm. With oil bath temperature at 116°, the product **37**, 348.3 g (56.2%), distilled smoothly at 61° (0.18 mm). At higher temperatures or in a spinning-band column, reversal of the Diels–Alder reaction and polymer formation in the head occurred.

Anal. Calcd for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.72, 67.62; H, 6.68, 6.23; N, 8.17, 8.08.

Ir analysis showed CH at 3.29 (w), 3.40 (w), and 3.50 (w), CN at 4.50 (m), ester at 5.75 (s), bicycloheptene at 13.77 (m, sh), 14.08 (m); nmr, approximately equal amounts of *endo* and *exo* isomers were present, =CH at 3.53 (m, 1.4 H) and 4.02 (m, 0.5 H), perhaps the 6-H with carbomethoxy *endo*, OCH_3 at 6.11 (s, 1.6 H) and 6.20 (s, 1.4 H), total 3 H, CH (m) at 6.49, 6.87, 7.49, 7.84, 8.30, total 6 H.

2-Aminomethyl-2-carbomethoxybicycloheptane (39). Hydrogenation of 100 g (0.564 mol) of unsaturated cyano ester **37** in ethanol over Raney nickel, starting at room temperature and ending at 60°, caused the absorption of 70% of the theoretical quantity of hydrogen. The mixture was filtered with Celite, which was rinsed with ethanol and discarded. The filtrate was evaporated on a rotary evaporator and distilled in a spinning band column to give 76.6 g (74.1%) of aminomethyl ester **39**, bp 68–69° (0.27 mm). [A small forerun of saturated cyanoester **38** was obtained. It solidified at 4° and melted by 27°: ir CH at 3.39 (m) and 3.49 (w), CN at 4.49 (w), C=O at 5.73 (s).]

Anal. Calcd for $C_{10}H_{17}O_2N$: C, 65.54; H, 9.35; N, 7.64; neut equiv, 183.2. Found: C, 65.67, 65.55; H, 9.26, 9.19; N (Kjeldahl), 7.5, 7.8; neut equiv, 185.4, 186.6.

Ir analysis showed $-NH_2$ at 2.95 (w) and 3.00 (w), CH at 3.40 (m) and 3.50 (m), ester C=O at 5.78 (s), and $-NH_2$ at 6.20 (m); nmr OCH_3 at 6.31 (s, 3 H) and NH_2 at 8.72 (s, 2 H) were present. CH_2NH_2 appeared as a singlet at 7.13 and as an AB quartet at 6.96 and 7.39, J = 12 cps, ratio $\sim$0.7, total 2 H.

Methanesulfonic Acid Salt of 2-Aminomethyl-2-carbomethoxybicycloheptane (39). Solutions of 19.73 g (0.0108 mol) of the amino ester **39** and of 9.61 g (0.100 mol) of methanesulfonic acid (E. K. Co.), each in 50 ml of ether, were made up separately and mixed with stirring and ice cooling. A gummy white solid formed and, in the refrigerator, slowly solidified. After 2 days, the solid was broken up, filtered, rinsed well with ether, and pumped dry to leave 27.6 g of white solid. Recrystallization from 100 ml of benzene–100 ml of hexane and then from 100 ml of ethyl acetate gave 14.7 g (52.6%) of white crystals of **30** which, dried in a pistol over P_2O_5 at 56° (0.3 mm), melted at 96.0–98.0° (bubbles clearing at 145°).

Anal. Calcd for $C_{11}H_{21}O_5NS$: C, 47.29; H, 7.58; S, 11.48. Found: C, 47.26, 47.12; H, 7.49, 7.46; S, 11.1, 11.2.

Formolysis and Deamination of the Methanesulfonic Acid Salt of 2-Carbomethoxy-2-aminomethylbicycloheptane. The salt, 12.69 g (0.0454 mol), was mixed with 4.74 g (0.0494 mol) of methanesulfonic acid and 49 ml of 90% formic acid and refluxed for 5 hr.[11] It was cooled and the solvents were evaporated at reduced pressure at 80–90°, final pressure being 0.4 mm. The resulting pale glass did not crystallize. It was dissolved in 50 ml of 10% sodium hydroxide solution and diluted to a final volume of 100 ml with water to give a solution of amino acid **40** as its sodium salt. Deamination of this solution by acetic acid and sodium nitrite[26] gave a gross mixture of liquids, bp 83–102° (0.65 mm), containing no β-lactone.

