Alkaline Hydrolysis of 6a and Decarboxylation to 12. To a refluxing solution of NaOH (3.0 g, 75 mmol) in H_2O (30 mL), which had been purged with N_2 for 0.5 h, was added 6 (2.5 g, 7.48 mmol). Reflux under N_2 was continued for 2.5 h; the solution was then cooled to 50 °C and acidified to pH 1.0 with 37% HCl (CO_2 evolution). After cooling to 5 °C, the solution was filtered and the solid washed with H_2O and dried in air to give the monohydrate of 12, mp 277–278 °C dec. Recrystallization was carried out by dissolving the solid in the minimum amount of 95% EtOH, treating with Norite, filtering, and adding two volumes of H_2O. Air drying gave pure 12 H_2O: mp 282–284 °C; M^+ *m/e* 262; IR (KBr) 3255, 1735, 1710, 1615, and 1600 cm^{-1}; UV λ_{max}(EtOH) 280 nm (ϵ 2200), 223 (8500, shoulder), and 210 (14 000). The NMR spectrum (acetone-d_6) of a sample that had been dried under high vacuum overnight (100 °C) showed absorptions at δ 1.95 (dd, 1 H, J = 17.0 and 11.0 Hz), 2.18–3.05 (m, 7 H), 3.52–3.82 (m, 1 H), 5.55 (s, broad, 1 H), 6.18 and 6.30 (AB system, J_{AB} = 2.3 Hz, meta ArH), and 3.46 (s, broad, 2 H).

Anal. Calcd for $C_{14}H_{14}O_5 \cdot H_2O$: C, 62.66; H, 6.02. Found: C, 62.60; H, 5.70.

Methylation of 12 to 13. To a solution of dimethyl sulfate (1.52 g, 12.0 mmol) in acetone (20 mL) were added 12 (800 mg, 3.05 mmol) and anhydrous K_2CO_3 (1.66 g, 12.0 mmol). The solution was refluxed during 5 h with stirring, cooled, filtered, and evaporated to give 13. Two recrystallizations from 2-propanol gave pure material: mp 107–109 °C; M^+ *m/e* 304; IR ($HCCl_3$) 1740, 1730, 1610, and 1590 cm^{-1}; UV λ_{max}(EtOH) 280 nm (ϵ 2100), 224 (8460, shoulder), and 209 nm (14 300); NMR ($DCCl_3$) δ 1.91 (dd, 1 H, J = 17.5 and 12.0 Hz), 2.29 (d, 1 H, J = 17.5 Hz), 2.45–3.07 (m, 6 H), 3.50–3.68 (m, 1 H), 3.75 (s, 3 H, OCH_3), 3.78 (s, 6 H, 2 OCH_3), 6.26 and 6.32 (AB system, J_{AB} = 2.4 Hz, meta ArH).

Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.14; H, 6.72.

X-Ray Crystallography. Preliminary experimental techniques and data collection methods were standard for this laboratory and have been described previously.[14] Details are given in Table I. As the crystal system was triclinic, there was a possible ambiguity as to the space group, but since the compound is racemic and there were two molecules in the unit cell, $P\bar{1}$ was assumed and appears confirmed by the successful refinement. Programs used for most computations were from the XRAY72 system,[15] but the structure was solved using MULTAN.[16]

All but two of the heavier atoms were visible in the *E* map. The missing atoms, including hydrogen, were found by a sequence of least-squares refinements and difference maps and the structure was finally refined using a partitioned full-matrix least squares approach with anisotropic thermal parameters for the heavier atoms, to an *R* factor of 4.5%. Final parameters are given in Tables II and III. (See paragraph at end of paper concerning supplementary material.)

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Registry No.—3, 58648-32-1; **6a,** 62562-54-3; **7,** 62562-55-4; **8,** 62562-56-5; **12,** 62562-57-6; **13,** 62562-58-7; dimethyl 3-ketoglutarate, 1830-54-2; glyoxal, 107-22-2.

Supplementary Material Available. Tables of final parameters and torsion angles (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 4: K. C. Rice, U. Weiss, T. Akiyama, R. J. Highet, T. Lee, and J. V. Silverton, *Tetrahedron Lett.*, 3767 (1975).

