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RELATIVE REACTIVITIES OF 1,2-CYCLOHEXADIENE WITH CONJUGATED DIENES AND STYRENE

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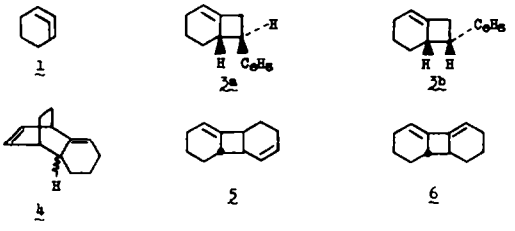
Abstract—Generation of 1,2-cyclohexadiene in the presence of conjugated dienes leads to (2 + 2) and/or (2 + 4) cycloaddition products. Methods used to generate 1,2-cyclohexadiene were: (1) treatment of 6,6-dibromobicyclo[3.1.0]hexane with methyllithium in tetrahydrofuran-ether at 0° and 60°; (2) treatment of 1,6-dichlorocyclohexene with magnesium in tetrahydrofuran at 60°; and (3) treatment of 1-bromocyclohexene with t-BuOK in THF at 60° or dimethyl sulfoxide at 40°. Comparison of relative reactivities with various dienes and styrene in ether solvents at 60° confirmed that the same intermediate, uncomplexed 1,2-cyclohexadiene, was involved in these reactions. Relative reactivities at 0° and 60° were found to be: 2-methylfuran (0·12, 0·14); furan (0·17, 0·16); 2,4-hexadiene (0·17, —); *cis*-pentadiene (0·53, 0·53); 2,3-dimethylbutadiene (2·35, 1·9); 1,3-cyclohexadiene (1·85, —); styrene (2·35, 1·9); and 1,3-cyclopentadiene (47, 14).

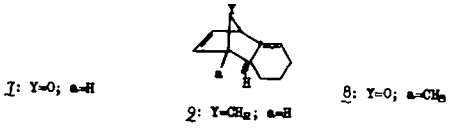
In 1965, Wittig and Fritze[1] reported that 1,2-cyclohexadiene (**1**), generated by the action of potassium t-butoxide (KO-t-Bu) on 1-bromocyclohexene, reacts with 1,3-diphenylisobenzofuran to give the *exo*- and *endo*-(2 + 4) cycloaddition products in a combined yield of about 40%. Boyden[2] obtained the same mixture of cycloaddition products in comparable yield when he treated 1,6-dibromocyclohexene with magnesium in the presence of 1,3-diphenylisobenzofuran. Moore and Moser[3] observed that **1**, generated from the reaction of 6,6-dibromobicyclo[3.1.0]hexane (**2**) with methyllithium (CH_3Li) in styrene, gives a 76% yield of a 2·2 : 1 mixture of the *exo*- and *endo*-(2 + 2) cycloaddition products **3a** and **3b**. It has also been observed that 1,2-cyclohexadiene, generated by either treatment of a 1-halocyclohexene with KO-t-Bu[4] or by treatment of 1,6-dichlorocyclohexene with magnesium,[5] and 1,3-cyclohexadiene react to give a mixture of the (2 + 4) and (2 + 2) cycloaddition products **4** and **5** in a ratio of about 3 : 1. In addition, all of these workers observed that 1,2-cyclohexadiene undergoes a competing dimerization to give the product of (2 + 2) cycloaddition, *trans*-tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene (**6**).



The work described here was undertaken in order to determine the scope of cycloaddition reactions of 1,2-cyclohexadiene (**1**) with conjugated dienes. After it was found that cycloaddition reactions are general reactions of **1** with unhindered conjugated dienes, the work was extended in an effort to determine if the **1** generated by the three methods was indeed the same chemical species. This was done by determining the relative reactivities with conjugated dienes and styrene of the 1,2-cyclohexadiene (**1**) generated at 60° in ether solvent by the reactions of (1) **2** with CH_3Li, (2) 1,6-dichlorocyclohexene with magnesium and (3) 1-bromocyclohexene with KO-t-Bu.

For synthetic purposes, the preferred method of generating **1** is the method of Moore and Moser, treatment of **2** with CH_3Li.