Saponification and Deamination of 2-Carbomethoxy-2-aminomethylbicycloheptane. To 500 ml of 2.06 *N* sodium hydroxide in 1:1 methanol–water solution (1.03 mol) was added 53.4 g (0.292 mol) of amino ester **39**. The solution was left for 48 hr at 27° and evaporated at 50° on a rotary evaporator. The resulting white slushy solid was made up to 400 ml with water and deaminated.[26] The product was a gross mixture of liquids, bp 62–136° (0.25–1.1 mm), containing negligible β-lactone but much ester (by infrared).

Ethanoanthracene Derivatives. 11-Chloromethylethanoanthracene-11-carbonyl Chloride (15). A solution of 76.6 g (0.43 mol) of anthracene, 69.5 g (0.50 mol) of α-chloromethylacrylyl chloride, 0.2 g of 2,5-di-*t*-butylquinone, and 1.65 l. of dry benzene was refluxed under nitrogen for 4.7 days.[27] The benzene was evaporated on a rotary evaporator and replaced with 200 ml of hot hexane. The dark solution crystallized well in the refrigerator. The hard crystalline mass was dissolved in 400 ml of hexane–benzene (1:1) containing Darco and Celite and filtered hot. Most of the solvent was boiled out and replaced with 200 ml of hot hexane and allowed to crystallize with magnetic stirring. After cooling to 4°, it was filtered and the hard crystals were pumped dry over paraffin to give 113.1 g (82.9%) of 11-chloromethylethanoanthracene-11-carbonyl chloride (**15**), mp 111.0–115.0°. Another recrystallization raised the melting point to 114.5–116.0°.

Anal. Calcd for $C_{18}H_{14}OCl_2$: C, 68.15; H, 4.45; Cl, 22.35. Found: C, 68.21; H, 4.47, 4.43; Cl, 22.6, 22.8.

Ir analysis showed CH at 3.45 (s) and 3.52 (m), C=O at 5.55 (s) and 5.72 (sh, w), nmr (CCl_4) ArH at τ 2.90 (m, 8 H), bridgehead H-9 at 5.36 (s, 1 H), bridgehead H-10 at 5.80 (overlapping doublets resembling a triplet, 1 H), CH_2Cl at 6.50 and 6.83 (J = 12 cps, 2 H), H-11 at 7.46 and 8.35 (J_{gem} = 13 cps, J_{vic} = 3 cps, 2 H).

11-Chloromethylethanoanthracene-11-carboxylic Acid (16). A solution of 75.0 g (0.236 mol) of 11-chloromethylethanoanthracene-11-carbonyl chloride in 980 ml of acetone, 400 ml of water, and 3 ml of 12 *N* hydrochloric acid was refluxed for 5 hr. The acetone was boiled out and the remaining suspension was extracted with 400 ml and then 200 ml of benzene. The benzene layers were dried with magnesium sulfate and rotary evaporated. The gummy residue was crystallized from 100 ml of hexane–180 ml of ether in the freezer to give 49.0 g (69.5%) of 11-chloromethylethanoanthracene-11-carboxylic acid (**16**), mp 185.8–186.6°. A second crop (16.5 g of chloro acid, mp 165–187°, mmp 185–188.5°) was gained by concentrating the filtrate to 50 ml and crystallizing in the freezer.

Anal. Calcd for $C_{18}H_{15}O_2Cl$: C, 72.35; H, 5.06; Cl, 11.86. Found: C, 72.55, 72.30; H, 5.24, 5.07; Cl, 11.4, 11.5.

Ir analysis showed CH at 3.30 (w), 3.43 (s), and 3.51 (m), HOOC at 3.7–4 (jagged, w), C=O at 5.85 (s); nmr HOOC at −1.35 (s, 0.2 H), ArH at 2.82 (m, 8 H), bridgehead H-9 at 5.46 (s, 1 H), bridghead H-10 at 5.72 (overlapping doublets resembling split s, 1 H), CH_2Cl at 6.45 and 6.95 (J = 11 cps, 2 H), bridge H-11 at 7.45 and 8.38, J_{gem} = 14 cps, J_{vic} = 3 cps, 2 H.