(2) All compounds described are racemic; for the formulas, one antipode has been chosen arbitrarily.

(3) For a recent example of a closely analogous reaction, see A. Gerhard, R. Muntwyler, and W. Keller-Schierlein, *Helv. Chim. Acta*, **58**, 1323 (1975). In the case described there, the need for activation of the proton by the double bonds was proven: hydrogenation yielded an alkali-stable compound.

(4) For a recent review of such processes, see R. Morrin Acheson, *Acc. Chem. Res.*, **4**, 177 (1971).

(5) N. E. Holden and A. Lapworth, *J. Chem. Soc.*, 2368 (1931).

(6) A. Michael and J. Ross, *J. Am. Chem. Soc.*, **52**, 4598 (1930).

(7) J. M. Edwards, I. H. Qureshi, U. Weiss, T. Akiyama, and J. V. Silverton, *J. Org. Chem.*, **38**, 2919 (1973).

(8) U. Weiss and J. M. Edwards, *Tetrahedron Lett.*, 4885 (1968).

(9) K. C. Rice, N. E. Sharpless, U. Weiss, and R. J. Highet, *Tetrahedron Lett.*, 3763 (1975).

(10) C. K. Johnson (1965), ORTEP, Oak Ridge National Laboratory, Report ORNL-3794.

(11) R. Bucourt, *Top. Stereochem.*, **8**, 159 (1974).

(12) C. Altona, H. L. Geise, and C. Romers, *Tetrahedron*, **24**, 13 (1968).

(13) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957). The correction factor used was 0.0004I^2.

(14) J. V. Silverton and H. A. Lloyd, *Acta Crystallogr., Sect. B*, **31**, 1576 (1975).

(15) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, "The X-Ray System", Technical Report TR-192, Computer Center, University of Maryland, 1972.

(16) P. Main, M. M. Woolfson, and G. Germain, "MULTAN. A Computer Program for the Automatic Solution of CRYSTAL Structures", Universities of York and Louvain, 1971.

1,3-Butadiene-2,3-dicarboxylic Acid Derivatives from Cyclohexene-1,2-dicarboxylic Acid Analogues

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Vapor-phase pyrolysis of dimethyl cyclohexene-1,2-dicarboxylate (1), and of cyclohexene-1,2-dicarbonitrile (3), at 700–800 °C and a few hundredths of a second contact time gave dimethyl 1,3-butadiene-2,3-dicarboxylate (4) and 1,3-butadiene-2,3-dicarbonitrile (12) in about 50 and 90% (ultimate) yields, respectively. Similar pyrolysis of *N*-methylcyclohexene-1,2-dicarboximide (2) gave a polymeric product, apparently arising from (labile) *N*-methyl-1,3-butadiene-2,3-dicarboximide (8). Evidence for the formation of 8 was obtained by isolation of its dimer *N,N'*-dimethyl-4-vinylcyclohexene-α,1,2,4-tetracarboxdiimide (9), and by trapping it with *N*-methylmaleimide, producing *N,N'*-dimethylcyclohexene-1,2,4,5-tetracarboxdiimide (10).

Derivatives of 1,3-butadiene-2,3-dicarboxylic acid are difficult to prepare; consequently, their chemistry has not been well studied. Esters of this type have been prepared by pyrolysis of dimethyl cyclohexene-1,2-dicarboxylate (1),[1] dimethyl 2,3-diacetoxy-2,3-dimethylsuccinate,[2] and diethyl 2,3-bis(1-piperidinomethyl)succinate dihydrochloride,[3] while the dinitrile has been prepared by pyrolysis of 2,3-diacetoxy-2,3-dimethylsuccinonitrile.[2,4,5] Because the method has not been well documented, and because of the potential value of these compounds, we have reinvestigated some of these pyrolytic syntheses. Very recently, the thermal rearrangement of derivatives of cyclobutene-1,2-dicarbonitrile has been shown to provide ready access to dienes of this type.[6,7]

