and thermally cross-linked as described previously. The ir is shown in Figure 2.

Acid-Catalyzed Cross-Linking Reaction. A solution of 0.318 g of the biscyanato phenylene prepolymer **13b** and 0.0058 g of *p*-toluenesulfonic acid in 4 ml of 20% ether in benzene was placed in a glass ampule, freeze dried, flushed with nitrogen, and sealed. The cross-linking reaction was carried out by heating the ampoule at 350 °C for 2 h. The T_g (Table III) was measured by DSC.

Pyrolysis of the Phenylene Polymer 19a. The phenylene polymer **19a** was pyrolyzed in a glass apparatus consisting of three side arms connected to a horizontal tube. The sample, 900 mg of **19a**, was introduced into the first side arm and the system was evacuated and sealed. The sample tube was then placed in a Wood's metal bath at 200 °C and the temperature was increased to 400 °C over a 20-min period while the second side arm, consisting of a mass spectrometer sample bulb, was cooled to dry ice temperature. After 45 min at 400–425 °C the apparatus was returned to room temperature while the third side arm, a break-seal tube with a fitting for the mass spectrometer gas inlet system, was cooled in liquid nitrogen and was sealed off from the remaining apparatus. The gas and solid samples thus obtained were analyzed by mass spectroscopy.

Gas sample: *m/e* (rel intensity[24]) benzene 73 (62) and hydrogen cyanide 27 (100). Major unidentified peaks distinguishable from an air sample occurred at: 91 (44), 71 (78), and 56 (31).

Solid sample: *m/e* (rel intensity[24]) cyanuric acid 129 (12), 86 (2), 56 (2), and 43 (100). No other major peaks (>5) distinguishable from an air sample were observed.

Pyrolysis of Triphenylcyanurate (4, Ar = Ph). Triphenyl cyanurate (**4**, Ar = Ph) was pyrolyzed in a glass apparatus consisting of a break-seal tube fitted with a ground glass fitting compatible with the mass spectrometer gas inlet system. Compound **4** (Ar = Ph) was placed in the tube which was then evacuated and sealed. The sample tube was then placed in a Wood's metal bath at 200 °C and heated to 400–425 °C for 1 h. The tube was allowed to cool before it was fitted to the mass spectrometer. The break-seal was broken and the mass spectral analysis of the volatile products revealed only fragments of phenyl cyanurate: mass spectrum *m/e* (rel intensity[24]) 162 (37) $C_8H_5N_2O_2$, 131 (3) C_8H_5NO, 93 (100) C_6H_5O, and 78 (6) C_6H_6. No peak at *m/e* 65 characteristic of phenol degradation.

Solubility and Hydrolytic Stability Studies. The polymer samples were weighed in coarse fritted glass filters which had been brought to constant weight. The filters were then placed into a Soxhlet extraction apparatus and continuously extracted for 24 hr with benzene or chloroform. The filters were placed in an oven at 100 °C for 12 h, then heated at 130 °C in vacuo for 12-h periods until constant weights were achieved (generally after 24 h). The percents sol were determined from the weights of the residues and the initial weights and are listed in Table V.

The polymer samples were weighed into test tubes that had been dried at 100 °C for several hours, and 5 ml of 1 N aqueous sulfuric acid or 5 ml of 1 N aqueous potassium hydroxide were added. After 100 h at room temperature, the polymer samples were collected in coarse fritted glass filters that were at constant weight. The samples were allowed to soak in water for 1–2 h then washed with 95% ethanol. The percents sol phase were determined as previously described and the results are reported in Table V.

The phenylene polymer **19b**, 0.4036 g, was placed in 10 ml of benzene, and 5 ml of 5 N aqueous potassium hydroxide and 100 mg of tetrabutylammonium hydrogen sulfate were added. After 48 h at room temperature, the benzene phase was homogeneous. The organic phase was separated and precipitated in 95% ethanol to afford an off-white powder which was dried in vacuo at 120 °C: ir ($CHCl_3$) 3680 cm^{-1} (OH) and aromatic features.