Ethanoanthracenespirolactone (17) by Reaction of Chloro Acid with Alkali. A mixture of 40.0 g (0.134 mol) of 11-chloromethylethanoanthracene-11-carboxylic acid, 69.5 ml (0.139 mol) of 2.00 *N* sodium hydroxide, 0.7 l. of trichloroethylene, and 0.52 l. of water was stirred at reflux for 18 hrs.[24] The mixture was cooled. The water layer was separated (pH 7) and extracted with 50 ml of trichloroethylene. A test sample gave a heavy precipitate upon acidification, so the main aqueous layer was mixed with 0.7 l. of trichloroethylene and refluxed with stirring for 24 hr more. After cooling, the aqueous layer upon acidification gave only ~3 g of oil which was discarded. The organic layers were separately dried, evaporated on a rotating evaporator, taken up in 250 ml of ether, and evaporated. Crystallization of fraction 1 from 100 ml of hexane gave 17.2 g of ethanoanthracenespirolactone (**17**), mp 148.0–151.0°. Evaporation of the filtrate gave 11.04 g of crude 11-methylene-ethanoanthracene (**23**), mp 95–100°. Similar treatment of fraction 2 gave 1.38 g of lactone, mp 156.5–157.5°, and 1.05 g of olefin, mp ~96°.

The lactone fractions were combined and recrystallized from 70 ml of heptane–80 ml of benzene, letting the solution cool with magnetic stirring. After final cooling at 4°, filtration, drying, and sublimation at 150–180° (0.18 mm) gave 14.34 g (40.6%) of pure lactone **17**, mp 153.0–155.5°, was obtained.

The olefin was passed through Florisil by hexane elution, and the crystals were recrystallized from 20 ml of hexane to give olefin **23**: yield 6.02 g (20.6%); mp 102.5–105.0°.

11-Bromomethylethanoanthracene-11-carboxylic Acid (22). A solution of 28.95 g (0.162 mol) of anthracene, 28.95 g (0.176 mol) of α-(bromomethyl)acrylic acid (**20**), and 0.10 g of hydroquinone in 580 ml of benzene was refluxed under nitrogen for 3 weeks.[27] Evaporation in a rotary evaporator gave a foamy solid. This was stirred vigorously twice with 300-ml portions of water containing a little acid, filtered, and rinsed well with water and with 300 ml of hexane to leave 52.4 g white solid. This was recrystallized from 200 ml of hexane–230 ml of benzene with Darco and Celite to give 30.8 g (55.3%) of white crystalline bromo acid **22**, mp 190.5–191.5°, mmp 172–207° with anthracene. Evaporation of the mother liquor left 11.9 g of white solid, mp 170–190°, probably mainly bromo acid.

Anal. Calcd for $C_{18}H_{15}O_2Br$: C, 62.99; H, 4.41; Br, 23.29; mol wt, 343.22. Found: C, 62.94, 62.81; H, 4.25, 4.38; Br, 23.69, 23.71; mol wt (in acetone), 351.

Ir analysis showed CH at 3.45 (m) and 3.53 (w), C=O at 5.90 (s); nmr (THF-*d*) HO_2C at 1.19 (broad s), ArH at 2.83 (m), bridgehead H-9 at 5.41 (s), bridgehead H-10 at 5.71 (overlapping doublets resembling triplet), $BrCH_2$ at 6.42 and 7.11 (J = 10 cps), bridgehead H-11 at 7.34 and 8.43, J_{gem} = 13 cps, J_{vic} = 3 cps (solvent interferred with intensity measurement).

Ethanoanthracenespirolactone from Reaction of Bromo Acid with Alkali. A mixture of 132.3 g (0.386 mol) of bromo acid **22**, 2.015 l. of trichloroethylene, and 1.5 l. of water was brought to reflux. With vigorous stirring, 200.0

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(26) E. Testa, L. Fontanella, G. F. Cristiani, and L. Mariani, *Helv. Chem. Acta.*, **44**, 1076 (1961).

(27) W. R. Vaughan and A. C. Schoenthaler, [*J. Amer. Chem. Soc.*, **80**, 1956 (1958)] used long reaction times for Diels–Alder reactions of anthracene.

