186. Synthesis and Polymerization of Trimethyl Bicyclobutane-1,2,2-Tricarboxylate

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(13. VI. 77)

Summary

Trimethyl bicyclobutane-1,2,2-tricarboxylate (**2**) was synthesized by a facile five-step route, beginning with the ferric chloride-catalyzed addition of chloroform to methyl acrylate to give methyl 2,4,4-trichlorobutyrate (**3**). Replacement of the 2-chloro group by iodide was followed by displacement with dimethyl malonate anion to give trimethyl 4,4-dichlorobutane-1,1,2-tricarboxylate (**5a**). Thermolysis of the corresponding sodium derivative **5b** gave trimethyl *cis, trans*-3-chlorocyclobutane-1,2,2-tricarboxylate (**6**). Closure of the bicyclobutane ring to yield **2** was accomplished by potassium hydride in ether with methanol as catalyst.

Bicyclobutane **2** polymerized under free radical initiation with breakage only of the 1,3-bond. The homopolymers, obtained in moderate yields, were of low molecular weight, probably owing to steric hindrance effects. Copolymerization occurred with vinyl monomers of varying polarity. The copolymers, obtained in moderate yields, had low molecular weights and consisted mostly of the vinyl comonomer units.

Introduction. - Bicyclobutane monomers [1] polymerize to high molecular weight polymers under free radical initiation [2]. For homopolymerizations, electronegative substituents at one or both bridgeheads are required. Alkyl groups at the bridgehead are unsatisfactory, but can be tolerated at the 2- and 4-positions if an electronegative substituent is at the bridgehead [3]. Bicyclobutanes with only methyl or hydrogen at the bridgehead did not give good polymers [4].

A wide variety of copolymers of bicyclobutanes with vinyl comonomers has been prepared [2]. To obtain alternating copolymers, synthesis of more electrophilic bicyclobutanes was attempted. A bicyclobutane with three electronegative substituents, trimethyl 4,4-dimethylbicyclobutane-1,2,2-tricarboxylate (**1**), was prepared [5], but it did not polymerize [6], probably owing to steric hindrance by the bulky groups at the 2- and 4-positions. Consequently the less hindered trimethyl bicyclobutane-1,2,2-tricarboxylate (**2**) has now been synthesized.

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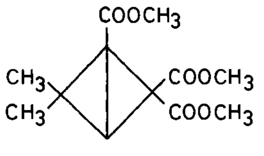

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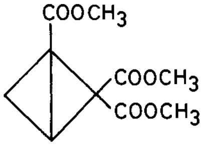

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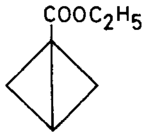

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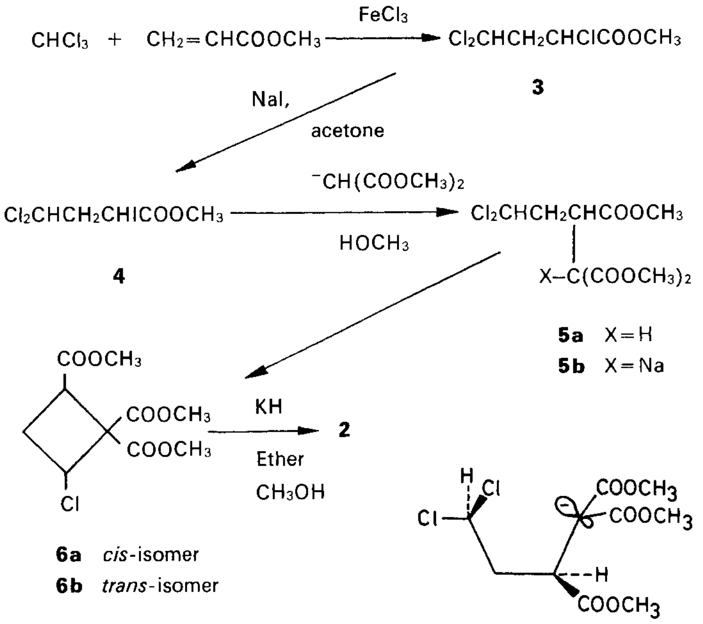
The first simple bicyclobutane, ethyl bicyclobutane-1-carboxylate (**10**), was synthesized by *Wiberg et al.* [1], using an internal alkylation of the substituted malonic ester to close the cyclobutane ring. Although the bicyclobutane monomers above [2] were synthesized by a different route, we have now returned to a malonic ester route for the synthesis of **2**.



