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RELATIVE REACTIVITIES OF BICYCLO[3.2.1]OCTA-2,3-DIENE AND 1,2-CYCLOHEPTADIENE WITH CONJUGATED DIENES AND STYRENE

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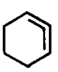
Abstract—Bicyclo[3.2.1]octa-2,3-diene (**2**) and 1,2-cycloheptadiene (**3**), generated by treatment of the corresponding dichlorides **4** and **5** with magnesium, were found to undergo cycloaddition reactions with 2,3-dimethylbutadiene, styrene, and 1,3-cyclopentadiene. **2**, but not **3**, was also found to undergo a (2 + 2) cycloaddition reaction with *cis*-pentadiene. The relative reactivities of **2** and **3** with *cis*-pentadiene, 2,3-dimethylbutadiene, styrene, and 1,3-cyclopentadiene at 60° in THF were found to be: 0·18, —; 1·0, 1·0; 0·60, 7·5; and 4·0, 150.

In an accompanying paper[1] we have reported our determinations of the relative reactivity of 1,2-cyclohexadiene (**1**) with several conjugated dienes and styrene. **1** was generated by three methods: treatment of 6,6 - dibromobicyclo[3.1.0]hexane with methyllithium; treatment of 1,6-dichlorocyclohexene with magnesium; and treatment of 1-bromocyclohexene with KO–t-Bu. In ether solvents at 60°, the same relative reactivities for **1** were observed regardless of the method by which it was generated.

As an extension of this work, we examined the reactions of bicyclo[3.2.1]octa - 2,3 - diene (**2**)[2] and 1,2-cycloheptadiene (**3**)[3] with several conjugated dienes and styrene. We describe here these reactions as well as our determinations of the relative reactivities of **2** and **3** with these reagents.



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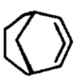

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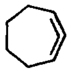

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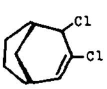
For our study, **2** and **3** were generated by treatment of the corresponding dichlorides **4**[4] and **5** with magnesium in THF. **5** was synthesized from the corresponding allylic alcohol, 2 - chloro - 2 - cyclohepten - 1 - ol,[5] and concentrated hydrochloric acid. For the preparative reaction of **3** with 2,3-dimethylbutadiene, **3** was formed from the action of KO–t-Bu on 1-chlorocycloheptene in DMSO. It should be noted that treatment of 7,7 - dibromobicyclo[4.1.0]heptane with methyllithium leads primarily to products of the corresponding carbene rather than of **3**.[6] However, similar treatment of 1 - methoxy - 7,7 - dibromobicyclo[4.1.0]heptane at −80° gives the dimer of 1 - methoxy - 1,2 - cycloheptadiene in yields up to 85%.[7]



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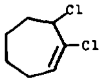

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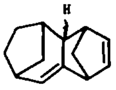
When 3,4 - dichlorobicyclo[3.2.1]oct - 2 - ene (**4**) was treated with magnesium in the presence of 1,3 - cyclopentadiene, three products were obtained in relative amounts 1·2:1·0:0·01. The principal products were assigned the *endo*- and *exo*-tetracyclo[7.2.1.1.^{4,7}0^{3,8}]trideca - 2,5 - diene (**6**) structures. These assignments and those to other new products described here were based on their elemental analysis as well as their 270-MHz NMR, IR, and mass spectra. The configurational assignments are tentative and made by analogy to the products from the reaction of **1** with 1,3-cyclopentadiene. The structure of the minor product was not determined.

Treatment of 1,7-dichlorocycloheptene (**5**) with magnesium in the presence of 1,3-cyclopentadiene gave two isomeric products in a ratio of *ca.* 2:1. These products, also by analogy with the reaction of 1,3-cyclopentadiene with **1**, are assigned, respectively, the *endo*- and *exo*-tricyclo[7.2.1.0^{2,8}]dodeca - 2,10 - diene (**7**) structures.