TABLE IV

Wt of lactone **17**, g	Vol of γ-butyrolactone, ml	Catalyst, ml	Time, hr	Yield of **5**·**10**, g	DTA mp, °C	η_{inh} (THF)
5.00		1.0	17.5	4.3	239 276 327	0.33
7.50		0.1	48	3.5	305	0.54
7.50	5.0	0.1	48	7.2	260	0.14

ml of 2.00 *N* sodium hydroxide solution (0.400 equiv) was added all at once. Vigorous stirring and refluxing were continued for 5.0 hr. The mixture was cooled and the neutral aqueous layer was separated and extracted with 250 ml of trichloroethylene. Acidification of the aqueous layer gave only ~2 g of sticky semisolid. The organic layers were dried and evaporated to a heavy oil. Crystallization from 150 ml of hexane gave 60.0 g of white solid. Concentration of the filtrate and crystallization gave a second crop of 21.7 g and a third crop of 0.3 g. These crops were dissolved in the minimum amount of benzene, about 50 ml, and transferred to a 9.5 × 50 cm chromatography column packed with 60–100 mesh Florisil under hexane. Hexane, 12 l., eluted 48.9 g of 11-methyleneethanoanthracene (**23**). Then ether, 12 l., eluted, after two small intermediate fractions, 28.9 g of lactone **17**.

The olefin was recrystallized from 100 ml of heptane to give 44.9 g (53.4%) of pure material, mp 100.0–103.0°.

Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.35, 93.20; H, 6.45, 6.42.

Ir analysis showed CH at 3.26 (w), 3.40 (w), 3.42 (s), and 3.50 (m), C=C at 6.09 (m); nmr (THF-*d*) ArH at 2.90 (m, 8 H), =CH at 4.92 (broad s, 1 H) and 5.38 (m, 1 H), bridgehead at 5.27 (s, 1 H) and 5.72 (apparent t, separation 2.5 cps, 1 H), bridgehead at 7.68 (apparent q, separation 2 cps, 2 H).

The lactone was crystallized from 460 ml of heptane–benzene (2:1), cooling with magnetic stirring to 4°, to give 24.4 g (24.1%), mp 151.0–152.5°. Sublimation at 160–170° (0.1 mm) gave almost complete recovery, mp 152.5–155.5°. A sample, supplied by Dr. G. Berezin of Du Pont, melted at 157.0–159.0°. A mixture melting point was undepressed and the infrared spectra of the two samples were identical.

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.46, 82.39; H, 5.45, 5.42.

Ir analysis showed CH at 3.29 (w), 3.31 (w), 3.41 (m), 3.45 (m), and 3.51 (m), C=O at 5.49 (s); nmr (THF-*d*) ArH at 2.79 (m, 8 H), bridgehead at 5.33 (s, 1 H), bridgehead at 5.61 (sl split t, 1 H), OCH_2 at 5.86 and 6.15 (*J* = 5 cps, 2 H), bridge at 7.50 (m) and 7.86 (m), 2 H total.

Therefore less lactone and more olefin formed from the bromo than the chloro acid.

11-Methyleneethanoanthracene (23) *via* **Bromo Acid with Silver Carbonate.** The bromo acid **22**, 13.72 g (0.040 mol), was stirred with 5.52 g (0.040 equiv) of silver carbonate and 100 ml of anhydrous acetonitrile at room temperature for 2 hr. The precipitate was filtered and rinsed with acetonitrile and the filtrate was evaporated to give 8.91 g of white solid. By ir this was shown to be a mixture of olefin and lactone, the former present in large excess. Therefore the SN1 reaction with Ag^- gave less lactone and more olefin.

Polyethanoanthracenespirolactone (18). Polymerization in sealed ampoules under nitrogen at 154° gave the results shown in Table IV. Anthracene could be sublimed from the polymer during 1–2 hr at 235° (0.1 mm).

11-Hydroxymethyl-11-carbethoxyethanoanthracene (34). Into a bomb were placed 78.1 g (0.60 mol) of ethyl (α-hdroxymethyl)acrylate, 106.9 g (0.60 mol) of anthracene, and a trace of 2,5-di-*t*-butylbenzoquinone. After maintaining the bomb at 200° for 12 hr and cooling, 178 g of crystalline solid was removed, mp 128–130°. The waxy product was taken up in hot methanol, filtered, and allowed to crystallize. Two recrystallizations from benzene–heptane (1:1) gave ester **34**, mp 136.5–138.0°, in 54.8% yield.

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.9; H, 6.5. Found: C, 77.61, 77.52; H, 6.33, 6.28.