At −15° or 0°, **1** from **2** and CH_3Li with furan, 2-methylfuran, and 1,3-cyclopentadiene gave, respectively, 57, 54 and 87% (VPC) yields of *ca.* 10 : 1, 3 : 1 and 1·5 : 1 mixtures, respectively, of the *endo*- and *exo*-(2 + 4) cycloaddition products **7**, **8** and **9**. The structures of these and other new products described here were assigned on the basis of their elemental analyses and their 270-MHz NMR, IR and mass spectra. The major products from these reactions were assigned the *endo* configuration because their NMR spectra possessed bands at high field (*ca.* δ 0·4 ppm), and these bands were most likely due to the *syn* C_5 proton of the *endo*-isomer, which is shielded by the π bond at C_9–C_{10}.



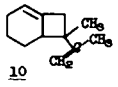
The reactions leading to **7**, **8** and **9** were accompanied by the formation of **6**, the dimer of **1** (*ca.* 40% together with **7** and **8**; 11% together with **9**).

Note that the reaction of **1** with 2-methylfuran was highly regioselective. A small amount (4%) of an unidentified product was formed together with **8**, and this may have been either the 1-methyl isomer of **8** or a (2 + 2) cycloaddition product. A small amount of (2%) of the product from 1,3-cyclopentadiene remained unidentified, and this may have been a (2 + 2) cycloaddition product.

It should also be noted that Moore and Moser[3] had attempted to trap 1,2-cyclohexadiene (**1**) with furan, but at −80°. Their lack of success was probably due to their choice of temperature. Even at 0°, only slightly more that 50% of the available **1** was trapped by furan; the rest was converted to dimer **6**. Dimerization of **1** certainly has a lower activation energy than the cycloaddition reaction of

1 with furan. Consequently, the rate constant for dimerization should decrease far less markedly with temperature than the rate constant for the cycloaddition reaction of 1 with furan.

The acyclic dienes 2,3-dimethylbutadiene, 2,4-hexadiene, and *cis*-pentadiene were found to undergo (2 + 2) cycloaddition reactions with 1 to give, respectively, **10**, **11** and **12**. Significantly, the yields of these (2 + 2) cycloaddition products appeared to be inversely related to the degree of steric hindrance at the terminal carbon of the diene system: **10**, 90%; **11**, 50%; and **12**, 35%. Unsuccessful attempts were made to trap 1 with *cis*- and *trans*-stilbene, 1,4-diphenylbutadiene, and thiophene. The lack of success with the former three reagents may well be due to steric hindrance of the carbon that would be expected to add to 1. The low reactivity of thiophene is probably due to its greater aromaticity relative to furan.[6] These unsuccessful attempts to trap 1 are described elsewhere.[7]



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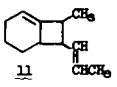

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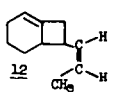


12

The products from 2,3-dimethylbutadiene and from *cis*-pentadiene at 0° (but not 60°) (**10** and **12**) appeared to be single products. That is: they each gave single VPC bands, even on a 500-ft Carbowax 20 M capillary column; they showed, respectively, only two and one discrete C-methyl resonances in their 270-MHz NMR spectra; and **12** obtained at 0° possessed no IR band at 967 cm^{-1}, which is characteristic of *cis*-substituted double bonds[8] and which is present in the spectrum of the product from 1 and *trans*-pentadiene at 0°.[9] By analogy with the stereochemistry of the ring closure of the bis-allylic diradical which gives *trans* **6**,[10] we tentatively assign **10** the *trans* C_6–H–C_7–CH_3 configuration and **12** the *trans* C_6–H–C_7–H configuration. **11** was obtained from a mixture of 2,4-hexadiene and was a 57:43 mixture of at least two isomers differing in the configuration of the 1-propenyl side chain at C_7.