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Synthesis and Ring-Opening Anionic Polymerization of a Paracyclophane Heterocycle

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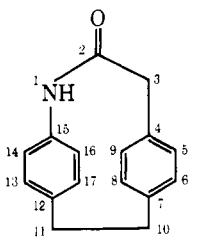
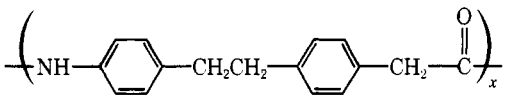
ABSTRACT: 1-Aza-2-keto[2.3]paracyclophane has been synthesized by two routes and has been polymerized with sodium hydride to poly(imino-1,4-phenylene-1,2-ethanediyl-1,4-phenylenemethylenecarbonyl).

Ring-opening anionic polymerization has been widely used to polymerize heterocycles to linear, high molecular weight polymers, often with low polydispersity. Such polymers invariably have aliphatic backbones. We wish to report the preparation of a polyamide containing aromatic rings in the backbone by ring-opening anionic polymerization of 1-aza-2-keto[2.3]paracyclophane (**1**). The lactam **1** was synthesized by Beckmann rearrangement of the oxime of 1-keto[2.2]paracyclophane[2] using sulfuric acid in dioxane. The preferred method of synthesis, however, was by the reaction of 1-keto[2.2]paracyclophane with hydrazoic acid (Schmidt reaction). The Schmidt reaction can also be carried out on 1,1-di-



1



(1)

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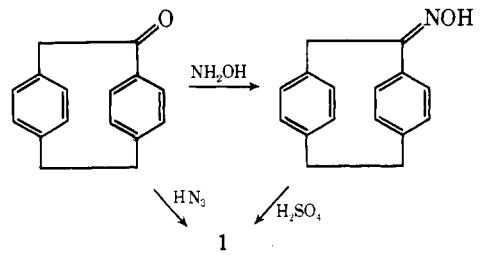
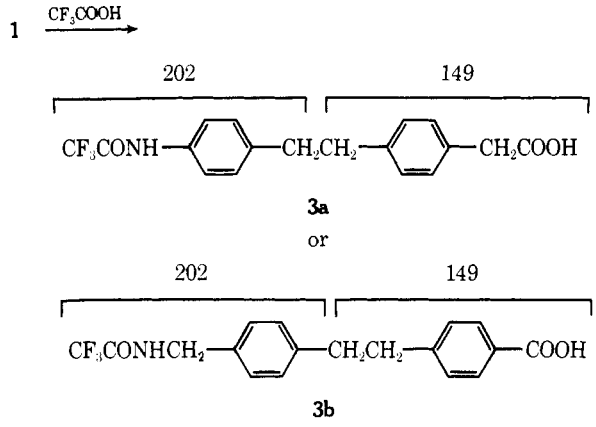


(2)

1

methoxy[2.2]paracyclophane prepared from 1-keto[2.2]-paracyclophane and methanol.

The structure of the lactam **1** is deduced from the mass spectrum of the trifluoroacetyl derivative, **3**, obtained by refluxing lactam **1** or 1-hydroxyimino[2.2]paracyclophane in trifluoroacetic acid. Strong peaks at 202 and 149 correspond respectively to $CF_3CONHC_6H_4CH_2$ (or $CF_3CONHCH_2C_6H_4$) and $CH_2C_6H_4CH_2COOH$ (or $CH_2CH_2C_6H_4COOH$). Since cleavage between adjacent benzylic CH_2 groups is much more probable than cleavage between phenyl and CH_2, structure



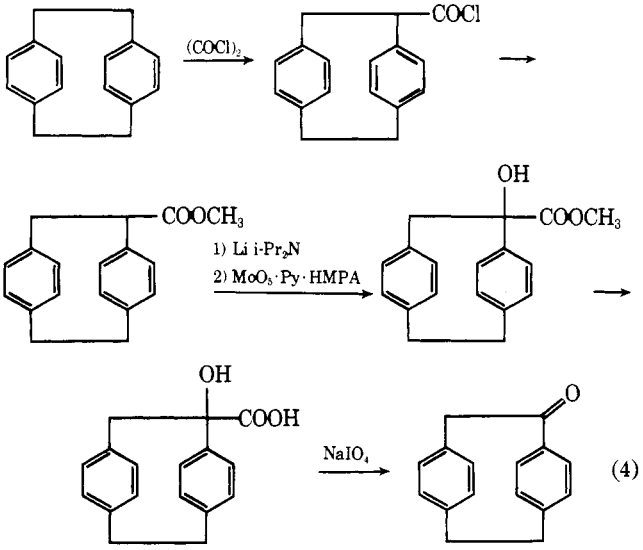
(3)

3a is assigned to the trifluoroacetyl derivative and, hence, structure **1** to the lactam.