Although the retro-Diels–Alder cleavage of cyclohexenes

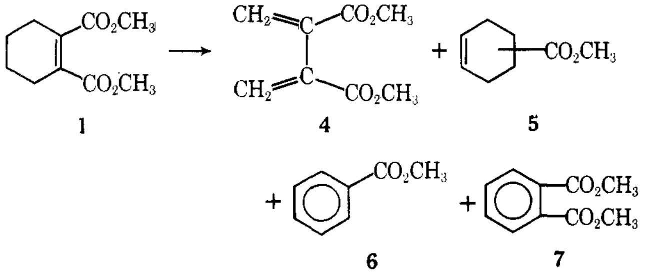
Table I. Pyrolysis of Dimethyl Cyclohexene-1,2-dicarboxylate (1)[a]

Temp, °C	Pressure, mmHg	Contact time, ms	% conversion (by VPC)[b]	VPC[b] % selectivity 4	5	6	7
600	~150[c]	50–60	4	23	32	5	
700	~150[c]	50–60	17	48	15	15	
750	~150[c]	50–60	22	38	9	21	
800	~150[c]	50–60	41	15	2	18	
900	~150[c]	50–60	60	10	0	10	
1000	~150[c]	50–60	87	11	0	3	
700	~12	25–30	17	47	21	9	2
750	~12	25–30	33	47	5	21	5
800	~12	25–30	60	40	1	42	

[a] Added neat to the system described in the Experimental Section. [b] Analysis on a 5 ft × 0.25 in. column packed with 5% Carbowax M on 40/60 mesh Chromosorb T. [c] Added as a 10 wt % solution in benzene; biphenyl formation interfered with VPC determination of 7.

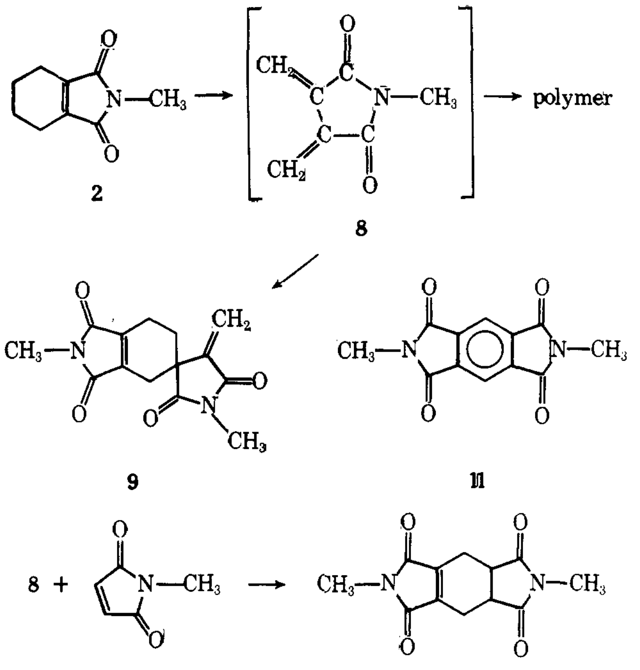
such as 1 is a relatively high energy process,[8] the ready availability of the necessary precursors (by isomerization of the Diels–Alder adduct of, e.g., butadiene and maleic anhydride) makes this at least potentially an attractive route to butadiene-2,3-dicarboxylic acid derivatives. We wish to report here the results of our work with 1, *N*-methylcyclohexene-1,2-dicarboximide (2), and cyclohexene-1,2-dicarbonitrile (3) as sources of dimethyl butadiene-2,3-dicarboxylate (4), *N*-methylbutadiene-2,3-dicarboximide (8), and butadiene-2,3-dicarbonitrile (12), respectively.

Gas-phase pyrolysis of 1 using very short contact times (Table I) gave 4 in about 50% (ultimate) yields. The retrograde Diels–Alder process occurred at temperatures somewhat above 600 °C. Competing processes seriously affected the desired reaction route, i.e., production of diene 4 and ethylene; these other major processes yielded, inter alia, methyl cyclohexenecarboxylate (5), methyl benzoate (6), dimethyl phthalate (7), and small amounts of dimethyl maleate and fumarate. For comparison, the thermal stabilities of materials related to 1 and some of the observed by-products were noted under the same conditions. Thus, at 700 °C and a contact time of 30–40 ms, 1 underwent ca. 30% conversion, 6 and 7 were essentially inert, dimethyl maleate isomerized to dimethyl fumarate but was otherwise unchanged, and dimethyl cyclohexane-1,2-dicarboxylate underwent ca. 7% conversion (at 150 ms contact time, to undetermined products). The relative instability of 1 may be a consequence of its ability to undergo a cycloreversion process, a reaction path unavailable to these other materials.



