The Synthesis and Polymerization of 1,3-Disubstituted Cyclohexanes. II. cis-1,3-Diformylcyclohexane and cis-1,3-Divinylcyclohexane

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The Synthesis and Polymerization of 1,3-Disubstituted Cyclohexanes. II. cis-1,3-Diformylcyclohexane and cis-1,3-Divinylcyclohexane*

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SUMMARY

The synthesis of cis-1,3-diformylcyclohexane by a hydride reduction of the dimethyl ester of cyclohexane-cis-1,3-dicarboxylic acid is described. An inversion of configuration occurred during an attempt to prepare trans-1,3-diformylcyclohexane by a similar route. cis-1,3-Divinylcyclohexane was prepared by a Wittig reaction on the corresponding dialdehyde. Polymerization of cis-1,3-diformylcyclohexane using a cationic catalyst gave high yields of thermally unstable polymers. Soluble fractions of the polymers contained some residual aldehyde groups. Spectroscopic data confirmed that these polymers contained 3-oxabicyclo[3,3,1]nonane rings formed through a cyclopolymerization mechanism. Polymerization of cis-1,3-divinylcyclohexane using a Ziegler catalyst resulted in soluble polymers containing little residual unsaturation. This soluble polymer, from the evidence, is a cyclopolymer containing bicyclo[3,3,1]nonane units.

INTRODUCTION

The cyclopolymerization of cis-1,3-diisocyanatocyclohexane has been described [1]. cis-1,3-Diformylcyclohexane and cis-1,3-divinylcyclohexane should present similar and unambiguous examples of cyclopolymerization. A 1,3-diformylcyclohexane is mentioned in the patent literature [2] but no details of preparation or stereochemistry are given. 1,3-Divinylcyclohexanes have not been reported.

RESULTS AND DISCUSSION

Synthesis

Brown and Tsukamoto [3] have prepared formylcyclohexane by the reduction of cyclohexane-N,N-dimethylcarbonamide with lithium di- or triethoxyaluminum hydride. The analogous bis-N,N-dimethylamide (III) of cyclohexane-cis-1,3-dicarboxylic acid was prepared, via the cyclic cis-anhydride (I) and the mono-N,N-dimethylamide (II), and its reduction was investigated using lithium di- and triethoxyaluminum hydride in tetrahydrofuran. The ether soluble products, obtained after hydrolysis of the reaction mixture, were shown by chemical tests to contain nitrogen and the aldehyde group and the IR spectra showed bands at 1625 cm^{-1} (identical to the carbonyl stretching absorption of III), 1720 cm^{-1} (presumably the carbonyl stretching absorption of the aldehyde group), and strong absorption in the hydroxyl stretching region. Substantial amounts of starting material were also recovered from these reductions. It is clear that very little reaction occurs under conditions which produce a good yield of aldehyde for the monosubstituted compound and that with only partial reduction of III further reduction of the aldehyde takes place. Similar results were obtained in this laboratory from attempts to selectively reduce cyclohexane-cis-1,3-di-N-methylcarbonanilide (IV) with lithium aluminum hydride [4].