5a X=H
5b X=Na

6a *cis*-isomer
6b *trans*-isomer

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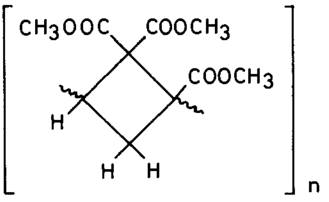
Synthesis. - Methyl 2,4,4-trichlorobutyrate (**3**) was prepared by addition of chloroform [7] to methyl acrylate [8] catalyzed by ferric chloride. To selectively increase the reactivity of the α-halogen towards sodium dimethyl malonate, methyl 4,4-dichloro-2-iodobutyrate (**4**) was prepared from **3** with sodium iodide in acetone. Only the chlorine at the 2-position was replaced at 25°; sodium chloride was precipitated, shifting the equilibrium completely to **4**. Iodide **4** reacted with excess sodium dimethyl malonate in methanol at 25° to give trimethyl 4,4-dichlorobutane-1,1,2-tricarboxylate (**5a**). The thermolysis of its sodium salt **5b** was catalyzed by crown ether and gave a 1:10 mixture (GC.) of trimethyl *cis*- and *trans*-3-chlorocyclobutane-1,2,2-tricarboxylate (**6**). The structures of both are confirmed by their ^{1}HMR. spectra where the –CHCl-Signal of *trans*-**6** is shifted to a lower field than that of the *cis*-compound. *Trans*-**6** is formed preferably, as expected, since the conformation that leads to the *cis*-compound is sterically less favorable (*cf.* **7**). The bicyclobutane **2** was prepared from the mixture of *cis*- and *trans*-**6** with potassium hydride in ether using methanol as catalyst. The *cis*-chloride forms the bicyclobutane faster, consistent with the fact that the –CH–COOR-proton is sterically less hindered in the *cis*-compound. Monomer **2** is a viscous oil which has not been crystallized, stable at 25° under nitrogen in the dark for several weeks, but polymerizing slowly on long storage. Perhaps because of its strongly electrophilic character it acts as a powerful lachrymator.

Homo- and Copolymerizations. - These were performed using standard conditions for free radical-induced polymerizations [9]. The inherent viscosities η_{inh} of solutions of the polymers were measured to obtain approximate molecular weights; the compositions of the copolymers were calculated from the elemental analyses (see *Table*).

Discussion. a) *Homopolymerizations.* The bicyclobutane **2** polymerized with radical initiation in fair yields to low molecular weight polymers. Addition of sulfolane had little effect on either yield or molecular weight. The polymers could be cast from chloroform solutions into clear brittle films. The ^{1}HMR. spectra indicate that only the 1,3-bond of the bicyclobutane **2** was broken during radical polymerizations. Thus only polymer **8** was formed (and not **9** by breaking the 2,3-bond). Similar results were found in radical polymerizations of other bicyclobutane monomers [2] [3]. This behavior is attributed to the high p-character of the 1,3-bond [10] which favors a radical attack, and to a stereoelectronic effect in which the bridgehead substituent, but not the side substituents, is able to stabilize the developing radical.



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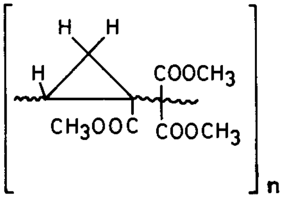

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The homopolymers were of low molecular weight, probably owing to the sterically hindered attack of the chain radical to the bicyclobutane during the polymerization. Strong polar interactions between the carbomethoxy groups of different macromolecules, the difficulty of bending the molecules because of steric hindrance, and the low molecular weights contribute to the brittleness of the polymers.

b) *Copolymerizations.* With the exception of *n*-butyl vinyl ether the bicyclobutane **2** copolymerized readily with all comonomers tried (see *Table*). Medium yields and poor to medium molecular weights were obtained. Brittle films could be cast from solutions in chloroform or DMF. They were cloudy in the cases of styrene and *p*-methoxystyrene copolymers. Although the feed ratio of bicyclobutane **2**/comonomer was usually 1:1, in one case even 2:1, usually much more of the comonomer was incorporated into the polymer. The fact that this occurs with the electron-rich *p*-methoxystyrene as well as with the electron-poor acrylonitrile shows that no polar effect but the high steric strain of the bicyclobutane [11] is probably the driving force in copolymerizations. Similar results were found earlier for the copolymerizations of bicyclobutane-1-carbonitrile and methyl bicyclobutane-1-carboxylate [12]. Only the copolymer of **2** and methyl vinyl ether give an approximately 1:1 composition (within the experimental error of the elemental analysis) but there is not yet direct evidence for an alternating 1:1 copolymer. The fact that there is no copolymer formed with *n*-butyl vinyl ether shows that the bulkiness of the vinyl substituent has a great influence on the copolymerization.

Conclusions. - A facile five-step synthesis of trimethyl bicyclobutane-1,2,2-tricarboxylate (**2**) from inexpensive starting materials has been worked out. This new monomer gave much better results in homo- and copolymerizations than the sterically more hindered bicyclobutane **1**. However, the steric hindrance of the carbomethoxy groups of **2** is still so dominant that no very good homo- and copolymers could be obtained.