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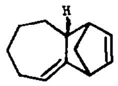

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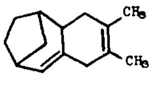
When bicyclo[3.2.1]octa-2,3-diene (**2**) was generated in the presence of 2,3 - dimethylbutadiene, 5,6 - dimethyltricyclo[7.2.1.0^{3,8}]dodeca - 2,5 - diene (**8**), the product of (2 + 4) cycloaddition, was obtained in *ca.* 35% vpc yield. Note that 1,2 - cyclohexadiene (**1**) gave a (2 + 2) cycloaddition product with this conjugated diene. It is conceivable that **8** was not the initial product formed in the reaction. The initial product, for which no evidence was obtained, may be the (2 + 2) cycloaddition product of **2** and 2,3-dimethylbutadiene, i.e. **9**, which, under the reaction conditions, isomerizes to **8**. Isomerization to **8**



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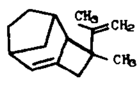

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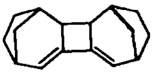
would lead to a relief of strain caused by steric interactions between the isopropenyl side chain and the C_7 and *cis*-C_{10} hydrogens. The major product that was isolated from the reaction of **4** with magnesium in the presence of 2,3-dimethylbutadiene had a molecular weight (mass spectrum) twice that of **2**. Vpc analysis showed three peaks in relative intensities of 3:3:1, and these compounds are probably three of the diastereomers of **10**.



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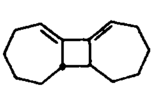
In order to prepare the cycloaddition product of 1,2-cycloheptadiene and 2,3-dimethylbutadiene in useful yield, 3 was generated from the reaction of 1-chlorocycloheptene with KO–t-Bu in the presence of the diene. In addition to 11, the dimer of 3,[3] which was the major product, the (2+2) cycloaddition product 8 - methyl - 8 - isopropenylbicyclo[5.2.0]non - 1 - ene (12) was formed in 21% VPC yield.



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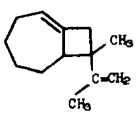

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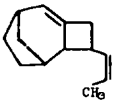
The major product from the reaction of 2 with *cis*-pentadiene was 5 - (cis - 1 - propenyl)tricyclo [5.2.1.0^{3,6}]deca - 2 - ene (13). A small amount (*ca.* 5%) of the product, which was not isolated, has been tentatively identified as the *trans*-isomer of 13 based on the presence of very weak bands at 953 and 970 cm^{-1} in the IR spectrum of the mixture and by analogy with the reaction of 1 with *cis*-pentadiene at 60°. Note that 13 and its *trans* isomer, unlike 9, possess no added strain due to steric interaction of the propenyl side chain with the C$_7$ and *cis*-C$_{10}$ hydrogens. This may well account for the different observed modes of cycloaddition of *cis*-pentadiene and 2,3-dimethylbutadiene with 2.



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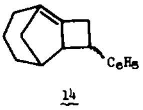
The reaction of 5 with magnesium in the presence of *cis*-pentadiene gave only 11, the dimer of 3.

2 and styrene gave a *ca.* 5:1 mixture of diastereomeric 5 - phenyltricyclo - [5.2.1.0^{3,6}]dec - 2 - enes (14). By analogy with the reaction of 1 with styrene,[8] we believe that these products are diastereomeric at C$_5$. On the basis of spectral data, we are unable to assign stereochemistry at C$_6$. Likewise 3 and styrene gave a mixture of diastereomeric 9 - phenylbicyclo[6.2.0]non - 6 - enes (15) in a ratio of *ca.* 1·5:1·0. Again by analogy with the reaction of 1 with styrene, the major product is assigned the *exo* - 8 - phenyl configuration.



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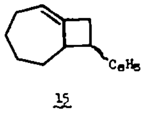

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The experiments to determine the relative rates of reactions of bicyclo[3.2.1]octa - 2,3 - diene (2) and 1,2-cycloheptadiene (3) with conjugated dienes and styrene were similar to those described in the accompanying paper. The strained cyclic allenes were generated in the presence of two reagents present in significant excess, and the relative amounts of the products from the two reagents were determined. When the two reagents are present in equal molar amounts, the ratio of rate constants is equal to the ratio of corresponding products, i.e.

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

These 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 cyclic allene 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.

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 was good ($\pm <$ 5%), and the rate constants relative to 2,3-dimethylbutadiene are considered accurate to ±10%.

The relative rate constants obtained for 2 and 3, as well as comparative data for 1, are summarized in Table 1.

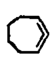
The order of reactivity of styrene and 2,3-dimethylbutadiene is different for 2 and the two monocyclic allenes. If these reactions are stepwise reactions involving intermediate diradicals,[1,8] the most important single factor affecting the relative reactivity would be the degree of allyl or benzyl resonance in the trapping agent part of the transition state. This resonance would be related to the dihedral angle defined by the two vinyl systems of the conjugated diene or the vinyl group and the phenyl ring at the instant of reaction. It seems reasonable to expect that this dihedral angle, and, therefore, the amount of resonance stabilization at the transition state, will differ with the amount of steric hindrance encountered by the reagent in its reaction with the strained allene system. Thus, although the same order of reactivity could be expected for the related allenes 1 and 3, and this was observed, a different reactivity order for the more hindered 2 is not incompatible with the diradical mechanism.