cis-1,3-Diformylcyclohexane was eventually prepared by reduction of the dimethyl ester of cyclohexane-cis-1,3-dicarboxylic acid (Va) using sodium aluminum hydride in tetrahydrofuran at −50°. Complete reduction of Va would produce cis-1,3-cyclohexanedimethanol (IX). Partial reduction, at −50° using sodium aluminum hydride, yielded either methyl cis-3-formylcyclohexanecarboxylate (VIa), cis-1,3-diformylcyclohexane (VII), or cis-3-formylcyclohexanemethanol (VIII), or a mixture of these.
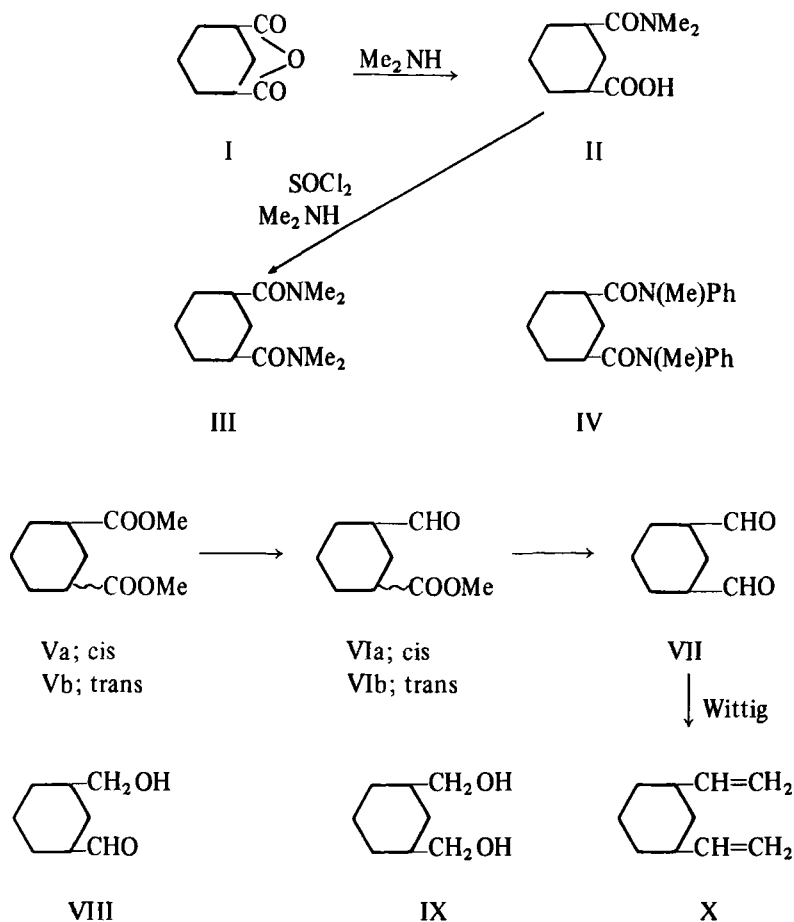
The extent of the reduction was dependent upon the amount of the re-
ducing agent present and to obtain the dialdehyde (VII) as the major
product a considerable excess of reducing agent was required. Increasing
the temperature decreased the yield of dialdehyde, and the alcohols (VIII
and IX) became the major products. To obtain reproducible results, the
activity of the sodium aluminum hydride was established, prior to its use,
by analysis for hydride (by hydrolysis) and aluminum (with 8-hydroxy-
quinoline).

Analysis of the products by vapor phase chromatography showed that,
in the usual case, three new compounds, with retention times distinct
from the starting material, were formed by this reduction. The compound

with the shortest retention time of the three was identified as cis-1,3-diformylcyclohexane (VII) by the preparation and analysis of the bis-2,4-dinitrophenylhydrazone derivative. Similarly the pure 2,4-dinitrophenyl-hydrazone and semicarbazone derivatives of VIa were prepared from the compound with the longest retention time. The third compound was identified as VIII from the strong hydroxyl bands in its IR spectrum. The relative proportions of VIa, VII, and VIII in the products obtained under the various reaction conditions were estimated from the peak areas in vapor phase chromatograms (Table 1).

Table 1

Reaction conditions		Product analysis (%)			Yield (%)[a]	
Excess NaAlH$_4$(%)	Time (hr)	VIa	VII	VIII	Total	VII
0	8	73	23	4	84	19
20	5	63	32	5	80	26
40	5	15	60	25	75	45
50	5	5	67	28	73	49

[a]Based on analysis.

Using the theoretically determined amount of sodium aluminum hydride and allowing the reaction to continue for 8 hr, the major product of the reaction was VIa. The proportion of the dialdehyde in the product was not significantly improved by increasing the reaction time to 14 hr. However, increasing the amount of the reagent present in the reaction mixture increased the proportion of the required dialdehyde (VII), and also of the alcohol (VIII), in the product. Spinning-band distillation of the product of the reaction using 50% in excess of the theoretical amount of reagent gave a first fraction which, after two redistillations, yielded pure cis-1,3-diformylcyclohexane (VII). Initially, considerable polymerization in the distillation flask led to low yields of VII but considerably improved yields were recorded when the distillation was carried out in the presence of m-dinitrobenzene. The IR spectrum of this compound showed the expected C–H stretching absorption at 2700 cm^{-1} and the C=O absorption at 1720 cm^{-1} (Fig. 1a).