The experiments to determine the relative rates of reactions of 1 with conjugated dienes and styrene were modeled after those of other workers[11] who have determined relative reactivities of reactive intermediates. They consisted of generating 1 in the presence of two reagents present in significant excess and then determining the relative amounts of products from 1 and the two reagents. Provided that three conditions are met, the relative rate constants k/k_0 are given by the expression

$$k/k_0 = (P/P_0)(R_0/R)$$

wherein P is the mole fraction of the product and R is the mole fraction of the reagent. The conditions are: the rate laws for the competing reactions are similar in form; the two reagents are in sufficient excess so that their mole ratio does not change significantly during the experiment; and the product ratio is not changed by succeeding reactions. The first condition was assumed. In our experiments, the second condition was met by using a combined mole ratio of reagents to 1,2-cyclohexadiene precursor of ten. By examination of product ratios in aliquots taken as the reactions were proceeding, we were able to determine that the third condition was also met. Note that when the two reagents are present in equal molar amounts, the ratio of rate constants becomes equal to the ratio of corresponding products, i.e.,

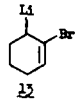
$$k/k_0 = P/P_0.$$

Product ratios were determined by means of high-precision VPC. In all cases, the experimental points used to construct the standard curves used in the analyses encompassed the experimental points from the various competition experiments. Reproducibility and internal consistency of data were good (± <7%), and the rate constants relative to 2,3-dimethylbutadiene, the arbitrary standard, are considered accurate to ±10%.

For purposes of determining relative rate constants in ether solvents, 1,2-cyclohexadiene (1) was generated under four sets of conditions: by treatment of 6,6-dibromobicyclo[3.1.0]hexane with MeLi at 0° and at 60°; by treatment of 1,6-dichlorocyclohexene with magnesium at 60°; and by treatment of 1-bromocyclohexene with KO-t-Bu at 60°. A limited series of experiments was also carried out by generating 1 from 1-bromocyclohexene and KO-t-Bu in DMSO at 40°. The relative rate constants obtained under the five sets of conditions are summarized in Table 1.

It was not possible to determine the relative reactivities of furan and 2-methylfuran with 1 generated from 1,6-dichlorocyclohexene and magnesium because the products, **7** and **8**, were unstable under the reaction conditions. We ascribe this instability to the presence of magnesium chloride, which is formed during the reaction. Because they were unstable under the reaction conditions, it was also not possible to determine the relative reactivities of styrene, 1,3-cyclohexadiene, and 1,3-cyclopentadiene with 1 from 1-bromocyclohexene and KO-t-Bu in THF or the former two compounds with 1 from the same reagents in DMSO. Styrene polymerized under the strong basic conditions; 1,3-cyclohexadiene was equilibrated with its 1,4-isomer;[12] and 1,3-cyclopentadiene underwent extensive dimerization during the long reaction time in THF.

We observed essentially the same relative reactivities at 60° for 2,3-dimethylbutadiene, styrene, and 1,3-cyclopentadiene with 1 generated from 6,6-dibromobicyclo[3.1.0]hexane and CH_3Li and with 1 generated from 1,6-dichlorocyclohexene and magnesium. These data indicate that the same reactive intermediate, uncomplexed 1,2-cyclohexadiene, is involved in these reactions rather than other species such as **13** or **14**. The limited data obtained with 1 generated from 1-bromocyclohexene and KO-t-Bu in THF at 60°, which is most likely to be uncomplexed 1, give support to this conclusion. Further support is added by the observations that the relative amounts of the major diastereomeric products and of the major and minor products from the furans, styrene, 1,3-cyclohexadiene,[4,5] and 1,3-cyclopentadiene are independent of the method of generating 1.



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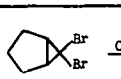
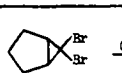
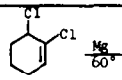
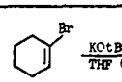
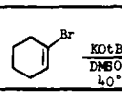
14

Interestingly, the relative reactivities in DMSO at 40° of 1,3-cyclopentadiene and 2,3-dimethyl butadiene (14:1) is about 70% of that calculated from the relative reactivities obtained at 0° and 60° in other solvents. Further study of

Table 1. Relative rate constants for reactions of 1,2-cyclohexadiene with conjugated dienes and styrene

