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A convenient route to a new bicyclobutane monomer: Isopropyl 1-bicyclobutanecarboxylate

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SUMMARY

Isopropyl 1-bicyclobutanecarboxylate was prepared over 5 steps in 24% overall yield from readily available materials. This monomer was highly reactive toward radical polymerization, and gave good yields of high polymers.

INTRODUCTION

Bridgehead substituted bicyclobutanes are known to undergo free radical polymerization and copolymerization with vinyl monomers.[1] The incorporation of a cyclobutane ring in a polymer chain confers desirable properties to the material, and indeed, bicyclobutane polymers and copolymers exhibit higher glass transition temperature, melting points, and improved mechanical properties than their vinylic analogs.[2]

In the original bicyclobutane synthesis of Wiberg et al.[3], the 1,3-disubstituted cyclobutane ring was closed using an internal alkylation of a substituted malonic ester. After several further steps, ethyl 1-bicyclobutanecarboxylate was synthesized. Although successful, this is a rather long route.

A different synthesis by Hall et al.[3] began with the cycloaddition of allene to acrylonitrile. The resulting 3-methylenecyclobutane carbonitrile was converted to a bridgehead substituted bicyclobutane after 4-6 more steps. This is a useful route to bicyclobutane monomers and is suited to large scale preparations. However, it is not without limitations: the cycloaddition requires specialized equipment, and may be hazardous.

Recently, Pigou et al.[4] reported a convenient synthesis of diisopropyl 3,3-dimethoxycyclobutane-1,1-dicarboxylate by condensation of diisopropyl malonate with 1,3-dibromo-2,2-dimethoxypropane. Based on this report, we have reexamined the malonic ester route for the synthesis of bicyclobutanes and then briefly investigated the polymerization of the title compound.

RESULTS AND DISCUSSION

Synthesis

Diisopropyl 3,3-dimethoxycyclobutane-1,1-dicarboxylate (1) was prepared according to Pigou et al.[4] As part of the traditional malonic ester synthesis, this diester was treated with 20% hydrochloric acid at reflux for concomitant ester hydrolysis, deketalization and decarboxylation. However we experienced some difficulties in isolating the resulting 3-oxocyclobutanecarboxylic acid, and decided to explore alternative routes.

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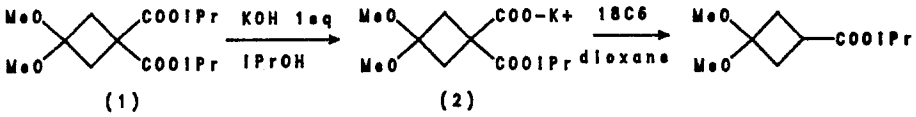
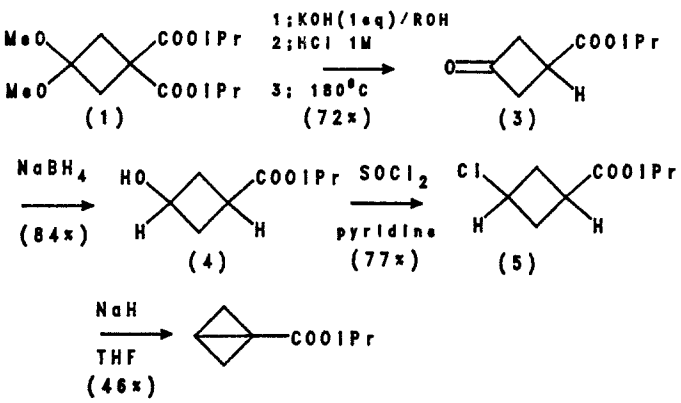


Decarbalkoxylation of the half ester (2)

The potassium salt of the half ester (2) was prepared by treating (1) with one equivalent of KOH in isopropanol in the presence of a catalytic amount of crown ether. In initial experiments, (2) was heated at reflux in dioxane in the presence of one equivalent of crown ether, according to the method of Hunter et al.[5] Decarbalkoxylation took place, and isopropyl 3,3-dimethoxycyclobutane-1-carboxylate was obtained in good yields. The use of one equivalent of crown ether discouraged any application of this method for large scale preparations, but its success encouraged us to investigate other routes starting from the half ester (2).

Finally, (1) was converted to isopropyl 3-oxocyclobutane-1-carboxylate (3) in good yield (72%) over three steps in two reaction flasks: the potassium salt of the half ester was treated with 1 M hydrochloric acid. When the resulting deketalized half ester was heated at 180°C under vacuum (10 mmHg), decarboxylation took place and (3) was directly distilled from the reaction mixture.

SYNTHESIS OF ISOPROPYL 1-BICYCLOBUTANECARBOXYLATE



Subsequent conversion of (3) to isopropyl 3-hydroxycyclobutane-carboxylate (4) with sodium borohydride proceeds smoothly in high yields (84%), as does the conversion of (4) to isopropyl 3-chlorocyclobutane-carboxylate (5)(77%). Both (4) and (5) were obtained as a mixture of cis and trans isomers. The title compound was prepared from the mixture of cis and trans (5) with sodium hydride in THF in 46% yield.