An attempt was made to isolate trans-1,3-diformylcyclohexane by the same route as that used for the preparation of the cis-isomer. The
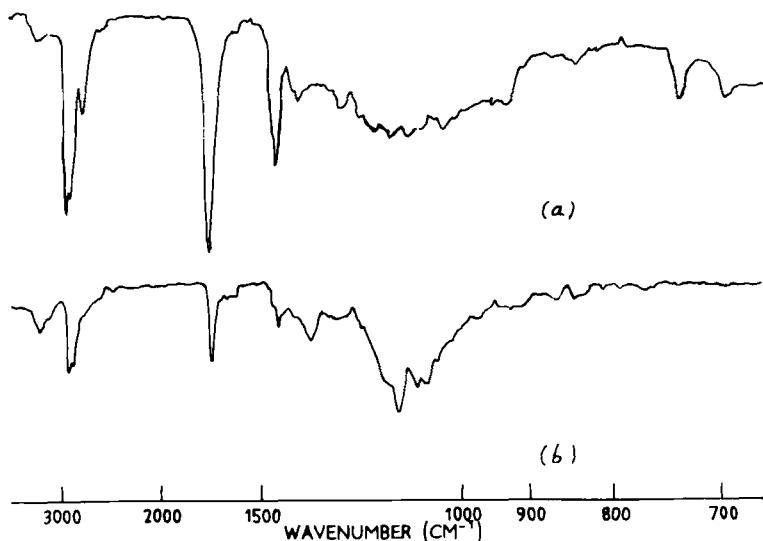
Fig. 1. Infrared spectrum of (a) cis-1,3-diformylcyclohexane and (b)
poly(cis-1,3-diformylcyclohexane).

dimethyl ester of cyclohexane—trans-1,3-dicarboxylic acid (Vb) was similarly
treated with sodium aluminum hydride in tetrahydrofuran at -50°. No re-
action occurred using 20% in excess of the theoretical amount of reagent
for 5½ hr, and using 50% excess and a reaction time of 8½ hr the product
was predominantly methyl trans-3-formylcyclohexanecarboxylate (VIb). The
difference between the reactivity of the dimethyl cis- and trans-hexahydroiso-
phthalates, Va and Vb, respectively, indicates the relative reactivity of equa-
torial and axial substituents. When the trans-diester (Vb) was treated for 8½
hr at -50° with a solution of sodium aluminum hydride (50% excess) in
tetrahydrofuran, which had been refluxed for 15 hr under a nitrogen atmos-
phere, the product of the reaction was predominantly the cis-dialdehyde.
Since the reductions of the cis- and trans-diesters, Va and Vb, produce
quite different mono-aldehydes, VIa and VIb, this inversion of configuration
must occur during the conversion of VIb to the dialdehyde.

cis-1,3-Diformylcyclohexane was converted by the Wittig reaction [5]
into cis-1,3-divinylcyclohexane, the IR spectrum of which showed strong
absorption bands at 912, 993, and 1645 cm^{-1} associated with the vinyl
groups (Fig. 2a). Minor products, identified from IR spectra as methyl
cis-3-vinylcyclohexanecarboxylate and cis-3-vinylcyclohexanemethanol, were
also isolated. Separation of cis-1,3-divinylcyclohexane from these compounds
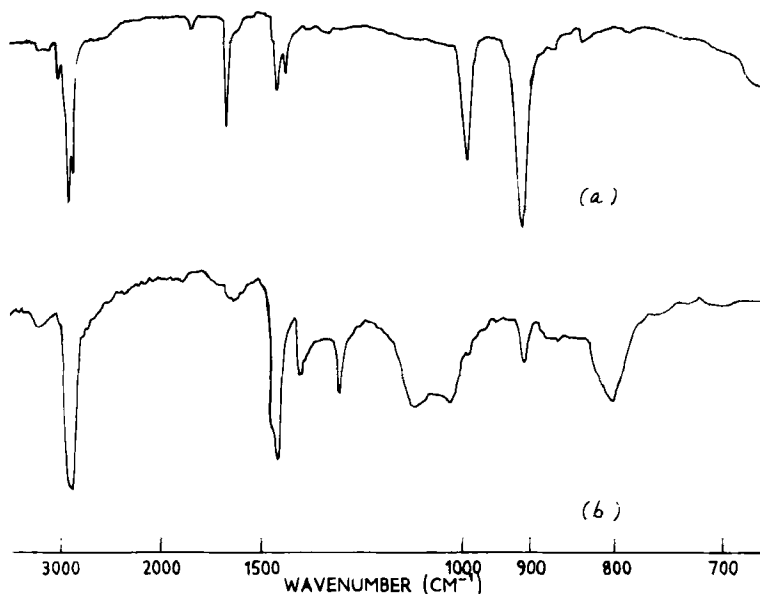was carried out by fractional distillation using a spinning-band column.