Lactam **1** undergoes polymerization in refluxing dioxane with initiation by sodium hydride–benzoic anhydride to give poly(imino-1,4-phenylene-1,2-ethanediyl-1,4-phenylenemethylenecarbonyl) (**2**). The conversion to polymer is generally low but this is believed to be related to experimental problems in the microscale polymerization rather than an equilibrium between monomer and polymer. The polyamide, **2**, which is soluble in hexamethylphosphoramide, sulfuric acid, and dimethylacetamide/lithium chloride has an inherent viscosity of 1.83 in hexamethylphosphoramide. In dimethylacetamide/lithium chloride, the inherent viscosity is 2.56. X-ray analysis of the polyamide shows a moderate degree of crystallinity. A film of the polyamide cast from hexamethylphosphoramide[3] solution by evaporation was translucent and, in the absence of residual solvent, brittle with a tensile strength of only 464 psi. The film was shown by x ray to be mostly crystalline. The polymer decomposes at about 270 °C as indicated by differential scanning calorimetry and thermogravimetric analysis. The low thermal stability of the polymer can probably be attributed to the bibenzyl linkage and the phenylacetyl group in the backbone.

Sodium hydride alone can also be used to initiate polymerization of lactam **1** to polyamide **2**. However, the resulting polymer has a lower molecular weight (η_{inh} 1.47 in dimethylacetamide/lithium chloride) than the polymer prepared with sodium hydride–benzoic anhydride (η_{inh} 2.56 in dimethylacetamide/lithium chloride).

Because the method used[2] to prepare 1-keto[2.2]paracyclophane (i.e., reaction of [2.2]paracyclophane with *N*-bromosuccinimide) was not readily amenable to large-scale preparation of the ketone, an alternative synthesis (eq 4) was



(4)

devised starting with [2.2]paracyclophane-1-carbonyl chloride which is readily prepared by the radical-initiated reaction of [2.2]paracyclophane with oxalyl chloride.[4] The corresponding methyl ester is then converted to its anion and oxidized to the α-hydroxy ester by the method recently reported by Vedejs.[5] Hydrolysis of the ester and oxidation of the α-hydroxycarboxylic acid so obtained with sodium periodate leads to 1-keto[2.2]paracyclophane. Unfortunately, the over-all yield from this route was low, and there appeared to be no advantage over the *N*-bromosuccinimide route of Cram and Helgeson.[2]

Experimental Section

1-Hydroxyimino[2.2]paracyclophane. A mixture of 502 mg of 1-keto[2.2]paracyclophane,[2] 558 mg of hydroxylamine hydrochloride, 2.8 ml of pyridine, and 2.8 ml of ethanol was stirred at reflux under argon for 2 h and then evaporated in a stream of nitrogen. The residue was treated with cold water and filtered. The filter cake was recrystallized from methanol to give 325.4 mg (61%) of crystals of 1-hydroxyimino[2.2]paracyclophane, mp 206–207.8 °C. From the mother liquor was obtained an additional 64.2 mg (12%) of the oxime, mp 193–195 °C.

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.95; H, 6.66; N, 5.62.

1-Aza-2-keto[2.3]paracyclophane by Beckmann Rearrangement of Oxime. To a stirred solution of 1 ml of sulfuric acid in 25 ml of dioxane was added 305 mg of 1-hydroxyimino[2.2]paracyclophane. After stirring for 3 h at ambient temperature, the solution was added carefully to excess ice–dilute aqueous sodium bicarbonate. The precipitate was collected by filtration to give 284.3 mg of colorless solid. Recrystallization from toluene–heptane gave 127 mg of plates of 1-aza-2-keto[2.3]paracyclophane, which darkens above 217 °C in air.

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.79; H, 6.42; N, 5.88.

The infrared spectrum of the product shows absorption at 3150 (N–H st), 1640 (amide C=O), and 1600 and 1500 cm^{-1} (aromatic).

The NMR spectrum of the product in chloroform-*d* (δ, ppm) shows absorption at 6.3–6.7 (m, intensity 9, paracyclophane-type aromatic), 4.0 (s, intensity 2, CH_2CO), 2.98 (s, intensity 3.5, $-CH_2CH_2-$), and 3.09 (s, intensity 1, N–H?). The mass spectrum of a similar sample (prepared from the oxime using thionyl chloride) showed the molecular ion to be 237.1144 ($C_{16}H_{15}NO$ requires 237.1153). A peak at 209 represents loss of CO, and a peak at 104 represents $CH_2C_6H_4CH_2$.