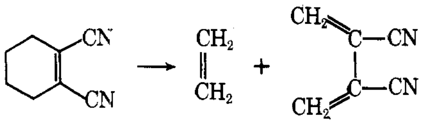
Pyrolysis of imide 2 occurred at temperatures above ca. 650–700 °C. Although VPC conversions were high at, e.g., ca. 800 °C and 15–20 ms contact time, diene 8 could not be isolated. Disproportionation of 2 giving *N*-methylphthalimide and its saturated derivative, and a degradation yielding hydrogen cyanide at higher temperatures, were noted. These two processes, however, contributed to no more than perhaps 10% of the total product.

All attempts to isolate monomeric diene 8 were futile. That it had been formed was demonstrated conclusively by the isolation of its dimer, *N,N'*-dimethyl-4-vinylcyclohexene-α,1,2,4-tetracarboxdiimide (9), although the major product was polymeric. Further, the diene 8 was "trapped" as the expected Diels–Alder adduct *N,N'*-dimethyl-1-cyclohexene-1,2,4,5-tetracarboxdiimide (10) when the pyrolysis was carried out in the presence of *N*-methylmaleimide (no 10 was noted in the absence of the latter). Although polymer formation and attendant separation difficulties prevented good yield data from being obtained, both the total (VPC) yield of 9 and 10 and the yield of 10 relative to 9 increased as the *N*-methylmaleimide concentration was increased. Thus, from VPC data, by assigning a value of 1.0 to the relative yield of 9 with no added maleimide, the total relative yield of 9 and 10 increased from 3.3 to 7.1 and the product ratio of 10 to 9 increased from 0.22 to 1.14 as the molar ratio of *N*-methylmaleimide to 2 was increased from 1.5 to 6.0. Another pyrolysis product of 2, isolated in very low yield in the absence of the maleimide, was *N,N'*-dimethylpyromellitdiimide (11).



The reasons for the instability of the exocyclic diene 8 are not clear. An earlier attempt to prepare the anhydride related to 8 by pyrolysis of 2,3-diacetoxy-2,3-dimethylsuccinic anhydride gave 2,3-dimethylmaleic anhydride.[2] Similarly, dehydration of 1,3-butadiene-2,3-dicarboxylic acid, even under mild conditions, gave only the dianhydride dimer related to 9.[3] Further unsuccessful attempts to isolate anhydrides of this type have been made.[9] In this connection, it may be noted that cyclobutane- and 3-cyclobutene-1,2-dicarboxylic anhydrides are known, while 1-cyclobutene-1,2-dicarboxylic anhydride (a valence tautomer of the anhydride analogous to 8) has never been reported and may be incapable of existence in a free state.[10]

Pyrolysis of the dinitrile **3** occurred smoothly at 750–800 °C and a 15-ms contact time to give 85–90% (VPC) yields of the diene **12**. Hydrogen cyanide was never detected in the gaseous by-products; indeed, there were no significant byproducts formed in this remarkably clean process. In some large-scale runs utilizing recycling of recovered cyclohexene **3**, isolated yields of recrystallized diene **12** were 72–83%.



3 **12**

Another theoretically possible, although energetically unfavorable,[8] mode of decomposition of the cyclohexene system is the formation of two molecules of ethylene and a molecule of acetylene. With cyclohexene **3**, such a process would yield dicyanoacetylene. This latter material (stable under the reaction conditions) could be detected in no more than trace amounts (if any at all, by VPC) among the pyrolysis products from **3**; it is thus doubtful[11] that this mode of degradation plays more than a minute role in the retro-Diels–Alder reaction of cyclohexenes of this type.