Fig. 2. Infrared spectrum of (a) cis-1,3-divinylcyclohexane and (b) poly(cis-1,3-divinylcyclohexane).

Polymerization

cis-1,3-Diformylcyclohexane, in contrast to glutaraldehyde [6, 7], did not spontaneously polymerize at room temperature and no change in the IR spectrum was observed for a sample stored in a sealed tube at 110° for 20 hr. Material containing considerable amounts of impurities showed a tendency to polymerize unless an inhibitor was present.

The polymerization of cis-1,3-diformylcyclohexane was initiated by boron trifluoride-diethyl etherate at -70° in toluene solution, the polymers being isolated by coagulation in n-heptane. Representative conditions and results are shown in Table 2. The white, powdery polymers were thermally unstable and were depolymerized completely to monomer by Soxhlet extraction with benzene. In general the polymers were largely soluble in such solvents as chloroform and tetrahydrofuran, the soluble fractions being recovered unchanged from solution by the addition of a nonsolvent such as n-heptane. Polymer B, for example, was soluble to the extent of 61.5% in hot chloroform and a further 11% was soluble in hot tetrahydrofuran. The capillary melting points of the polymers, occurring with decomposition

Table 2. Polymerization of cis-1,3-Diformylcyclohexane

Experiment	Catalyst (mmole)	Solvent (ml)	Monomer g	Monomer mmole	Catalyst concentration (mole %)	Temp (°C)	Time (hr)	Yield (%)
A	$BF_3O(C_2H_5)_2$ (0.85)	Toluene (8.5)	1.2	8.5	10	-70	2	94
B	$BF_3O(C_2H_5)_2$ (0.71)	Toluene (7.1)	1.0	7.1	10	-70	2	100
C	$BF_3O(C_2H_5)_2$ (0.25)	Toluene (5.0)	0.7	5.0	5	-70	2	81
D	$BF_3O(C_2H_5)_2$ (0.09)	Toluene (8.5)	1.2	8.5	1	-70	2	43

to monomer, varied from 120 to 200°. The solubility of the polymers is
evidence of their linear structure.

A linear polymer of cis-1,3-diformylcyclohexane may be formed either
by cyclopolymerization, with the formation of a 3-oxabicyclo[3,3,1] nonane
ring in the structural unit XI, or by polymerization occurring only through
one of the aldehyde groups to form the structural unit XII. The IR spec-
trum of the soluble fraction of the polymer (Fig. 1b) showed a band at
1720 cm^{-1} due to the carbonyl group, indicating the presence of some
residual aldehyde groups, and strong bands in the acetal region between
1050 and 1150 cm^{-1}. It is clear that the polymer contains both structural
units XI and XII. The IR spectra of the polymer fractions which were in-
soluble in chloroform and tetrahydrofuran were identical to those of the
soluble fractions. The decrease in solubility, and an observed increase in
melting point, may be due to the presence of some cross-linking in the
structure or merely to an increase in the molecular weight.

XI   XII
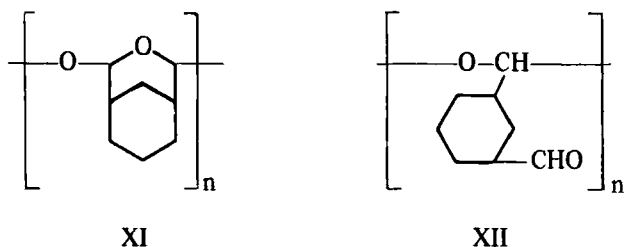
A chemical method for the determination of the pendant aldehyde con-
tent by preparation of the 2,4-dinitrophenylhydrazone was of no practical
use because the polymer depolymerized under these conditions and the
derivative of the monomer was obtained in quantitative yield. The pend-
ant aldehyde content was determined from the NMR spectrum of the
polymer. The spectrum showed a small peak at 0.4 τ due to the formyl
protons and a broad band between 7.5 and 9.4 τ due to protons in the
cyclohexane ring. The spectrum also showed broad peaks in the region 5.3
to 6.9 τ which did not appear in the spectrum of the monomer. Bands in
this region of the spectrum may be assigned to protons which are deshielded
by the presence of oxygen atoms. The observed ratio of the formyl protons
to all other protons present in the spectrum of the polymer was 1:39.
Structure XII requires the ratio of the formyl protons to the other protons
to be 1:11 and a 1:1 ratio of Structures XI and XII requires a ratio of 1:23.
It is clear that the cyclized units XI predominate in the polymer structure.