4-((2-(4-Trifluoroacetamido)phenyl)ethyl)phenylacetic Acid (3a). A mixture of 295 mg of 1-hydroxyimino[2.2]paracyclophane and 7 ml of trifluoroacetic acid was stirred at reflux for 1 h and evaporated in a stream of nitrogen with gentle warming. Recrystallization of the residue from toluene gave 308 mg of crystals, mp 175–177 °C. The product was stirred with excess aqueous sodium bicarbonate and filtered. The filtrate was slowly added to excess cold hydrochloric acid, and the resulting precipitate was collected by filtration (75 mg) and recrystallized from toluene to give 45 mg of 4-((2-(4-trifluoroacetamido)phenyl)ethyl)phenylacetic acid, mp 184–184.5 °C.

Anal. Calcd for $C_{18}H_{16}NF_3O_3$: C, 61.53; H, 4.59; N, 3.99; F, 16.22. Found: C, 61.85; H, 4.51; N, 4.06; F, 16.13.

The infrared spectrum of the product shows absorption at 3310 (N–H st), 2640 (broad, COOH), 1700 (C=O), 1590 and 1510 (aromatic), and 1540 cm^{-1} (amide II). The NMR spectrum of the product in acetonitrile shows absorption (δ, ppm) at 7.19 (s, aromatic) and 7.4 (quartet, $J = 9$ Hz, aromatic), 3.56 (s, $CH_2C=O$, unaffected by added D_2O–Et_3N), and 2.91 (s, $-CH_2CH_2-$).

The mass spectrum of the product shows a molecular ion of 351.1082 (Calcd for $C_{18}H_{16}NO_3F_3$: 351.1081). A very strong peak at 202 corresponds to $CF_3CONHC_6H_4CH_2$ or $CF_3CONHCH_2C_6H_4$ and a strong peak at 149 corresponds to $CH_2C_6H_4CH_2COOH$ or $CH_2CH_2C_6H_4COOH$. Since cleavage between adjacent benzylic CH_2 groups is much more favorable than cleavage between phenyl and CH_2, the correct structure must be $CF_3CONHC_6H_4CH_2 \cdot C_6H_4CH_2COOH$.

Refluxing 23 mg of 1-aza-2-keto[2.2]paracyclophane in trifluoroacetic acid until solution was complete gave, after addition of toluene and heptane while boiling off trifluoroacetic acid, 3.8 mg of 4-((2-(4-trifluoroacetamido)phenyl)ethyl)phenylacetic acid. The infrared spectrum of the product is identical with that of authentic amido acid.

1,1-Dimethoxy[2.2]paracyclophane. A sample of 1-keto-[2.2]paracyclophane prepared from 19 g of [2.2]paracyclophane and chromatographed by the procedure of Cram[2] was recrystallized from methanol to give 2 g of crystals of 1,1-dimethoxy[2.2]paracyclophane, mp 81.5–82.5 °C.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.99; 81.06; H, 7.09, 7.03.

The ^1H NMR spectrum in chloroform-*d* (δ, ppm.) showed absorption at 6.43–6.90 (m, paracyclophane-type aromatic, 8 H), 3.47 (singlet, CH_3O, 6 H), 3.29 (singlet, $CH_2C[OR]_2$, 2 H), and 3.08 (singlet, CH_2CH_2, 4 H).

From the mother liquor was obtained 664 mg of 1-keto[2.2]paracyclophane.

1-Aza-2-keto[2.3]paracyclophane by Schmidt Reaction of 1-Keto[2.2]paracyclophane. To a stirred solution of 1.66 g of 1-keto[2.2]paracyclophane in 50 ml of dioxane was added 4 ml of sulfuric acid. The solution was cooled to 15 °C and 3.2 g of sodium azide was added portionwise, and the temperature was allowed slowly to rise. When half of the sodium azide had been added, an additional 4.5 ml of sulfuric acid was added. The remaining sodium azide was added portionwise at 30 °C. After 30 min, 4 ml of sulfuric acid was added and the temperature was allowed to rise to 45 °C while 0.5 g of sodium azide was added. After 45 min, two 0.1-g portions of sodium azide were added. After 1 h, evolution of nitrogen appeared to have ceased, and the mixture was added to excess cold aqueous sodium bicarbonate. Filtration gave 1.53 g of colorless solid. Recrystallization from toluene gave 901 mg of 1-aza-2-keto[2.3]paracyclophane. The infrared spectrum of the product is identical with that of authentic 1-aza-2-keto-[2.3]paracyclophane.