Because of isolation and analytical problems, a direct comparison of the relative stabilities of the cyclohexenes **1**, **2**, and **3** toward a retro-Diels–Alder cycloreversion may not be entirely practical. However, from some representative runs at 750 °C and a contact time of ca. 40 ms, these cyclohexenes underwent conversions of 38, 72, and 95%, respectively, suggesting that the order of thermal stability is ester **1** > imide **2** > nitrile **3**.

Experimental Section[13]

Dimethyl cyclohexene-1,2-dicarboxylate (1) was prepared by esterification of cyclohexene-1,2-dicarboxylic anhydride with methanol in the presence of TsOH at 125 °C (autoclave): ^{1}H NMR ($CDCl_3$) δ 3.74 (s, CH_3, 6), 2.32 and 1.65 (m, CH_2, 4 each). The anhydride was prepared by the P_2O_5-catalyzed isomerization[14] of readily available 4-cyclohexene-1,2-dicarboxylic anhydride.

***N*-Methylcyclohexene-1,2-dicarboximide (2).** A solution of 304 g (2 mol) of cyclohexene-1,2-dicarboxylic anhydride in 500 mL of ethanol was stirred while 62 g (2 mol) of gaseous methylamine was added below the liquid level under a dry ice–acetone condensor. Complete solution occurred shortly with a mildly exothermic reaction. The solution was heated under reflux overnight. After removal of the ethanol in vacuo, the residual syrup was taken up in ether. Chilling the ether at −70 °C gave the imide **2** in several crops[15] (total yield of 320 g, 96%) as white crystals: mp 51–52 °C (from ether); IR (KBr) 1730, 1785 cm^{-1} (s and w, C=O); ^{1}H NMR ($CDCl_3$) δ 2.96 (s, CH_3, 3), 2.34 and 1.77 (m, CH_2, 4 each). Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.47. Found: C, 65.38; H, 6.63; N, 8.56.

Cyclohexene-1,2-dicarbonitrile (3) was prepared in a multistep synthesis[16] from cyclohexene-1,2-dicarboxylic anhydride via the imide [by treatment with urea in refluxing xylene, removing water azeotropically; mp 172–174 °C; IR (KBr) 3330 (NH), 1755 and 1725 cm^{-1} (w and vs, C=O)] and the diamide [by treating the imide with aqueous ammonium hydroxide and ammonia at 0 °C; mp 230–231 °C; IR (KBr) 3360 and 3170 (NH_2), 1640 and 1610 cm^{-1} (C=O)]. Reaction of the diamide with phosgene in pyridine at 80 °C on a large scale (1–2 mol) gave a reaction mixture that was worked up by the published procedure[16b] with great difficulty. The following modification allowed a much easier isolation of **3**. The pyridine reaction mixture, after addition of phosgene, was dissolved in a mixture of chloroform and toluene. After addition of cyclohexane, the solution was heated at 100 °C to remove the chloroform. This gave pyridine hydrochloride as a granular solid that was easily removed. The solution was then washed successively several times with hot water, hot aqueous potassium hydroxide, and hot water. After drying over magnesium sulfate, the solvents were removed to give the solid dinitrile **3** (50–75% yields): mp 95–96 °C (from cyclohexane and tetrahydrofuran); IR (KBr) 2210 (CN), 1580 cm^{-1} (C=C); UV (acetonitrile) λ_{max} 232 nm (ϵ 12 200); ^{1}H NMR ($CDCl_3$) δ 2.45 (m, CH_2, 4), 1.84 (m, CH_2, 4).

General Pyrolysis Procedures. The reactor consisted of a 1 × 12 in. quartz tube packed with quartz chips, and was held at an angle of ca. 30° from the horizontal. Heating was by a two-element electrical tube furnace controlled by Thermo Electric 400 controllers. The cyclohexene to be pyrolyzed was vaporized neat or in a solvent by dropping via a pressure-equalized dropping funnel into a pot packed with glass beads held at about 250 °C; the vaporization pot was connected to the upper end of the pyrolysis tube by an adaptor heated with a heating tape. Provision was also made for addition of nitrogen, controlled via a flow meter, through the vaporization pot into the system. Effluent from the furnace was collected in suitable traps.