The observed relative reactivities of 1,2-cyclohexadiene (1) and bicyclo[3.2.1] - octa - 2,3 - diene (2) with the most reactive reagent, 1,3 - cyclopentadiene, and the least reactive, *cis*-pentadiene, were 26 and 22, respectively. This similarity in selectivity of 1 and 2 shows that the strain added to 2 by the ethylene bridge has, at most, only a slight effect on the reactivity of the allene system. The reduced strain of the allene system of 1,2-cycloheptadiene (3) relative to that of 1 or 2 is reflected in its apparent reduced reactivity toward *cis*-pentadiene as well as its greater selectivity toward the other reagents. Thus, 3 reacts 7·5 times and 150 times more rapidly with styrene and 1,3-cyclopentadiene than with 2,3-dimethylbutadiene, whereas the comparable relative reactivities for 1 are 1·9 and 14.

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-MH-100 system, or with

Table 1. Relative rate constants for reactions of cyclic allenes with styrene and conjugated dienes in THF at 60°

Reagent	Relative Rate Constants with		
			 a
Cis-pentadiene	0.53	0.18	–
2,3-dimethylbutadiene	1.0	1.0	1.0
styrene	1.9	0.60	7.5
1,3-cyclopentadiene	14	4.0	150

[a] From ref. 1.

Table 2. Relative rate constants from reactions of 3,4 - dichlorobicyclo[3.2.1]oct - 2 - ene with magnesium at 60°

Reagent Pair[a]	Mole Fraction of Products	Relative Rate Constants
2,3-dimethylbutadiene cis-pentadiene	$\frac{0.846}{0.154}$	5.5
styrene cis-pentadiene	$\frac{0.766}{0.234}$	3.3
1,3-cyclopentadiene styrene	$\frac{0.870}{0.130}$	6.7

[a] Molar ratio was 1·0.

Table 3. Relative rate constants from reactions of 1,7-dichlorocycloheptene with magnesium at 60°

Reagent Pair[a]	Mole Fraction of Products	Relative Rate Constants
styrene 2,3-dimethylbutadiene	$\frac{0.882}{0.118}$	7.5
1,3-cyclopentadiene styrene	$\frac{0.952}{0.048}$	20

[a] Molar ratio was 1·0.

a Bruker-270; the 270-MHz spectra were obtained by Prof. 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, with a Finnigan 3200 GC/MS, and a Varian M-66 mass spectrometer by Mr. K. Miyano. Selected values of *m/e* are given; the complete mass spectra are reported elsehwere.[9] 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. Solvents were dried by standard methods and stored over Linde 4A molecular sieves. All reactions were run under a positive N_2 atmosphere.

1 - *Acetoxy - 7,7 - dichlorobicyclo*[4.1.0]*heptane.* A mixture of 1-acetoxycyclohexene,[10] (15·5 g; 0·11 mole), 96% phenyl(dichlorobromomethyl)mercury (50 g; 0·11 mole) and 100 ml benzene was stirred and heated under reflux for 21 hr. The suspension was cooled and filtered, and the filtrate was distilled to give of 1 - acetoxy - 7,7 - dichlorobicyclo[4.1.0]heptane (19·5 g; 92%) b.p. 66–68° (0·2 mm) [lit.[5a] b.p. 60–61° (0·15 mm)].

1,7-*Dichlorocycloheptene.* 2 - Chloro - 2 - cyclohepten - 1 - ol was prepared in 77% yield from 1 - acetoxy - 7,7 - dichlorobicyclo[4.1.0]heptane.[5] A mixture of 55 ml conc. HCl, 2 - chloro - 2 - cyclohepten - 1 - ol, (10·0 g; 0·068 mole) and 15 ml pentane was stirred rapidly for 1 hr.[11] The phases were separated, and the aqueous phase was extracted with pentane (15 ml). The pentane solns were combined, washed with 5% $NaHCO_3$ (25 ml) and water until the wash water gave a neutral reaction with litmus, dried (Na_2SO_4), and distilled to give of 1,7 - dichlorocycloheptene (10·3 g; 92%) b.p. 68–70° (2·5 mm), NMR δ 6·06 (t, 1, $J = 6·7$, C=CH), 4·67 (m, 1, C_7–H), and 2·45–1·35 ppm (complex, 8); ms, *m/e* (rel. intensity) 166(7), 164(11), 131(6), 130(6), 129(13), 128(14), 122(6), 115(7), 113(13), 93(100), 91(34), 77(42). (Found: C, 51·06; H, 6·00. $C_7H_{10}Cl_2$ requires: C, 50·93; H, 6·11%).