Table. *Trimethyl bicyclobutane-1,2,2-tricarboxylate* (**2**): *Homo- and copolymers*[a]

Comonomer	Solvent[d]	Conversion	η_{inh}	Elemental composition[e] C	Elemental composition[e] H	Composition **2**: Comonomer
-[b]	-	66%	0.08	51.61% (52.63)	5.30% (5.30)	-
-[b]	S	68%	0.04	51.78	5.11	-
n-Butyl vinyl ether[b]	-	no polymer formed				
Methyl vinyl ether[b]	S	40%	0.17	54.29 (54.54)	6.10 (6.34)	1:0.84
p-Methoxy-styrene[b]	-	66%	0.23	76.88 (62.97)	7.04 (6.12)	1:10.6
Styrene[b]	S	50%	0.17	81.37 (65.05)	3.86 (6.07)	1:5.6
Styrene[c]	S	41%	0.14	73.59 (65.05)	6.94 (6.07)	1:2.5
Acrylonitrile[b]	-	51%	1.22	59.58 (55.51)	5.61 (5.38)	1:3.6

[a] Initiation by 1% of AIBN (2,2'-azo-bis(2-methylpropionitrile)) at 72° for 24 h. [b] 2 mmol of **2**, in copolymerizations 2 mmol of comonomer (feed ratio 1:1). [c] 2 mmol of **2**, 1 mmol of styrene (ratio 2:1). [d] S: 0.5 ml of sulfolane added. [e] Numbers in parentheses are the theoretical elemental analysis of the homopolymer, or for the 1:1 copolymer, respectively.

Experimental Part

Instrumentation. - Boiling points are uncorrected. IR. spectra were taken on a *Perkin-Elmer* 337 spectrophotometer and ^{1}HMR. spectra were obtained on a *Varian* T60 (δ_{TMS} = O). Viscosities were run in DMF at 30° at a concentration of 50 mg of polymer in 10 ml of solution. The purity of intermediates and monomers was checked on a *Varian Aerograph* 1700 gas chromatograph on a 3% *SE-30* 80-100 mesh *Chromosorb W* column (He carrier gas).

Methyl 2,4,4-trichlorobutyrate (**3**). Methyl acrylate (345 g, 4 mol), $CHCl_3$ (1432 g, 12 mol), $FeCl_3$, $6H_2O$ (21.6 g, 0.08 mol), and CH_3CN (270 g, 6.5 mol), were heated to 145° in a steel autoclave for 24 h. The solvents were evaporated and some tar and ferric chloride removed by dissolving the residue in ether, drying with $MgSO_4$ and evaporating. Distillation of the black viscous oil gave 211 g (26%) of a colorless liquid, b.p. 94-98°/26 Torr. Distillation on a 1 m spinning band column gave 140 g (17%) of pure **3**, b.p. 60-61°/0.9 Torr. - ^{1}HMR. (CCl_4): 2.6-3.0 (*m*, 2H, CH_2); 3.75 (*s*, 3H, $COOCH_3$); 4.48 (*m*, 1H, CHCl); 5.90 (*m*, 1H, $CHCl_2$).

$C_5H_7Cl_3O_2$ (205.47) Calc. C 29.23 H 3.43 Cl 51.76% Found C 29.02 H 3.45 Cl 51.87%

Methyl 4,4-dichloro-2-iodo-butyrate (**4**). Chloroester **3** (48.9 g, 0.238 mol), and NaI (90 g, 0.6 mol) were allowed to react in abs. acetone (350 ml) at 25° under N_2 in the dark for 3 days (monitored by GC.). The mixture was evaporated, the residue dissolved in hexane (800 ml), the NaCl and excess of NaI (with some I_2 on the surface) filtered off and washed with hexane (500 ml), and the solutions evaporated. Distillation gave 67.6 g (96%) of almost colorless **4**, b.p. 55-60°/0.16 Torr. - ^{1}HMR. (CCl_4): 2.81 (*m*, 2H, CH_2); 3.74 (*s*, 3H, $COOCH_3$); 4.49 (*m*, 1H, CHI); 5.71 (*m*, 1H, $CHCl_2$).