Calculation of the % cyclization was accomplished using the equation [8]:

$$\frac{100(dc - b)}{dc - b + a} = \% \text{ cyclization}$$

where a = number of protons in the cyclized unit; b = number of protons, other than formyl, in the acyclic unit; c = number of formyl protons in the acyclic unit; and d = ratio of protons, other than formyl, to formyl protons as determined by NMR.

A value of 70% cyclization was obtained, although this represents only a good approximation since the values used in the calculation are not based on very accurate experimental data. Thus, the polymerization of cis-1,3-diformylcyclohexane, using a cationic catalyst, leads to polymers which, from their spectroscopic and chemical properties, consist mainly of structural units XI containing the 3-oxabicyclo[3,3,1]nonane ring, formed by a cyclopolymerization mechanism.

cis-1,3-Divinylcyclohexane would be expected to undergo cyclopolymerization to produce a polymer possessing the structural units XIII if polymerization proceeds exclusively by this mechanism. If cyclization fails to occur, a linear polymer containing unreacted vinyl groups (XIV) or a cross-linked polymer may result.

Polymerization was accomplished with a Ziegler catalyst prepared from triisobutylaluminum and titanium tetrachloride in 1:1 molar ratio in n-heptane solution. Other initiators tried, boron trifluoride-diethyl etherate,

XIII   XIV
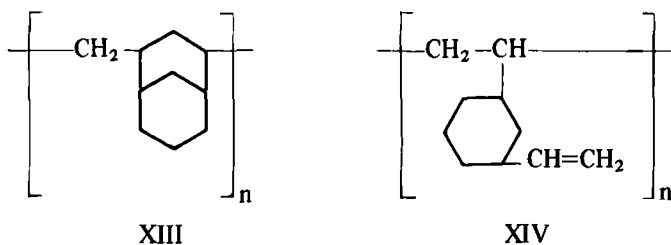
α,α'-azobisisobutyronitrile and benzoyl peroxide, were ineffective in initiating polymerization of this monomer. The polymers obtained by Ziegler catalyst initiations were almost completely soluble in cold benzene with melting points varying from 90 to 150° and so were essentially linear in structure. The IR spectra of the purified polymers showed the presence of some residual vinyl groups (Fig. 2b). The NMR spectrum of the polymer containing the maximum amount of residual unsaturation gave a broad peak

at a chemical shift of $8.6 \pm 1 \tau$ for the sp^3 bonded hydrogens and peaks at ap-
proximately 4.2 and 5.0 τ for sp^2 bonded hydrogens. The observed $sp^2 : sp^3$
ratio was 1:28. Structure XIII requires a $sp^2 : sp^3$ ratio of 1:4.3 and a 1:1 co-
polymer of XIII and XIV requires a ratio of 1:9.7. The % cyclization was ob-
tained using the equation given earlier where a = number of sp^3 hydrogens in
the saturated unit, b = number of sp^3 hydrogens in the unsaturated unit, c =
number of sp^2 hydrogens in the unsaturated unit, and d = sp^2 hydrogens ratio
as determined by NMR. A minimum value of 82% cyclization was obtained,
but again these calculations represent only a good approximation.

The condition used and results of the polymerization experiments are re-
corded in Table 3. X-ray diffraction studies on these polymers indicated
some degree of crystallinity. An X-ray powder photograph showed one dif-
fuse band, almost certainly containing more than one diffraction peak.
Measurement of the diffraction line using the maximum intensity portion
of the band gave a d-spacing of 5.58 ± 1 Å.

EXPERIMENTAL

Melting points, determined on a Gallenkamp apparatus (design no. 889,
339), are uncorrected. Refractive indices were determined on a Bellingham
and Stanley Abbe 60 refractometer. Vapor phase chromatograms were re-
corded on a Pye Argon chromatograph with 20% silicone elastomer E301
on a 30/80 mesh celite column 1.2 m long. IR spectra were recorded as
liquid films or as potassium bromide disks on a Perkin-Elmer Infracord.
NMR spectra were determined for deuterochloroform solutions with tetra-
methylsilane as internal standard on a Varian Associates HA-100 high
resolution spectrometer.