Cycloaddition reactions of bicyclo[3.2.1]*octa - 2,3 - diene and of 1,2 - cycloheptadiene generated from the corresponding dichlorides and magnesium.* The following procedure is representative. To a rapidly stirred suspension of mg (8·6 g, 0·36 g atom) in 100 ml THF and freshly "cracked" 1,3 - cyclopentadiene (18·7 g; 0·283 mole) at 60° 4[4] (10 g; 0·056 mole) was added dropwise in 20 min. After 5 hr, the mixture was cooled to 0° and 100 ml water was added. The phases were separated, 20 ml 10% H_2SO_4 was added to the aqueous phase, and the acidic soln was extracted with ether (3 × 50 ml). The organic solns were combined, washed successively with water (50 ml) and sat NaCl aq (2 × 50 ml), dried (Na_2SO_4), and concentrated by distillation. The products were isolated by prep VPC on a 4′ × ⅜″ 10% SE 30 column at 150°; they were 3 - chlorobicyclo[3.2.1]oct - 2 - ene[2,4] (VPC yield <5%) and a 1·2 : 1 mixture of *endo* - and *exo* - **6** (VPC yield *ca* 95%): NMR, δ 6·84–5·84 (complex, 3, vinyl H), 3·39 (m, 4, bridge head H), and 3·08–1·10 ppm (complex, 9); ms, *m/e* (rel. intensity) 172(57), 171(4), 157(10), 153(11), 152(11), 144(48), 147(70), 131(35), 130(100), 129(43), 117(27), 115(41), 90(48). (Found: *m/e*, 172·1220; C, 90·37; H, 9·25. $C_{13}H_{16}$ requires: *m/e* 172·1252; C, 90·64; H, 9·36%).

5,6 - *Dimethyltricyclo*[7.2.1.0^{3,6}]*dodeca* - 2,5 - *diene* (**8**) was prepared in *ca* 35% VPC yield from mg (8·6 g; 0·36 g. atom),**4** (10 g, 0·056 mole) and 2,3-dimethylbutadiene, (24·2 g; 0·285 mole) and isolated by prep VPC on a $6' \times \frac{1}{4}''$ 10% Carbowax 20M column at 140°. The following data were obtained for **8**: NMR, δ 5·53 (m, 1, C=CH), 2·88–0·80 with s (CH_3) at 1·57 ppm (complex, 19); ms, *m/e* (ref. intensity) 188(78), 173(16), 160(16), 159(100), 145(32), 143(9), 131(26), 129(18), 127(18), 119(46), 117(48), 105(54), 91(54). (Found: C, 89·06; H, 10·48. $C_{14}H_{20}$ requires: C, 89·29; H, 10·71%).

5 - *Phenyltricyclo*[5.2.1.0^{3,6}]*dec* - 2 - *ene* (**14**) was prepared in 82% yield (isolated) from mg (4·8 g; 0·20 g. atom) **4**, (7·0 g; 0·040 mole) **4**, and styrene (20·5 g; 0·197 mole), and isolated by distillation. The following data were obtained for **14**: b.p. 91–93° (0·5 mm); NMR, δ 7·17 (s, 5, C_6H_5), 5·83 and 5·85 (two d, 1, *J* = 7 Hz, C=CH), 3·30–1·25 ppm (complex, 12); ms, *m/e* (rel. intensity) 210(26), 181(10x, 169(7), 167(9), 165(8), 156(8), 120(25), 105(4), 104(90), 103(27), 91(100), 79(32), 78(40), 77(65). (Found: C, 91·08; H, 8·43. $C_{16}H_{18}$ requires: C, 91·37; H, 8·63%).

5 - (cis)1 - *Propenyl*)*tricyclo*[5.2.1.0^{3,6})*dec* - 2 - *ene* (**13**) was prepared in 90% VPC yield from mg (4·3 g; 0·18 g atom), 99% *cis*-pentadiene, (9·3 g; 0·14 mole) and **4** (5·0 g; 0·028 mole), and isolated by prep VPC on a $5' \times \frac{3}{8}''$ 5% SE 30 column at 135°. The following data were obtained for **13**: NMR, δ 5·75–5·10 (complex, 3, vinyl H), 3·15–0·90 (complex, 12), and 1·63 ppm (overlapping d, *J* = 5 Hz, C=C–C$\underline{H}_3$); IR, 695 (s, *cis* olefin), 953 (vw), 970 cm^{-1} (vw); ms, *m/e* (rel. intensity) 174(40), 159(21), 146(15), 145(52), 131(28), 117(40), 91(100). (Found: C, 89·44; H, 10·25. $C_{13}H_{18}$ requires: C, 89·59; H, 10·41%). There was a minor component (*ca* 5% of **13**) which was not purified. The GC–MS of this component indicated that it was isomeric with **13**.