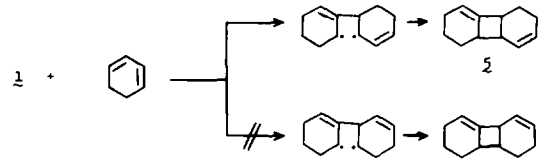
Reagent					
	0.12	—	—	0.14	—
	0.17	0.17	—	0.16	0.15
$CH_3CH{=}CH{-}CH{=}CHCH_3$	0.17	—	—	—	—
cis-$CH_2{=}CH{-}CH{=}CHCH_3$	0.53	—	0.53	—	—
$CH_2{=}C(CH_3){-}C(CH_3){=}CH_2$	1.00	1.00	1.00	1.00	1.00
	1.85	—	—	—	—
	2.35	1.9	1.9	—	—
	47	14	14	—	14

the dependence on solvent of relative reactivities of **1** as well as other strained cyclic allenes and cycloalkynes with conjugated dienes and with nucleophiles is contemplated.

We believe that the cycloaddition reactions studied, as was found for the dimerization of **1** to give **6**,[10] and as was proposed for the reaction of 1 with styrene,[3] are stepwise reactions involving intermediate diallylic diradicals. The most important single factor that would result in enhancement of the rate of cycloaddition by this mechanism is the degree of allyl resonance in the trapping agent part at the transition state. This resonance would be expected to be greatest for reactions with 1,3-cyclopentadiene, the most reactive diene. In 1,3-cyclopentadiene, the dihedral angle defined by $H_1C_1C_2H_2$ and $H_3C_3C_4H_4$ is nearly 0°. The corresponding dihedral angle of the preferred conformation of 1,3-cyclohexadiene, the next most reactive diene, is about 18°,[13] and similar angles for the less reactive acyclic dienes are expected to be somewhat greater.

Our belief that these cycloaddition reactions occur by a stepwise mechanism is on firmer ground with the (2 + 2) cycloadditions observed with the acyclic dienes and, in part, with 1,3-cyclohexadiene. There are very few examples of thermally allowed (2 + 2) cycloaddition reactions which are believed to be concerted.[14] Indeed, (2 + 2) cycloaddition reactions which have been studied in detail have been shown to proceed through diradicals.[15,16] Note that the mode of (2 + 2) cycloaddition of 1,2- and 1,3-cyclohexadiene is much more easily rationalized on the basis of a stepwise mechanism involving intermediate diradicals. The only (2 + 2) cycloaddition product formed from these reagents is tricyclo[6.4.0.0^{2,7}]2,9-dodecadiene (**5**), which can be pictured as arising from a diallylic diradical intermediate. Note that formation of the isomeric 2,11-diene **15**, which seems reasonable via a concerted pathway, requires intermediacy of a less stable monoallylic diradical.

Although similar strong or convincing arguments are lacking as to whether the (2 + 4) cycloadditions of **1** are stepwise or concerted, the high degree of regioselectivity in the reaction of **1** with 2-methylfuran and the low degree



of stereoselectivity seen in that reaction as well as the reactions of **1** with 1,3-cyclopentadiene seem more compatible with the stepwise mechanism.

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were obtained with a Beckman IR-8 with polystyrene calibration points, and only selected frequencies are reported. NMR spectra were obtained of *ca.* 10–20% solns in CCl_4 containing 1–2% TMS with a Varian Associates A-60A system, a JEOL JNM-MN-100 system, or with a Bruker-270; the 270-MHz spectra were obtained by Professor R. Kluger at the University of Chicago. Mass Spectra were determined with a Consolidated Electrodynamics Corporation Type 21-104 Mass Spectrometer by Mr. J. L. Voth or with a Finnigan 3200 Gas Chromatograph/Mass Spectrometer by Mr. J. Fleming. Selected values of *m/e* are given; the complete mass spectra are reported elsewhere.[7] Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona, or by the Microanalytical Laboratory, University of California, Berkeley. Gas chromatograms were obtained with an aerograph Model 600-D HY-FI, Varian Aerograph Model 90-P, or an F and M Research Chromatograph Model 810. All solvents were dried by standard methods and stored over Linde 4A molecular sieves. KO-t-Bu was obtained from MSA Research Corporation and resublimed before use. MeLi was obtained from Foote Mineral Company in an ether solution and was standardized by routine techniques. All reactions were run under a positive N_2 atmosphere.