Cyclohexane-cis-1-N,N-dimethylcarbonamide-3-carboxylic acid II. Cyclo-
hexane-cis-1,3-dicarboxylic anhydride (I) [1] (25 g) in benzene (250 ml)
was cooled in ice and N,N-dimethylamine (20 ml) was added with stirring.
A Dry Ice-acetone condenser was attached to the flask and the mixture
allowed to warm to room temperature. After standing for 2 hr the precipi-
tate which had formed was filtered off, dissolved in the minimum amount
of water, acidified with concentrated hydrochloric acid, and the precipitate
filtered off to yield cyclohexane-cis-1-N,N-dimethylcarbonamide-3-carboxylic
acid (25 g), mp 165-167° (from acetone-ether) (found: N, 7.13;
$C_{10}H_{17}NO_3$ requires N, 7.03%).

Cyclohexane-cis-1,3-di-N,N-dimethylcarbonamide (III). (II) (15 g) in benzene (20 ml) and thionyl chloride (8 ml) were stirred and warmed on water bath under an air condenser for 2 hr. This solution was added dropwise with stirring, over 1 hr, to N,N-dimethylamine (18 ml) in benzene (25 ml) under a Dry Ice-acetone condenser. The mixture was stirred for 1 hr after completion of the addition, poured into water, extracted with chloroform and, after drying over anhydrous sodium sulfate, solvent was removed under reduced pressure to yield cyclohexane-cis-1,3-di-N,N-dimethylcarbonamide (16 g), mp 127-128° (from isopropanol-petrol, 60-80°) (found: N, 12.17; $C_{12}H_{22}N_2O_2$ requires N, 12.38%).

cis-1,3-Diformylcyclohexane (VII). In a 500-ml conical flask equipped with a magnetic stirrer, dropping funnel, nitrogen inlet, and calcium chloride tube and surrounded by a Dry Ice-acetone bath at -75°, was placed sodium aluminum hydride (0.0375 mole, weight based on analysis) and dry tetrahydrofuran (150 ml). Dimethyl cis-hexahydroisophthalate [1] (10 g, 0.05 mole) in tetrahydrofuran (100 ml) was added dropwise, over 30 min. with stirring to the slurry of the hydride. The cooling bath was allowed to warm to -50° and maintained at -50 to -60°. After 5 hr at this temperature the reaction mixture was decomposed by careful addition of 2 N sulfuric acid, extracted with ether, and after drying over anhydrous magnesium sulfate the solvent removed under reduced pressure to yield a pale yellow liquid (5.2 g). Vpc analysis showed that the product contained 67% dialdehyde and distillation, in the presence of m-dinitrobenze (50 mg), gave a first fraction which, after two redistillations, yielded cis-1,3-diformylcyclohexane, bp 80°/0.8 mm, n_D^{20} 1.4735 characterized as the bis-2,4-dinitrophenylhydrazone, mp 253-253.5° (from nitromethane) (found: C, 47.84; H, 4.19; N, 22.05; $C_{20}H_{20}N_8O_8$ requires C, 48.00; H, 4.03; N, 22.39%).

The product from a reduction using 0.025 mole of sodium aluminum hydride and maintained at -50° for 8 hr contained 73% methyl cis-3-formylcyclohexane carboxylate (VIa), bp 97°/2 mm, n_D^{20} 1.4631 characterized as the 2,4-dinitrophenylhydrazone, mp 147-148° (from absolute alcohol), (found: C, 51.58; H, 5.37; N, 15.95; $C_{15}H_{18}N_4O_6$ requires C, 51.42; H, 5.18; N, 15.99%), and as the semicarbazone, mp 132-133° (from petroleum ether, 100-120°) (found: C, 53.06; H, 7.42; N, 18.41; $C_{10}H_{17}N_3O_3$ requires C, 52.85; H, 7.54; N, 18.49%).