Homopolymerization of isopropyl 1-bicyclobutanecarboxylate

The title compound was subjected to conventional solution radical polymerization. DMSO was chosen as the solvent, and AIBN (3 mol% vs monomer) as the initiator. High yields of polymer were obtained. The white material was soluble in common organic solvents (DMSO, DMF, acetone, chloroform, toluene, hot methanol..), but insoluble in water.

Polymerization of Isopropyl 1-Bicyclobutane Carboxylate (DMSO, 60°C)

Monomer (g)	DMSO (ml)	AIBN (mol % vs monomer)	Transfert Agent (mol % vs monomer)	Yield (%)	$[\eta]_{inh}$ (dL\g, Chloroform, 30°C)
0.5	2.6	3%	none	66%	2.99
0.5	2.6	5%	none	86%	1.11
0.5	2.6	3%	i-Butyraldehyde 3%	78%	1.20
0.5	2.6	3%	t-Butyl Tin Hydride 3%	66%	0.84

It was reported that mild chain transfer agents are necessary during the polymerization of bicyclobutane monomers to avoid gel formation[1] Apparently, steric hindrance of the bulky isopropyl group prevents excessive abstraction of tertiary hydrogens from adjacent chains. Nevertheless, highly branched products were obtained, as indicated by the high inherent viscosities and the large molecular weight distributions, so transfer still competes with propagation during the polymerization.

EXPERIMENTAL

All reaction solvents were reagent grade and were distilled prior to use. GC-MS were performed on a system consisting of a Hewlett Packard model 5890 gas chromatograph, a model 5970 mass spectrometer and an RTE-G/VM data system. ^{1}H and ^{13}C NMR spectras were obtained by using a Bruker WM 250 NMR spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer 983 spectrometer. Microanalysis were performed by Desert Analtyics, Tucson, AZ.

Isopropyl 3-oxocyclobutanecarboxylate

Diisopropyl 1,1-dimethoxycyclobutane-3,3-dicarboxylate (78g, 0.27 mol) (5) was added to a solution of potassium hydroxide (17.8g, 1 equivalent) in dry isopropanol, and the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure to give a foam which was dissolved in 200 ml of a 3N HCl solution saturated with KCl. Distilled water (20 ml) was added, and the aqueous phase was extracted with ethyl acetate (2 x 150 ml). The organic layer was washed with water (50 ml), dried with anhydrous magnesium sulfate, and the solvent removed under

reduced pressure. The oily residue was poured in a vacuum distillation apparatus. The pressure was set at 10 mmHg. Decarboxylation began at 180°C, and the resulting isopropyl 1,1-dimethoxycyclobutane-3- carboxylate distilled as produced. The distillate was then treated with 200 ml of 1 M hydrochloric acid for two hours at room temperature to achieve the deacetalization. The aqueous phase was extracted with ethyl acetate (2 x 100 ml) and the solvent was removed at reduced pressure. The resulting oil was distilled through a Vigreux column.
Yield: 30.42 g (72%).
Physical Data: BP 88°C (3mmHg); IR (neat) 1732 cm^{-1} (ester) 1801 cm^{-1} (cyclobutanone); ^1H NMR ($CDCl_3$) δ 5.07 (1H, sextuplet, J=6 Hz), 3.3 (5H, m), 1.28 (6H, d, J=6Hz); ^{13}C NMR (DMSO d_6) 204.22 (C_3), 173.34 (CO_2), 67.80 (OCH), 50.95 ($C_{2,4}$), 26.93 (C_1), 21.28 (CH_3); Anal. Calcd for $C_8O_3H_{12}$: C, 61.53; H, 7.69 Found C,61.18 ; H,7.64.

Isopropyl 3-hydroxycyclobutane-1-carboxylate

To a stirred solution of 1.26 g (0.033 mol) of sodium borohydride in 50 ml of water was added with stirring and crushed ice bath cooling, a slurry of 19 g (0.12 mol) of isopropyl 3-oxocyclobutane-1-carboxylate in 50 ml of water. When the addition was complete, the solution was stirred at room temperature overnight. The product was extracted with ethyl acetate. The ethyl acetate extract was dried and distilled to give 15.92 g (84%) of a colorless oil. Analysis shows the product to be a 75/25 mixture of the trans and cis isomers.
Physical Data: BP 121°C (0.5 mmHg) ^1H NMR ($CDCl_3$) δ 5.00 (1H,sept), 4.53 (0.25H,m), 4.16 (0.75H,m), 2.53 (3H,m), 2.15 (2H,m), 1.24 (6H,d); Mass spectrum, m/e : 143 (2), 116 (26), 99 (276), 98 (236), 88 (117), 73 (873), 55 (364), 43 (886). Anal. Calcd for $C_8O_3H_{14}$: C, 60.75 ; H, 8.86 Found: C, 60.18 ; H,8.95.