Ir analysis showed OH at 2.83 (s), CH at 3.25 (w), 3.40 (w), and 3.49 (w), C=O at 5.81 (s); nmr ($CDCl_3$) ArH at 2.83 (m, 8 H), bridgehead H-9 at 5.36 (s, 1 H), bridgehead H-10 at 5.75 (split s, 1 H), OCH_2CH_3 at 6.09 (quartet, *J* = 7.5 cps, 2 H), OCH_2 at 6.78 (s, 2 H), HO at 7.30 (s, 1 H), bridgehead H-11 at 7.52 and 8.65, J_{gem} = 13 cps, J_{vic} = 2 cps, 2 H, CH_3 at 9.00 (t, *J* = 7 cps, 3 H), nmr (THF-*d*) ArH at 2.88 (m), bridgehead H-9 at 5.40 (s), bridgehead H-10 at 5.74 (apparent t, separation 2 cps), OCH_2CH_3 at 6.18 and 6.38, *J* = 7 cps, 2 H, $HOCH_2$ at 6.81 and 7.13 (*J* = separation 10 cps), bridgehead H-11 at 7.69 and 8.71, J_{gem} = 14 cps, J_{vic} = 3 cps, 2 H, HO at 8.00 (s), CH_3 at 9.95 (t, *J* = 7 cps).

11-Benzenesulfonyloxymethyl-11-carbethoxyethanoanthracene (35). To a solution of 119.0 g (0.386 mol) of hydroxy ester **34** in 1.2 l. of purified tetrahydrofuran under nitrogen was added at −5 to 0° with stirring, 164.5 g (0.386 mol) of a solution of a 15.05% butyllithium solution in hexane (Foote Co.) during 34 min. The solution remained homogeneous. Benzenesulfonyl chloride, 81.8 g (0.463 mol), was added similarly during 42 min. The solution was left at 4° overnight and was poured onto 1 kg of ice and water with stirring. The tetrahydrofuran was evaporated on the steam bath with a nitrogen stream. Clumps of solid were broken up, washed thoroughly with water, dried, and recrystallized from 500 ml of ethyl acetate to give 127.7 g (73.8%) of white crystals of sulfonyloxy ester **35**, mp 144.5–146.5°.

Anal. Calcd for $C_{26}H_{24}O_5S$: C, 69.62; H, 5.39; S, 7.15. Found: C, 69.63, 69.63; H, 5.43, 5.37; S, 7.1, 7.3.

A second crop of 14.99 g (8.7%), mp 137–142°, was obtained by evaporation, trituration with ether, and drying: nmr (THF-*d*) ArH at 2.38 (m) and 2.88 (m), bridgehead H-9 at 5.42 (s), bridgehead H-10 at 5.75 (apparent t, separation 3 cps), OCH_2CH_3 at 6.16 (q, *J* = 8 cps), SO_2OCH_2 at 6.11 and 6.42 cps bridgehead H-11 at 8.57 and 7.51, J_{gem} = 14 cps, J_{vic} = 3 cps.

11-Acetoxymethyl-11-carbethoxyethanoanthracene. An attempt to convert the hydroxy ester to the bromo acid gave only acetoxy ester, reflecting the high degree of steric hindrance in these compounds. A mixture of 10 g (0.032 mol) of hydroxy ester **34**, 100 ml of glacial acetic acid, and 5 ml of water was brought to reflux and gaseous HBr was passed in for 1.25 hr. After stirring overnight, the mixture was poured into 1 l. of cold water. The blue precipitated solid was filtered, taken up in hot benzene, and filtered through Celite into a separatory funnel. Following a wash with water and drying over $MgSO_4$, the benzene was removed, leaving an oil which crystallized in hexane–acetone. Two recrystallizations from hexane–acetone gave the acetoxy ester as white crystals, mp 183–184° in 20% yield.

Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 74.02, 73.95; H, 5.44, 5.36.

Ir analysis showed CH at 3.45 (s) and 3.51 (m), C=O at 5.71 (s) and 5.91 (s).

11-Hydroxymethylethanoanthracene-11-carboxylic Acid (52). A solution of 25.0 g (0.0811 mol) of hydroxy ester **34** and 7.1 g of potassium hydroxide in 50 ml of water and 100 ml of dimethyl sulfoxide[28,29] was heated under nitrogen on the steam bath for 60 hr. A white solid crust formed. The mixture was cooled and filtered. The solid was dissolved in 500 ml of water, extracted three times with 250-ml portions of ether, and acidified with 30 ml of 12 *N* hydrochloric acid. The oil was taken up in two 250-ml portions of ether, dried with magnesium sulfate, and evaporated gently on the steam bath. It was then heated vigorously on the steam bath to drive out the last traces of solvent. Foaming and crystallization occurred. The solid was cooled and broken up to give 16.2 of white solid, mp 90–95°. This was recrystallized from ethyl acetate–hexane (1:1) to give 12.72 g (55.9%) of white crystals, which adhered tenaciously to solvent. Drying for 17 hr in a pistol at 107° (0.5 mm) over P_2O_5 caused a little wax to sublime out. The white crystalline residue of hydroxy acid melted at 146.3–148.0°.