Typically, the system was evacuated to the desired pressure, with the furnace and vaporization system preheated to the desired temperature. The reactant was then added dropwise at a rate such as to give the desired contact time. This was calculated by the expression

$$\text{contact time (ms)} = \frac{1000 \times \text{reactor void space (mL)} \times \text{addition time (s)}}{\text{volume of gas added (mL)}}$$

with the gas volume described as

$$\frac{760}{\text{mm pressure}}\,\frac{\text{T (K)}}{273}\left[22\,400\left(\frac{\text{g reactant}}{\text{mol wt}} + \frac{\text{g diluent}}{\text{mol wt}}\right)\right]$$

and the reactor void space calculated as the volume of the reactor less the "net" volume of the quartz chip packing (by measurement of the displaced liquid in a graduate cylinder). After addition of reactant was completed, and a few (10–15) minutes had elapsed, the reactor was opened in a stream of nitrogen. The reactor system was cleaned as desired by burning out in a stream of air.

Pyrolysis of Diester 1. The ester **1** (150 g) was added dropwise to the reactor system at 700 °C and 10 mm pressure over a period of 105 min (the reactor was packed with 50 mL of quartz chips; contact time was ca. 40 ms). The effluent was passed through two traps, cooled in ice and dry ice–acetone, respectively, to give a total of 114.5 g of product. This material was rapidly distilled through a 6-in. Vigreux column from a steam bath under high vacuum, removing 18.4 g of a distillate (VPC analysis on the column described in the footnote to Table I indicated about 12% diester **1**, 3% dimethyl fumarate, 18–19% **5**, 22% **6**, and 34% diene **4**), leaving 87 g of residual oil (analyzing 91–92% diester **1**, 4% diene **4**, and 4% dimethyl phthalate **7**). The latter was recycled through the reactor. Material distilled in this manner from several runs was combined (ca. 40 g), diluted with an equal volume of ether, and chilled at −70 °C to give a crystalline solid. Filtering gave 12.6 g of diene **4** (low melting, purity about 90% by VPC). This was distilled under high vacuum, after addition of a little hydroquinone, to give pure (99.7% by VPC) diene **4**: bp 62 °C (0.3 mm); mp 17–18 °C; IR (neat) 1725 (C=O), 1620 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ 6.26 and 5.83 (CH_2=, J_{gem} = 1.5 Hz), 3.75 (s, CH_3); mass spectrum *m/e* (rel intensity) 170 (55, M$^+$). Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.45; H, 5.95.

Pyrolysis of Imide 2. A 50% solution of **2** in dimethyl phthalate was pyrolyzed at 750 °C and 10 mm pressure. The effluent, a viscous and sticky liquid (similar in consistency to a heavy rubber cement), was collected in the manner described for the pyrolysis of **1**. Combined product from several runs was distilled under high vacuum through a short-path column, removing solvent and small amounts of easily volatilized products. The residue, from a mixture of tetrahydrofuran and ether, gave a tarry solid that was removed. Further standing allowed slow deposition of the diene dimer **9** as almost white crystals: mp 139–140 °C (from tetrahydrofuran); IR (KBr) 1690 and 1760 cm^{-1} (s and w, imide C=O); ^{1}H NMR (DMF-d_6) δ 6.23 and 5.81 (2 s, CH_2=, 2), 3.01 and 2.93 (2 s, CH_3, 6), 2.67 (m, CH_2, 4), 2.09 (m, CH_2, 2); ^{13}C NMR (Me_2SO-d_6) δ 177.9, 169.8, and 167.6 (C=O), 142.4, 140.1, and 138.4 (C=), 119.2 (H_2C=), 43.2 (quaternary C), 28.7, 26.9, and 17.2 (CH_2), 24.5 and 23.2 (CH_3); mass spectrum *m/e* (rel intensity) 274 (100, M$^+$), 259 (15), 245 (10), 217 (17), 189 (28), 132 (29), 104 (20). Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.30; H, 5.15; N, 10.21. Found: C, 61.42; H, 5.27; N, 10.93.