Isopropyl 3-chlorocyclobutane-1-carboxylate

A 500 ml three necked flask was equipped with a sealed stirrer unit, a reflux condenser and an addition funnel; 36g (0.227 moles) of isopropyl 3-hydroxycyclobutane-1-carboxylate and 18g (0.227 moles) of pyridine were introduced in the flask, while 55g (0.4 moles) of redistilled thionyl chloride was placed in the addition funnel. The content of the funnel was added over 20 minutes. The mixture was then heated to reflux for one hour, until no more sulfur dioxide evolved, and all the solid was dissolved. The mixture was cooled and poured in a separatory funnel. The upper layer was removed, carefully washed with water and sodium carbonate solution, then dried with calcium chloride before distillation. Yield 30.85g (77%)

Physical Data. BP 105°C (15mm Hg) ; ^1H NMR ($CDCl_3$) δ 5.03 (1H,sept), 4.59 (0,65H, quint), 4.31 (0.35H, quint), 3.24 (0.35H,m), 2.78 (2,65H,m), 2.53 (2H,m), 1.23 (6H,d) ; ^{13}C NMR ($CDCl_3$) δ 174.04 (C=O), 67.99 (CH cis),67.91 (CH trans), 51.00 (C_3 cis), 47.71 (C_3 trans), 37.47 ($C_{2,4}$ cis), 36.34 ($C_{2,4}$ trans), 34.39 (C_1 cis), 32.83 (C_1 trans), 21.56 (-CH_3); IR (neat): 1725 cm^{-1} (ester) ; mass spectrum, m/e : 161 (1), 135 (20), 117 (23), 99 (18), 83 (20.5), 43 (31); Anal. Calcd for $C_8H_{13}O_2Cl$: C, 54.89 ; H, 7.36 found: C, 55.01 ; H, 7.5 .

Isopropyl Bicyclobutanecarboxylate

A 200ml three-necked flask was fitted with a condenser, an addition funnel and a thermometer. The setting was heated with a heat gun and cooled to room temperature under vacuum. Sodium hydride (0.75g, 0.255 eq),

3-ter-butyl-4-hydroxy-5-methylphenyl sulfide (0.05 g), and 40 ml of dry THF were introduced in the flask and magnetically stirred. A solution of 3-chloro-isopropylcyclobutane-1-carboxylate (5.188g, 1 eq) in 10 ml of dry THF was introduced in the addition funnel. As the addition began, the temperature of the mixture raised to 55°C. After the end of the addition, the mixture was heated at 60°C for 2 hours, until no more evolution of hydrogen was observed.

The mixture was cooled with a ice/acetone bath and washed with 10 ml of a saturated solution of potassium chloride. The aqueous phase was washed with 20 ml of THF; the organic layers were combined, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure (0^0C, 10mmHg). The pure bicyclobutane distilled at 30^0C (3mmHg), the receiver being chilled with dry ice . Yield 1.55g (45%)

Physical data: BP 28/30°C (3mmHg); ^{1}H NMR ($CDCl_3$) δ 5.02 (1H,sept), 2.34 (2H,dd), 2.03 (1H,m), 1.23 (6H,d), 1.12 (2H,dd); ^{13}C NMR ($CDCl_3$): 172.34 (-C=O), 67.51 (CH), 35.19 ($C_{2,4}$), 21.60 (CH_3), 15.87 (C_1), 9.05 (C_3); mass spectrum m/e : 140 (13), 98 (175), 81 (87), 69 (50), 53 (165), 43 (262); Anal. Calcd for $C_8O_2H_{12}$: C, 68.57 ; H, 8.57 found: C, 68.42 ; H, 8.55 .

Poly isopropyl 1-bicyclobutanecarboxylate

In a polymerization tube were introduced via syringe 1.5 ml of DMSO , 0.5 ml of isopropyl 1-bicyclobutanecarboxylate , 16 mg of AIBN (3 mol %), and a magnetic stirrer. The mixture was degassed by three freeze/thaw cycles, and then placed in an oil bath and heated at 60°C for 16 hours. After this period of time, the solution was very viscous. Ethyl ether (10 ml) was added and the polymer was precipitated in 200 ml of a mixture methanol / water (75 / 25). The filtered polymer was dried overnight in an Abderhalden drying pistol (3mm Hg, in presence of phosphorus pentoxide, heated with water) before analysis. Physical data: Anal. Cald for $(C_8O_2H_{12})_n$: C, 68.57% ; H, 8.57% . Found: C, 68.18% ; H, 8.65%. ^{1}H NMR ($CDCl_3$) δ (ppm) : 4.9 (1H), 2.2 (5H), 1.2(6H). ^{13}C NMR ($CDCl_3$) δ (ppm) : 176 (COO), 67.7 (CH), 46.8, 44.2 (C_1), 35.3, 33.3 (C_3), 28.67 ($C_{2,4}$), 21.80 (CH_3). IR (film cast from $CHCl_3$) : 1709 cm^{-1} (ester). DSC (heating rate 20°C/min) : Tg = 85°C. Inherent Viscosity ($CHCl_3$,T=30°C) : $[\eta]_{inh}$ = 2.99 dL/g. GPC ($CHCl_3$, polystyrene standards) : Mn = 310000, Mw = 700000, PDI=2.3.

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