Preparation of cycloaddition products by the reaction of 6,6-dibromo[3.1.0]*hexane with* MeLi *in the presence of conjugated dienes or styrene.* The following synthesis is representative. To a rapidly stirred soln of 2·7 (10 g; 0·042 mole) in furan (30 ml; 0·42 mole) (freshly distilled from LAH) at −15° 1·3 M MeLi (39 ml; 0·051 mole) was added in 1·5 hr. After the addition was complete, the mixture was stirred for 15 min at −15°. It was then allowed to warm to room temp., and the reaction was quenched by the cautious dropwise addition of H_2O. The two phases that

resulted were separated, and the aqueous phase was extracted with ether (2 × 50 ml). The organic solns were combined, washed successively with H_2O (50 ml) and satd NaCl aq (50 ml), dried (Na_2SO_4), and distilled to give 3·5 g (57%) of **7**, b.p. 59–62° (1·2 mm), and 1·0 g (30%) of *trans*-**6**,[1,10] b.p. 49–52° (3 mm). The following data were obtained for **7**: NMR, δ 6·17 (d of d, 1, J = 5·5 Hz, C_{10}–H), 5·85 (d of d, 1, J = 5·5 Hz, C_9–H), 5·42 (m, 1, C_3–H), 4·79 (m, 2, HCOCH), 2·45–1·1 (m, 6), and 0·45–0·22 ppm (m, 1, *endo* C_5–H); ms, *m/e* (rel. intensity) 149(3), 148(28), 147(5), 133(8), 132(2), 131(3), 130(5), 129(6), 120(25), 119(88), 92(28), 91(100), 79(39), 77(30). (Found: C, 81·31; H, 7·96. $C_{10}H_{12}O$ requires: C, 81·04; H, 8·16%).

8-*Methyl*-11-*oxatricyclo*[6.2.1.$0^{2,7}$]*undeca*-2,9-*diene* (**8**) was prepared in 56% yield (as determined by VPC) from **2** (7·5 g; 0·031 mole) 1·3 *M* MeLi (29 ml; 0·038 mole), and freshly distilled 2-methylfuran (26 g; 0·31 mole). The following data were obtained for **8**: b.p. 70° (6 mm); NMR, δ 6·06 (m, 1, C_{10}–H), 5·73 (d, 1, J = 5 Hz, C_9–H), 5·42 (m, 1, C_3–H), 4·87 (m, 1, C_1–H), 2·5–1·6 (m, with s [CH_3] at 1·59 ppm, 9), and 0·5–0·2 ppm (m, 0·8, *endo* C_5–H); ms, *m/e* (rel. intensity) 163(5), 162(43), 161(4), 147(17), 134(31), 133(78), 119(55), 105(63), 92(17), 91(100), 79(25), 77(38). (Found: C, 81·28; H, 8·77. $C_{11}H_{14}O$ requires: C, 81·44; H, 8·70%).

endo- *and* exo-*Tricyclo*[6.2.1.$0^{2,7}$]*undeca*-2,9-*diene* (**9a** and **9b**) were prepared in a combined yield of 84% (as determined by VPC) from **2** (7·5 g; 0·031 mole), 29 ml 1·3 M MeLi (29 ml; 0·038 mole) and freshly "cracked" 1,3-cyclopentadiene (15·3 g; 0·23 mole). The following data for **9a** and **9b** were obtained: ms, *m/e* (rel. intensity) 147(8), 146(79), 145(18), 132(9), 131(80), 119(6), 118(52), 117(100), 115(25), 105(44), 104(42), 92(19), 91(60). (Found: C, 90·59; H, 9·79. $C_{11}H_{14}$ requires: C, 90·35; H, 9·65%). **9a** and **9b** were separated by gas chromatography (12′ × 1/4″; 15% TCEPE; 98°). **9a** had NMR: δ 6·32–5·63 (m, 2, HC=CH), 5·48–5·25 (m, 1, C_3H); 3·23–3·02 (m, 1, C_1–H), 2·66–2·42 (m, 1, *syn* C_{11}–H), 2·20–1·10 (m, 8), and 1·10–0·80 ppm (m, 1, *endo* C_5–H). **9b** had NMR: δ 6·07–5·55 (m, 2, HC=CH), 5·44–5·22 (m, 1, C_3–H), 3·16–2·93 (m, 1, C_1–H), 2·97–2·73 (m, 1, *syn* C_{11}–H), 2·24–1·12 (m, 8), and 0·42–0·23 ppm (m, 1, *endo* C_5–H).