In a run utilizing no solvent, imide **2** at 700 °C, 25 mm pressure, and a contact time of about 120 ms, gave a dark-colored effluent oil that deposited a crystalline solid upon standing. This product was collected and recrystallized from tetrahydrofuran to give *N,N'*-dimethylpyromellitdiimide (**11**) as large, hard plates: mp 375–378 °C (sealed tube); IR (KBr) 1690 and 1750 cm^{-1} (imide C=O); mass spectrum *m/e* 244 (M$^+$). Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47. Found: C, 59.12; H, 3.39; N, 11.59.

Representative of the runs utilizing *N*-methylmaleimide, a solution of 5 g of imide **2**, 5 g of *N*-methylmaleimide, and 25 g of dimethyl phthalate was vaporized into the furnace at 750 °C, 2.5 mm pressure, and a contact time of ca. 10 ms. Effluent[17] from the traps was poured slowly into 600 mL of ether, giving several crops of crystalline solid upon standing. These were combined and recrystallized twice from tetrahydrofuran to give the Diels–Alder adduct **10** as flocculent, cream-colored crystals: mp 202–203 °C; IR (KBr) 1695 and 1760 cm^{-1} (s and w, imide C=O); ^{1}H NMR (DMF-d_6) δ 3.4–3.7 (m, CH, 2), overlapping resonances at 2.90 and 2.87 (2 s, CH$_3$), and 2.7–3.1 (m, CH$_2$) (total of 10 H); mass spectrum *m/e* (rel intensity) 248 (40, M$^+$), 244 (26), 200 (15), 191 (23), 163 (36), 106 (100), 105 (65). Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.09; H 4.90; N, 12.05.

Pyrolysis of Dinitrile 3. In a typical run, a solution of 25 g of dinitrile **3** and 25 g of benzonitrile was vaporized into the pyrolysis apparatus at 775 °C, 10 mm pressure, and a contact time of ca. 21 ms. The effluent (ca. 29 g) from a series of traps at −70 °C was taken up in 30 mL of tetrahydrofuran. Chilling at −20 °C gave 4.4 g of diene **12**, which, from ether, gave almost white needles of the pure (by VPC on a 5 ft × 0.25 in. Apiezon on Chromosorb T column) diene, mp 126–127 °C (by placing the capillary in the apparatus preheated to ca. 125 °C) (lit.[4] mp 125–127 °C). Dilution of the tetrahydrofuran mother liquor with ether gave an additional 1.44 g of the diene **12**: IR (KBr) 2220 (CN), 1570 (C=C), 950 cm^{-1} (=CH$_2$, overtone at 1900); ^{1}H NMR (CDCl$_3$) δ 6.45 and 6.33 (2 s, J_{gem} = 0 Hz); mass spectrum *m/e* (rel intensity) 104 (26, M$^+$), 77 (95), 64 (48), 52 (100). Anal. Calcd for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.91. Found: C, 69.2; H, 4.0; N, 27.1.

Registry No.—**1**, 4336-19-0; **2**, 28839-49-8; **3**, 52477-67-5; **4**, 38818-30-3; **9**, 59082-62-1; **10**, 59120-88-6; **11**, 26011-79-0; **12**, 19652-57-4; cyclohexene-1,2-dicarboxylic anhydride, 4720-86-9; cyclohexene-1,2-dicarboxamide, 62601-01-8.

References and Notes

(1) A. L. Barney and H. B. Stevenson, U.S. Patent 2 870 196 (E. I. du Pont de Nemours and Co.) (Jan 20, 1959).

(2) W. J. Bailey. R. L. Hudson, and E. T. Yates, *J. Org. Chem.*, **28**, 828 (1963).

(3) U.-I. Záhorszky and H. Musso, *Justus Liebigs Ann. Chem.*, 1777 (1973).

(4) P. O. Tawney, U.S. Patent 2 444 882 (U.S. Rubber Co.), (July 6, 1945).

(5) E. J. Prill, U.S. Patent 2 480 961 (U.S. Rubber Co.), (Sept 6, 1949).

(6) D. Belluš, K. von Bredow, H. Sauter, and C. D. Weis, *Helv. Chim. Acta*, **56**, 3004 (1973).

(7) We independently confirmed the facile synthesis of dienes of this type from the cyclobutene derivatives.

(8) H. Kwart and K. King, *Chem. Rev.*, **68**, 416 (1968).