The ultraviolet spectrum of the product in 95% ethanol shows absorption at 219 mμ (ε 13 444) with shoulders at 265 mμ (ε 2940) and 305 mμ (ε 195). In ether solution, the spectrum is the same but with slightly lower extinction coefficients.

1-Aza-2-keto[2.3]paracyclophane by Schmidt Reaction of 1,1,-Dimethoxy[2.2]paracyclophane. To a stirred solution of 1.95 g of 1,1-dimethoxy[2.2]paracyclophane in 50 ml of dioxan at 15 °C under argon was added 4 ml of sulfuric acid. Then 1.6 g of sodium azide was added portionwise while allowing the mixture to warm to 35–40 °C. An additional 4 ml of sulfuric acid was added followed by portionwise addition of 1.6 g of sodium azide with the temperature at 40 °C. After 30 min 0.2 g of sodium azide and 0.8 ml of sulfuric acid were added. After 2 h, the mixture was added to excess aqueous sodium biccarbonate, and the precipitate was collected by filtration to give 1.498 g (87%) of 1-aza-2-keto[2.3]paracyclophane. Recrystallization from toluene gave 1.044 g of colorless plates. The infrared spectrum of the product is identical with that of authentic 1-aza-2-keto[2.3]paracyclophane.

Polymerization of 1-Aza-2-keto[2.3]paracyclophane with NaH/Benzoic Anhydride. To a stirred solution of 237.3 mg of 1-aza-2-keto[2.3]paracyclophane in 5.5 ml of anhydrous dioxane at 90 °C under argon was added 1.3 mg of benzoic anhydride and 0.4 mg of 57.1% sodium hydride dispersion in mineral oil. As soon as the sodium hydride was added, swollen polymer began to separate. The mixture was refluxed for 3 h and then added to excess dioxane containing a little acetic acid and filtered. After washing with dioxane and with ether, 55.2 mg of polymer was obtained.

Anal. Calcd for $(C_{16}H_{15}NO)_x$: C, 80.98; H, 6.37; N, 5.90. Found: C, 78.61, 77.91; H, 6.61, 6.30; N, 5.53, 5.45.

From the filtrate was obtained 132 mg of 1-aza-2-keto[2.3]paracyclophane.

The polymer is soluble in dimethylacetamide/3% lithium chloride, sulfuric acid (warming at 100 °C), and hexamethylphosphoramide.[3]

The infrared spectrum (Nujol) of the polymer shows absorption at 3289 (N–H st, H bonded), 1667 (C=O), 1605 and 1534 (shoulder), and 1515 cm^{-1} (aromatic C=C and amide II). η_{inh} 1.93 (hexamethylphosphoramide, 0.5% at 30 °C). A sample of polymer having η_{inh} 1.83 in hexamethylphosphoramide (0.5% at 30 °C) has η_{inh} 2.56 in dimethylacetamide containing 3% lithium chloride (0.5% at 30 °C). Differential scanning calorimetry shows an exotherm peaking at 279 °C. Thermogravimetric analysis in air shows weight loss beginning at 275 °C, with 52% weight loss at 490 °C. In nitrogen, weight loss begins at 290 °C, with 37% weight loss at 470 °C. A hazy film can be cast from hexamethylphosphoramide solution by baking out the solvent. The film is strong and flexible until the last traces of solvent are removed and then becomes brittle. X-ray analysis of the film shows it to be mostly crystalline.

When the polymerization experiment was repeated without using any benzoic anhydride, the polymerization began instantaneously giving 37 mg of polymer (after 17 h) and 122.2 mg of recovered lactam after recrystallization from dioxane. The polymer has η_{inh} 1.47 (0.5% in dimethylacetamide with 3% lithium chloride at 30 °C).