Dimethyl trans-hexahydroisophthalate [1] (0.05 mole) treated with sodium aluminum hydride (0.0375 mole) in tetrahydrofuran (250 ml) at -50° for 8½ hr yielded methyl trans-3-formylcyclohexanecarboxylate (VIb), bp 82°/0.7 mm, n_D^{20} 1.4640 characterized as the 2,4-dinitrophenylhydrazone, mp 120-121° (from methanol), mixed melting point with

Table 3. Polymerization of cis-1,3-Divinylcyclohexane

Experiment	mmoles	Solvent (ml)	Initiator (mmoles)	Reaction conditions		Polymer	
				Temp ($^\circ$C)	Time (hr)	Yield (%)	Soluble (%)
1	5		BP^a (0.25)	75	100		
2	5		ABIB^b (0.25)	75	300		
3	5	CH$_2$Cl$_2$ (2.5)	BF$_3$. (C$_2$H$_5$)$_2$O (0.25)	-10	100		
4^{c,d}	1.6	n-Heptane (5)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	25	138	20	86
5^{c,d}	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	55	89	47	90
6^{c,d}	2.5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	63	87	68	100
7^{c,d}	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	75	84	81	91
8^c	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	25	120	1.5	90^f

9[c]	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$	75	156	6	90
10[c,d]	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	25	48	1	90[f]
11[e,d]	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	25	96	1.5	90[f]
12[e,d]	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	25	182	2	90[f]
13[e,d]	5	n-Heptane (10)	TiCl$_4$ (1) Al(i-Bu)$_3$ (1)	61	75	7	90

[a] Benzoyl peroxide.
[b] α,α'-Azobisisobutyronitrile.
[c] Reaction mixture was continuously stirred.
[d] Catalyst "aged" for 20 min at room temperature.
[e] Reaction carried out in pear-shaped flask.
[f] Total yield too small to calculate this percentage accurately.

cis-derivative, 104-110° (found: C, 51.62; H, 5.32; N, 16.10; $C_{15}H_{18}N_4O_6$ requires C, 51.42; H, 51.8; N, 15.99%).

When the sodium aluminum hydride was refluxed overnight in tetrahydrofuran the above conditions yielded cis-1,3-diformylcyclohexane, identified from the bis-2,4-dinitrophenylhydrazone (melting point and mixed melting point). When added to an authentic sample of cis-1,3-formylcyclohexane the mixture gave a single peak in vpc.

cis-1,3-Divinylcyclohexane (X). In a 500-ml conical flask equipped with a magnetic stirrer, dropping funnel, reflux condenser, and dry nitrogen cover, methyltriphenylphosphonium bromide (40 g) and sodamide (5 g) was dispersed in dry tetrahydrofuran (200 ml). After stirring overnight, a solution of cis-1,3-diformylcyclohexane (7 g) in dry tetrahydrofuran (50 ml) was added to the resulting orange solution of the ylid. After stirring overnight, 200 ml of solvent was removed by distillation at atmospheric pressure. The residue was taken up in water, extracted with petroleum ether (30-40°), dried over anhydrous magnesium sulfate, and after removal of solvent at atmospheric pressure, the residue distilled to yield cis-1,3-divinylcyclohexane (4.1 g), bp 164.5°, n_D^{20} 1.4615 (found: C, 87.92; H, 11.51; $C_{10}H_{16}$ requires C, 88.16; H, 11.84%).

Polymerization of cis-1,3-Diformylcyclohexane. Representative conditions and results are summarized in Table 2; the following is a typical polymerization procedure. In a 20-ml three-necked conical flask equipped with a magnetic stirrer, dropping funnel, nitrogen inlet, and calcium chloride tube and surrounded by a Dry Ice-acetone bath at -70°, was placed boron trifluoride-diethyl etherate (0.09 ml, 0.7 mmole) in toluene (4 ml). cis-1,3-Diformylcyclohexane (1.0 g, 7 mmole) in toluene (3 ml) was added to the vigorously stirred catalyst solution and the mixture maintained at -70°. After 2 hr, n-heptane was added to yield poly(cis-1,3-diformylcyclohexane) (1.0 g).

Polymerization of cis-1,3-Divinylcyclohexane. Conditions and results are given in Table 3, the following is a typical polymerization procedure. To a 25-ml conical flask was added n-heptane (5 ml), triisobutylaluminum (0.20 g, 1 mmole), and titanium tetrachloride (0.20 g, 1 mmole). After the catalyst had aged for 20 min, cis-1,3-divinylcyclohexane (0.48 g, 3.5 mmole) in n-heptane (5 ml) was added. All operations were carried out under a dry nitrogen cover in a dry box. The mixture was stirred for 84 hr at 75° under nitrogen and decomposed by pouring into methanol

(200 ml) to yield poly(cis-1,3-divinylcyclohexane)(0.355 g), melt temperature 115° (found: C, 87.36; H, 11.94; $(C_{10}H_{16})_n$ requires C, 88.16; H, 11.84%).

ACKNOWLEDGMENTS

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