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found (using WO_3): C, 77.01, 76.93; H, 5.71, 5.70.

Ir analysis showed OH at 2.95 (m), CH at 3.35 (w), 3.45 (s), and 3.51 (w), HOOC at 3.7–4 (jagged, w), C=O at 5.82 (s); nmr (THF-*d*) ArH at 2.85 (m), bridgehead H-9 at 5.38 (s), H-10 at 5.75 (apparent t, separation 2 cps), OCH_2 at 6.69 and 6.90 (J = 11 cps, 2 H), bridgehead H-11 at 7.50 and 8.5 (J_{gem} = 14 cps, J_{vic} = 3 cps, 2 H), possible OH at 8.01 (s).

Triphenylphosphoniopivalate, $(C_6H_5)_3P^+CH_2C(CH_3)_2COO^-$. To 104.9 g of triphenylphosphine at 160° was added with stirring under nitrogen a solution of 18.1 g of bromopivalic acid in 10.0 g of pivalolactone during 31 min. The solution was held at 160° for 8 hr. The cooled reaction mixture was ground up, extracted thoroughly with ether, and filtered. The insoluble solid weighed 12.2 g.

Of this solid, 6.1 g was heated for 2 hr with 60 ml of 48% hydrobromic acid to hydrolyze any oligomers. The cooled mixture was washed twice with 50-ml portions of chloroform to remove triphenylphosphine and its hydrobromide. The aqueous extract was neutralized with sodium bicarbonate and extracted twice with 100-ml portions of methylene chloride. Drying and evaporation left 1.41 g of betaine, mp 207–217° (bubbles). The ir spectrum showed carboxylate absorption at 6.25 μ.[30,31] Recrystallization from ethyl acetate gave 0.37 g (1.4% yield) of pure betaine, mp 217–220° (bubbles). It was dried at 80° (0.3 mm) over P_2O_5.

Anal. Calcd for $C_{23}H_{23}O_2P$: C, 76.22; H, 6.40; P, 8.55. Found: C, 76.68, 76.45; H, 6.39; P, 7.41, 7.98, 8.73, 8.26.

TGA measurements of solid samples showed that weight loss from this betaine began at 200°, whereas tetrabutylammonium pivalate began at 137°.

The betaine was an active catalyst for pivalolactone polymerization. For polymerizations of the slow spirolactones it was used as a 0.0094 *M* solution in γ-butyrolactone.

Acknowledgments. The authors are deeply indebted to Dr. G. Berezin of the Du Pont Industrial and Biochemicals Department and Dr. F. W. Knobloch of the Du Pont Textile Fibers Department for samples and discussion, to Professor S. J. Cristol and Dr. S. C. Cherkofsky for helpful suggestions, and to Mrs. Janet Willoughby and Mr. J. F. Grezlikowski for excellent technical assistance.

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The Nucleophile-Initiated Polymerization of α,α-Disubstituted β-Lactones

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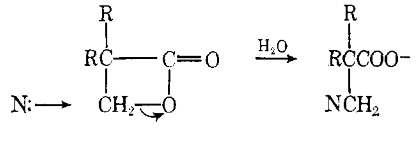
Received February 28, 1969

ABSTRACT: The rate constants for reactions of α,α-dialkyl-β-lactones with quaternary ammonium carboxylates in organic solvents were measured. The heat of polymerization of pivalolactone was -20.1 kcal mol^{-1}, allowing calorimetric determination of the rate constants. The rates were much higher in acetonitrile or tetrahydrofuran than in water and correspond to the fastest ring opening polymerizations recorded. Polar substituents in the alkyl groups accelerated the rates, whereas branched alkyls or bridged rings retarded. Pivalate ion was the most reactive nucleophile, followed by acetate, fluoride, and benzoate. Other halide ions and *p*-toluenesulfonate were extremely slow. Chloropivalolactone reacted with carboxylates to generate chloride ion and an intermediate acyloxypivalolactone, a reaction which can lead to branching.

Physical organic investigations[2] have shown that a β-lactone in aqueous solution can react at any of three places in the molecule. Strong acid protonates the carbonyl oxygen while alkali attacks the C=O at carbon. In intermediate pH ranges, other anions or water itself attack the CH_2 group with alkyl–oxygen cleavage (Sn2), in general with simple second-order



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