Larger Scale Polymerization of 1-Aza-2-keto[2.3]paracyclophane. To a mechanically stirred solution of 787 mg of 1-aza-2-keto[2.3]paracyclophane in 20 ml of hot dioxane was added 3.7 mg of benzoic anhydride followed by 10 mg of 57% sodium hydride dispersion in mineral oil. The mixture was stirred at reflux for 18 h. Polymer began to precipitate soon after the sodium hydride was added. The mixture was added to 100 ml of hot dioxane containing 1 ml of acetic acid and filtered. The filter cake was washed well with methanol and dried to give 551 mg (70%) of polymer which is soluble in hexamethylphosphoramide. η_{inh} 1.83 (0.5% in hexamethylphosphoramide at 30 °C).

Anal. Calcd for $(C_{16}H_{15}NO)_x$: C, 80.98; H, 6.37; N, 5.90. Found: C, 79.79, 79.99; H, 6.43, 6.42; N, 5.87, 5.78.

Methyl 1-Hydroxy[2.2]paracyclophane-1-carboxylate. To 3.60 ml of diisopropylamine in 25 ml of ether was added dropwise 16 ml of 1.56 M methyllithium in hexane while cooling in an ice–water bath. The resulting solution was then stirred for 15 min at 0–5 °C. To a stirred mixture of 5.8 ml of the lithium diisopropylamide solution and 15 ml of 2:1 tetrahydrofuran–hexane at −70 °C was added from a dropping funnel a solution of 672.6 mg of methyl [2.2]paracyclophane-1-carboxylate[4] in 12 ml of tetrahydrofuran. After 30 min at −70 °C, 1.4226 g (3.25 mmol) of MoO_5/pyridine/hexamethylphosphoramide[5] was added in one portion with stirring. After 1 h at −70 °C, the mixture was allowed to warm to −10 °C (mixture became homogeneous at −40 °C and a precipitate formed above that temperature) and was then treated with water and extracted with ether. The ether extract was washed with 5% sodium carbonate and 5% hydrochloric acid, dried, and evaporated to an oil which partially crystallized. The product was chromatographed on Florisil (20 g). Elution with 7% ether in petroleum ether (1.4 liters) and 20% ether in petroleum ether (200 ml) followed by recrystallization from heptane gave 82.2 mg of methyl 1-hydroxy[2.2]paracyclohexane-1-carboxylate, mp 79–81.5 °C.

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.60; H, 6.54.

1-Hydroxy[2.2]paracyclophane-1-carboxylic Acid. A mixture of 73.2 mg of methyl 1-hydroxy[2.2]paracyclophane-1-carboxylate, 5 ml of 95% ethanol, and 1 pellet of sodium hydroxide was stirred at room temperature under nitrogen for 24 h and then concentrated in a stream of nitrogen; the residue was treated with 10% hydrochloric acid and filtered. The filter cake was washed with water to give 55.1 mg of 1-hydroxy[2.2]paracyclophane-1-carboxylic acid. Recrystalli-

zation from benzene gave 25.6 mg of crystals, mp 159–163 °C.

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 77.56, 77.34; H, 6.38, 6.21.

The infrared spectrum of the product shows absorption at 3400 (OH st), 2600–2700 (COOH), and 1700 cm^{-1} (C=O).

1-Keto[2.2]paracyclophane from 1-Hydroxy[2.2]paracyclophane-1-carboxylic Acid. A mixture of 130 mg of 1-hydroxy-[2.2]paracyclophane-1-carboxylic acid, 2.4 ml of acetone, 2.4 ml of acetic acid, 0.6 ml of water, and 600 mg of powdered sodium periodate was stirred at 45 °C for 20 h, concentrated in a stream of nitrogen, treated with cold water, and filtered to give 80.7 mg (75%) of 1-keto-[2.2]paracyclophane.

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(3) In recent inhalation studies at our Haskell Laboratory for Toxicology and Industrail Medicine, hexamethylphosphoramide has been found to be carcinogenic in rats. Accordingly, any work with hexamethylphosphoramide should be carried out in an efficient hood to avoid inhalation of vapors. Since it is absorbed by the skin, care should be taken to avoid contact with hexamethylphosphoramide.
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Kinetic Study of Polymerization of 2-*tert*-Butyl-7-oxabicyclo[2.2.1]heptane

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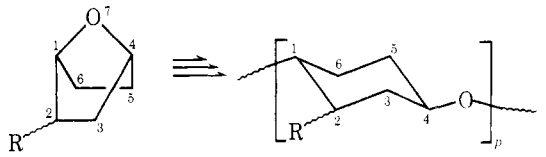
ABSTRACT: Kinetics of the polymerizations of *exo*- and *endo*-2-*tert*-butyl-7-oxabicyclo[2.2.1]heptanes (**1a** and **1b**) were studied by means of the Phenoxyl End-Capping method. The propagation rate constants and the activation parameters were determined. The reactivities of **1a** and **1b** were discussed and compared with those of the methyl homologues.