(9) R. K. Huff, C. E. Moppett, and J. K. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 2584 (1972).

(10) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 1773 (1957).

(11) The reactivity of dicyanoacetylene with diene **12**, which could account for its absence, was not assessed. However, diene **12** reacts only extremely slowly with the related dimethyl acetylenedicarboxylate.[12]

(12) R. L. Cobb and J. E. Mahan, to be published.

(13) Melting points, determined in a Mel-Temp apparatus, are uncorrected; IR spectra were determined on a Perkin-Elmer Model 137 Infracord; NMR spectra were determined vs. internal Me$_4$Si on Varian T60 or XL100 instruments.

(14) M. E. Bailey and E. D. Amstutz, *J. Am. Chem. Soc.*, **78**, 3828 (1956).

(15) Recrystallization of the first product crop, 269 g, from ether gave a small amount of insoluble *N*-methylcyclohexene-1,2-dicarboxamic acid: mp 178–179 °C (from isopropyl alcohol–ether); IR (KBr) 3280 (sharp, strong, NH), 1630, 1540, and 1290 (amide), 1670 and 930 cm^{-1} (acid). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.11; H, 7.19; N, 7.13.

(16) (a) G. E. Ficken and R. P. Linstead, *J. Chem. Soc.*, 4846 (1952); (b) G. E. Ficken, H. France, and R. P. Linstead, *ibid.*, 3730 (1954).

(17) VPC analyses for **9** and **10** were made utilizing the Carbowax column described in footnote *b* of Table I and a similar silicone rubber column.

Organoboranes. 21. Facile Syntheses of *cis*-Bicyclo[3.3.0]oct-1-yl Derivatives from Lithium Dialkyl-9-borabicyclo[3.3.1]nonane "Ate" Complexes[1]

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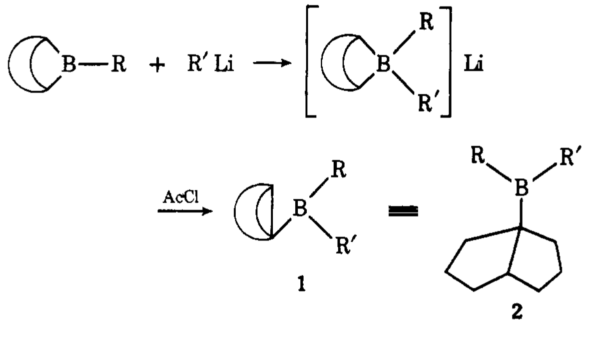
Lithium dialkyl-9-borabicyclo[3.3.1]nonane "ate" complexes react with acetyl chloride via hydride transfer to form *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes. These organoboranes are valuable intermediates for the preparation of a variety of 1-substituted *cis*-bicyclo[3.3.0]octanes. Many of these derivatives have heretofore been difficult to prepare. However, the ready availability of the organoborane precursor now permits their convenient preparation in high yield.

We recently reported that lithium "ate" complexes (**1**), derived from the addition of alkyllithiums to *B*-alkyl-9-borabicyclo[3.3.1]nonanes (*B*-alkyl-9-BBN), react with acetyl chloride via hydride transfer to form *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes (**2**) (eq 1).[2,3] These organoboranes are valuable intermediates for the preparation of a variety of 1-substituted *cis*-bicyclo[3.3.0]octanes. Since many of these derivatives have heretofore been difficult to prepare, we explored the synthetic utility of these organoboranes (**2**).[4] Employing several common reaction sequences from the organoborane arsenal, we prepared and isolated in high yield several representative 1-substituted *cis*-bicyclo[3.3.0]octanes (**3–7**).



(1)

The preparations of compounds **5–7** deserve further discussion. These synthetic procedures are known to proceed via free-radical reaction paths.[6-9] Accordingly, we felt that the proper choice of the other alkyl groups (R and R′ in **2**) would be important to the overall success in effecting preferential transfer of the bicyclic moiety. To demonstrate this point, we carried out 1,4-additions to methyl vinyl ketone with several derivatives of **2** with varying alkyl substituents. The results (Table I) clearly show, as anticipated, that selective migration