Tricyclo[6.2.$20^{2,7}$]*dodeca*-2,9-*diene* (**4**) and trans-*tricyclo*-[6.4.0.$0^{2,7}$]*dodeca*-2,9-*diene* (**5**) were prepared in yields of 63% and 20%, respectively, as determined by VPC, from **2** (7·5 g; 0·031 mole), 1·3 M MeLi (29 ml; 0·038 mole), and 99% 1,3-cyclohexadiene (25 g; 0·31 mole). **4** and **5** were identical with the products described previously.[4] **6** was also obtained in 17% yield as determined by VPC.

endo- *and* exo-7-*Phenylbicyclo*[4.2.0]*oct*-1-*ene* (**3a** and **3b**) were prepared by the method of Moore and Moser.[3]

7-*Methyl*-7-*isopropenylbicyclo*[4.2.0]*oct*-1-*ene* (**10**) was prepared in 46% isolated yield from **2** (7·5 g; 0·031 mole), 1·3 M MeLi (29 ml; 0·038 mole), and 2,3-dimethyl-1,13-butadiene (25 g; 0·31 mole). The following data were obtained for **10**: b.p. 62–64° (5·9 mm); NMR, δ 5·21 (m, 1, C_2H), 4·55 (m, 2, $=CH_2$), 2·93–2·41 (m, 2, C_8H_2), 1·62 (s, 3, C=C–CH_3), 1·00 (s, 3, C_7CH_3), and 2·28–1·12 ppm (m, 7); ms, *m/e* (rel. intensity) 163(9), 162(70), 161(3), 148(8), 147(61), 145(4), 121(11), 120(100), 105(96), 91(58), 79(29), 78(12), 77(33). (Found: C, 88·91; H, 11·19. $C_{12}H_{18}$ requires: C, 88·82; H, 11·18%).

7-(cis-1-*Propenyl*)*bicyclo*[4.2.0]*oct*-1-*ene* (**12**) was prepared in 50% yield (as determined) by VPC; 1·1 g or 26% isolated) from **2** (7·5 g; 0·031 mole), 1·3 M MeLi (29 ml; 0·038 mole), and *cis*-1,3-pentadiene (21·0 g; 0·31 mole). The following data were obtained for **12**: NMR δ 5·33 (m, 2, HC=CH), 5·13 (m, 1, C_2H), 2·60 (m, 4), 2·20–0·85 (m, 6), and 1·58 ppm (d, 3, J = 5 Hz, CH_3); IR (neat) 701 cm^{-1} (*cis*-olefin), no band at 967 cm^{-1} (*trans*-olefin); ms, *m/e* (rel. intensity) 148(7), 133(25), 120(9), 119(28), 107(8), 106(21), 105(50), 103(5), 93(12), 92(19), 91(100), 79(45), 77(35). (Found: C, 88·59; H, 11·38. $C_{11}H_{16}$ requires: C, 88·32; H, 11·68%).

8-*Methyl*-7-(cis- *and* trans-1-*propenyl*)*bicyclo*[4.2.0]*oct*-1-*ene* (**11**) was prepared in 35% yield, as determined by VPC, from **2** (7·5 g; 0·031 mole), mixed 2,4-hexadienes (25 g; 0·31 mole), and 1·3 M MeLi (29 ml; 0·038 mole). A 65% (VPC) yield of **6** was also obtained. The following data were obtained for **11**: b.p. 65–66° (4·7 mm); NMR, δ 5·45–5·23 (m, 2, HC=CH), 5·12 (m, 1, C_2H), 2·92–1·60 (m, 8), 1·64 and 1·45 (pair of doublets, J = 2 Hz, 1·7:1·3, C=CCH_3), and 1·02 ppm (overlapping doublets, C_8CH_3); ms, *m/e* (rel. intensity), 163(2), 162(32), 148(7), 147(60), 134(10), 133(44), 121(7), 120(19), 119(54), 107(26), 105(100), 91(66), 79(60), 77(38). (Found: C, 85·30; H, 10·92. $C_{12}H_{18}$ requires: C, 88·82; H, 11·18%). A satisfactory analysis for carbon was not obtained).