This paper describes a kinetic study of the cationic polymerizations of *exo*- (**1a**) and *endo*-2-*tert*-butyl-7-oxabicyclo-[2.2.1]heptanes (**1b**) in CH_2Cl_2 with BF_3–tetrahydrofuran (THF) complex–epichlorohydrin (ECH) system as initiator. As reported in our preceding paper,[1] propagation in the polymerization of *tert*-butyl monomers proceeds via an SN2 reaction between the monomer and the propagating oxonium ion. Polymerizations of the *tert*-butyl monomers suffered from fairly rapid termination to generate olefinic ends. Such termination was not significant in the polymerizations of the methyl homologues. In our previous papers,[2,3] the polymerization reactivities of **2a** and **2b** (the methyl homologues) were



1a, R = *exo*-$(CH_3)_3C$ **2a**, R = *exo*-CH_3
b, R = *endo*-$(CH_3)_3C$ **b**, R = *endo*-CH_3

also examined. The effects of size and geometric position (exo or endo) of the alkyl substituent of bicyclic ether monomer on the polymerization reactivity are of great interest. In the present paper, the polymerization reactivities of **1a** and **1b** are examined and compared with those of the methyl homologues.

Solution polymerizations of **1a** and **1b** were carried out in CH_2Cl_2 at temperatures in the range between −40 and 0 °C. Figures 1 and 2 show the time–[P*] (concentration of propagating species) profiles of their polymerizations, in which [P*] was determined by the "Phenoxyl End-Capping" method.[4] It is indicated that the decrease of [P*] becomes pronounced at higher reaction temperatures. This observation is in agreement with the result of our previous study in which the olefin contents of the product polymers prepared at various temperatures were analyzed by ir spectroscopy.[1]

The polymer yield was low as shown in time–conversion curves (Figures 3 and 4). The kinetic analysis was performed in an early stage of polymerization, because the concentration of olefinic linkages formed by termination became significant as polymerization progressed. This disturbed the determination of [P*] by uv absorption of phenoxyl group at 272 nm in the "Phenoxyl End-Capping" method. As shown in the spectra of the polymers obtained under varying conditions (Figure 5), the absorption curve for the phenoxyl group was deformed as polymerization proceeded, especially at elevated temperatures. The points in parentheses in Figures 1 and 2 were obtained on the basis of the deformed uv spectra. Therefore, these points were not used in the subsequent kinetic analysis. The formation of olefinic linkage was observed at similar concentrations when the polymerization mixture was not treated with sodium phenoxide. Thus, the olefinic group at the polymer end is not generated by "Phenoxyl End-Capping" reaction.

The rate of monomer consumption in the propagation step is formulated according to the SN2 reaction between the propagating species and the monomer:

$$-d[M]/dt = k_p[P^*][M] \quad (1)$$

where [M] and k_p are the monomer concentration and the propagation rate constant, and [P*] has already been described above. In the cases of **2a** and **2b**, the propagation step was established to be irreversible by a depolymerization experiment in which the purified polymers of **2a** and **2b** were treated with $Et_3O^+SbCl_6^-$ at −20 °C for 96 h to generate no monomer by gas chromatographic analysis.[2,3] In poly(**1a**) and poly(**1b**), the depolymerization by the cyclization of the monomeric unit of polymer into the monomer is also deemed impossible. Therefore, the propagations of **1a** and **1b** are considered to be irreversible processes. Integration of eq 1 between times t_1 and t_2 gives eq 2, where $[M]_{t_1}$ and $[M]_{t_2}$ are monomer concentrations at times t_1 and t_2. The integrated value of [P*] could be obtained by graphical integration of the time–[P*] curve, and the monomer concentrations were calculated from the amount of polymer produced. A plot of $\int_{t_1}^{t_2}[P^*]\,dt$ vs. $\ln([M]_{t_1}/[M]_{t_2})$ gave a linear relationship as exemplified in Figures 6 and 7. The k_p value was obtained from the slope of the line. Arrhenius plots of the k_p values gave the activation parameters (Figure 8). In Table I, the k_p's and