$C_5H_7Cl_2IO_2$ (296.92) Calc. C 20.23 H 2.38% Found C 20.52 H 2.34%

Trimethyl 4,4-dichlorobutane-1,1,2-tricarboxylate (**5**). Na (10.5 g, 0.456 mol), dissolved in abs. methanol (250 ml), was added at 0° during 30 min to a stirred mixture of iodoester **4** (67.6 g, 0.228 mol), and dimethyl malonate (93 g, 0.7 mol). The mixture was stirred at 25° for 24 h, neutralized with 5% aq. H_2SO_4, evaporated, diluted with water, extracted with ether; the ether phase was washed with 1M $NaHSO_3$- and saturated KCl-solutions, dried with magnesium sulfate, evaporated and fractionated to give 49.1 g (72%) of pure **5**, b.p. 124-125°/0.11 Torr. - ^{1}HMR. (CCl_4): 2.0-3.0 (br. *m*, 2H, CH_2); 3.05-3.50 (br. *m*, 1H, CH); 3.74 (*m*, 10H, 3 $COOCH_3$ and CH); 5.90 (*d*×*d*, 1H, $CHCl_2$).

$C_{10}H_{14}Cl_2O_6$ (301.12) Calc. C 39.89 H 4.69% Found C 40.10 H 4.78%

Trimethyl 3-chlorocyclobutane-1,2,2-tricarboxylate (**6**). Chloroester **5** (15.05 g, 50 mmol), was dissolved in abs. methanol (25 ml) containing Na (1.20 g, 52 mmol); dry benzene (50 ml) was added, and the mixture evaporated (foams). The residue was dissolved in benzene (50 ml), dicyclohexyl-18-crown-6 *(Aldrich)* (343 mg, 1 mmol), added, and the mixture evaporated at 70°/0.06 Torr to give a yellow dry foam (sodium salt of **5**) which was powdered and transferred to a 25 ml short-path distillation apparatus without exposure to air. The powder was heated gradually under high vacuum until melting occurred and the product **6** distilled (max. bath temp. 146°, b.p. 110-117°/0.2 Torr). Fractionation gave 8.79 g of a pure mixture of *cis*- and *trans*-**6** (71%) (GC. 1:10), b.p. 97-99°/0.03 Torr. - ^{1}HMR. (CCl_4): 2.3-2.8 (*m*, 2H, CH_2); 3.65, 3.70 and 3.79 (3 *s*, 9H, 3 $COOCH_3$); 3.88 (*m*, 1H, CH-COOR); 4.66 and 5.04 (2 *m*, tot. 1H, ratio 1:10, *cis*- and *trans*-CHCl).

$C_{10}H_{13}ClO_6$ (264.66) Calc. C 45.52 H 4.81 Cl 13.58% Found C 45.38 H 4.95 Cl 13.40%

Trimethyl bicyclobutane-1,2,2-tricarboxylate (**2**). A24% suspension of KH in mineral oil (14 g, *ca.* 70 mmol), was washed under N_2 on a sintered glass filter funnel with pentane (6× 20 ml) and abs. ether (3× 20 ml), and suspended in abs. ether (20 ml). The mixture of *cis*- and *trans*-cyclobutyl chlorides **6** (9.37 g, 35.4 mmol) was added under N_2 with stirring. The reaction was started by adding abs. methanol drop by drop at intervals of 3-5 min (22 drops), the reaction being followed by GC., *cis*-**6** was consumed faster than *trans*-**6**. The mixture was immediately filtered under N_2, the precipitate washed with ether and the ether phases evaporated. Fractionation in a short-path distillation apparatus gave 5.21 g (65%) of pure **2**, b.p. 88-89°/0.03 Torr. - IR. (neat) in cm^{-1}: 3100*w*, 2990*w*, 2940*m* (CH);

1730, 1740 and 1755*s* (COOR). - ¹HMR. (CCl_4): 1.41 (*m*, 1H, *endo*-H); 2.37 (*m*, 1H, *exo*-H); 3.19 (*m*, 1H, bridgehead-H); 3.67 and 3.72 (2*s*, 6H and 3H resp., 3 $COOCH_3$).

$C_{10}H_{12}O_6$ (228.20) Calc. C 52.63 H 5.30% Found C 52.65 H 5.23%

Comonomers were passed through a basic *Woelm* alumina column, then distilled before use. Methyl vinyl ether was used directly from the cylinder.

Homo- and copolymerizations. The indicated amounts of monomer **2**, comonomer, 2,2'-azo-bis(2-methylpropionitrile) (=AIBN), and solvent (see *Table*) were mixed below 40° to a homogeneous mixture. The sample was flushed with N_2 and sealed. The polymerization vessel was placed in an oven at 72° for 24 h. The resulting solid plug was dissolved in $CHCl_3$ (1 ml), and the solution added dropwise to vigorously stirred abs. methanol (40 ml). The polymer was collected on a sintered glass filter, dried, ground, and dried for 24 h at 50°/0.1 Torr over P_2O_5.

We are deeply indebted to the *US Army Research Office* (Durham, NH) and to the *«Stiftung für Stipendien auf dem Gebiete der Chemie»* (Switzerland) for financial support of this work and a travel grant to W.F.

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