Standard VPC curves for determination of product ratios from competition reactions with 1,2-*cyclohexadiene.* All standard solns were prepared gravimetrically using purified samples of cycloaddition products. At least four standard solns of each two sets of cycloaddition products were examined by VPC (500′ × 0·03″ Carbowax 20 M), and corresponding plots were prepared using apparent weight % vs actual weight % as the coordinates. In all cases, standard points on these curves encompassed the experimental points from the various competition experiments.

Competition experiments. The following experiments are representative.

(a) *Reactions of* 6,6-*dibromobicyclo*[3.1.0]*hexane with* MeLi *at* 0°. To a 25-ml round-bottomed flask equipped with a dry ice-acetone condenser and a pressure equalizing addition funnel **2** (2·4 g; 10 mmoles), freshly distilled furan (3·4 g; 50 mmoles), and freshly distilled 2-methylfuran (4·1 g; 50 mmoles) was added. The soln was stirred vigorously and cooled to 0° ± 1°, and 11 ml of 1·3 M (14 mmoles) MeLi soln was added dropwise in 90 min. When the addition was complete, the mixture was stirred for an additional 15 min and then allowed to warm to room temp. The excess MeLi was destroyed by the cautious dropwise addition of 10 ml water, the phases were separated, and the aqueous phase was extracted with ether (3 × 10 ml). The organic solns were combined, washed successively with water (10 ml) and satd NaCl aq (10 ml), dried (Na_2SO_4), and analyzed by VPC. The results of these competition experiments are summarized in Table 2, and the corresponding relative reactivities of the various trapping reagents are summarized in Table 1.

Table 2. Relative rate constants from reactions of 6,6-dibromobicyclo[3.1.0]hexane with CH_3Li at 0°

Reagent Pair[a]	Mole Fraction of Products	Relative Rate Constants
furan / 2-methylfuran	0.583 / 0.417	1.40
2,3-dimethylbutadiene / furan	0.853 / 0.147	5.80
2,3-dimethyl-butadiene / 2,4-hexadiene	0.853 / 0.147	5.80
styrene / 2,3-dimethylbutadiene	0.693 / 0.307	2.26
2,3-dimethyl-butadiene / cis-pentadiene	0.650 / 0.350	1.86
1,3-cyclohexadiene / 2,4-hexadiene	0.915 / 0.085	10.8
1,3-cyclopentadiene / 1,3-cyclohexadiene	0.96 / 0.040	24
1,3-cyclopentadiene[b] / 1,3-cyclohexadiene	0.93 / 0.068	27

[a] Molar ratio was 1.0 unless noted otherwise [b] Molar ratio was 0.50

(b) *Reactions of* 6,6-*dibromobicyclo*[3.1.0]*hexane with* MeLi *at* 60° *in* THF-*ether.* To a 50-ml round-bottomed flask equipped with a dry ice-acetone condenser and a pressure equalizing dropping funnel 20 ml dry THF, freshly distilled 2,3-dimethylbutadiene (1·75 g; 21 mmoles), freshly distilled styrene (2·2 g; 21 moles), and **2** (1·0 g; 4·2 mmoles) was added. The soln was stirred rapidly and heated to 60° ± 2°, and 1·3 M MeLi (4·6 ml; 6·0 mmoles) was added dropwise in 35 min. When the addition was complete, the mixture was stirred for an additional 15 min, cooled to room temp., and

quenched, worked-up, and analyzed as described above. The results of the competition experiments are summarized in Table 3, and the corresponding relative reactivities of the various trapping reagents are summarized in Table 2.

Table 3. Relative rate constants from reactions of 6,6-dibromobicyclo[3.1.0]hexane with CH_3Li at 60° in THF-ether

Reagent Pair[a]	Mole Fraction of Products	Relative Rate Constants
2,3-dimethyl-butadiene / furan	0.853 / 0.147	5.8
styrene / furan	0.911 / 0.089	10.2
styrene / 2,3-dimethyl-butadiene	0.654 / 0.346	1.89
1,3-cyclopentadiene / styrene	0.885 / 0.115	7.70

[a] Molar ratio was 1.00

(c) *Reactions of 1,6-dichlorocyclohexene and magnesium at 60° in THF.* A mixture was prepared from 20 ml dry THF, Mg (1·0 g; 43 mmoles), 2,3-dimethylbutadiene (2·75 g; 33·5 mmoles), and freshly distilled styrene (3·5 g; 33·5 mmoles). The mixture was heated rapidly to 60° ± 2°, rapid magnetic stirring was begun, 1,6-dichlorocyclohexene[18] (1·10 g; 6·7 mmoles) was added, and a few drops of MeI was added to initiate the reaction. When most of the Mg was consumed, the reaction was stopped by the cautious dropwise addition of water (25 ml total). The mixture was cooled, filtered, and the phases were separated. The organic phase was washed successively with water (25 ml) and satd NaCl aq (25 ml), dried (Na_2SO_4) and analyzed. The results of the competition experiments are summarized in Table 4, and the corresponding relative reactivities of the various trapping reagents are summarized in Table 1.

Table 4. Relative rate constants from reactions of 1,6-dichlorocyclohexene with magnesium at 60°

Reagent Pair[a]	Mole Fraction of Products	Relative Rate Constants
2,3-dimethyl-butadiene / cis-pentadiene	0.653 / 0.347	1.88
styrene / cis-pentadiene	0.769 / 0.231	3.15
styrene / 2,3-dimethyl-butadiene	0.654 / 0.346	1.88
1,3-cyclopentadiene / styrene	0.886 / 0.114	7.78

[a] Molar ratio was 1.0

(d) *Reactions of 1-bromocyclohexene and* KO-t-Bu *at 60° in THF.* To a rapidly stirred mixture of KO-t-Bu (1·04 g; 9·3 mmoles), 20 ml freshly dried THF, 2,3-dimethyl-1,3-butadiene (2·54 g; 31 mmoles), and furan (freshly distilled from LAH) (2·11 g; 31 mmoles) at 60° was added 1-bromocyclohexene[4] (1·0 g; 6·2 mmoles) in 30 min. After 20 hr, the reaction was stopped by the dropwise addition of 10 ml of sat K_2CO_3 aq. The mixture was cooled, the phases were separated, and the aqueous phase was extracted with ether (3 × 10 ml). The organic solns were combined, washed with sat K_2CO_3 aq (3 × 30 ml), dried, and analyzed. The ratio of the mole fractions of products from 2,3-dimethylbutadiene and furan was found to be 0·866:0·134, which corresponds to relative reactivities of 6·45:1·00. A similar experiment with 2,3-dimethylbutadiene and 2-methylfuran gave a ratio of mole fractions of products of 0·878:0·122, which corresponds to relative reactivities of 7·20:1·00. The relative reactivities of the three trapping reagents are summarized in Table 1.

(e) *Reactions of 1-bromocyclohexene and* KO-t-Bu *at 40° in DMSO.* To a rapidly stirred soln of KO-t-Bu (1·04 g; 9·3 mmoles), furan (freshly distilled from LAH) (2·11 g; 31 mmoles), 2,3-dimethylbutadiene (2·54 g; 31 mmoles), and 20 ml DMSO at 40° was added 1-bromocyclohexene[4] (1·0 g; 6·2 mmoles) in 10 min. After 1 hr, the reaction was stopped by the addition of 10 ml water. The mixture was cooled and extracted continuously with ether for 24 hr. The ether soln was dried (Na_2SO_4) and analyzed. The ratio of the mole fractions of products from 2,3-dimethylbutadiene and furan was found to be 0·869:0·131, which corresponds to relative reactivities of 6·62:1·00. A similar experiment with 1,3-cyclopentadiene and 2,3-dimethylbutadiene gave a ratio of mole fractions of products of 0·931:0·069, which corresponds to relative reactivities of 13·5:1·00. The relative reactivities of the three trapping reagents are summarized in Table 1.

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