endo - *and* exo - *Tricyclo*[7.2.1.0^{2,8}]*dodeca* - 2,10 - *diene* (**7**), in a ratio of *ca* 2 : 1, were prepared in 85% VPC yield from mg (1·8 g; 0·075 g atom) **5**, (2·5 g; 0·015 mole), and freshly "cracked" 1,3-cyclopentadiene (10·0 g; 0·15 mole), and isolated by prep VPC on the SE 30 column at 165°. The following data were obtained for **7**: NMR, δ 6·13–5·99 (m, 2, $\underline{H}$C=C$\underline{H}$), 5·83–5·51 (m, 1, C=C$\underline{H}$), 3·13–2·95 (m, 1, C_1-H), and 2·85–1·05 ppm (complex, 12); ms, *m/e* (ref. intensity) 160(69), 145(31), 132(33), 131(43), 127(86), 114(45), 92(62), 91(100), 79(52), 77(42). (Found: C, 89·75; H, 10·10. $C_{12}H_{16}$ requires: C, 89·94; H, 10·06%).

8 - *Phenylbicyclo*[6.2.0]*non* - 6 - *ene* (**15**) was prepared in 30% VPC yield from mg (1·8 g, 0·075 g atom), styrene, (15·6 g; 0·15 mole) and **5** (2·5 g; 0·015 mole), and isolated by prep VPC on the SE 30 column at 165°. The following data were obtained for **15**: NMR, δ 6·92 (app. s, 5, $C_6\underline{H}_5$), 5·27 (m, 1, C=CH), 2·75–2·45 (m, 3, cyclobutane $\underline{H}$'s), 1·95–9·90 (complex, 9); ms, *m/e* (rel. intensity) 199(8), 198(48), 183(12), 169(14), 155(29), 142(25), 141(37), 130(27), 129(57), 128(30), 115(33), 107(39), 104(50), 103(24), 95(36), 94(31), 91(100), 79(64), 78(32), 77(48). (Found: C, 90·47; H, 9·04, $C_{15}H_{18}$ requires: C, 90·85; H, 9·15%).

Reaction of 1-*chlorocycloheptene with* KO–t-Bu *in the presence of* 2,3-*dimethylbutadiene*. To a stirred soln of resublimed KO–t-Bu (18·9 g; 0·169 mole) in 90 ml THF and 2,3-dimethylbutadiene (31·0 g; 0·384 mole) at 60° was added dropwise 1-chlorocycloheptene[3] (10·0 g; 0·077 mole) in 25 min. After 18 hr, the mixture was cooled to room temp. and 30 ml of sat K_2CO_3 aq was added dropwise. The mixture that resulted was added to 200 ml water, and the phases were separated. The aqueous phase was extracted with ether (3 × 100 ml), and the organic solns were combined, washed successively with water (2 × 50 ml) and sat K_2CO_3 aq (2 × 100 ml), dried (K_2CO_3), and concentrated by distillation. 8 - *Methyl* - 8 - *isopropenylbicyclo*[5.2.0]*non* - 1 - *ene* (**12**) (21% VPC yield) was isolated by prep VPC on a $5' \times \frac{1}{4}''$ 5% Carbowax 20M column. The following data were obtained for **12**: NMR, δ 5·30 (m, 1, C=C$\underline{H}$), 4·55 (m, 2, C=C$\underline{H}_2$), 2·95–2·43 (m, 2, cyclobutane H's), 2·30–1·15 (complex with s [C=C–CH_3] at 1·62, 12), and 1·04 ppm (s, 3, C_8–C$\underline{H}_3$); ms, *m/e* (rel. intensity) 186(30), 161(38), 148(6), 147(14), 133(32), 119(100), 107(43), 105(92), 91(61). (Found: C, 88·36; H, 11·38; *m/e* 176·1586. $C_{13}H_{20}$ requires: C, 88·56; H, 11·44%; *m/e* 176·1586.)

Reaction of 1,7-*dichlorocycloheptene with magnesium in the presence of* cis-*pentadiene*. To a rapidly stirred mixture of mg (1·8 g; 0·075 g atom) *cis*-pentadiene, (10·2 g; 0·15 mole) and 25 ml THF at 60° was added 1,7-dichlorocycloheptene (2·5 g; 0·015 mole) in 30 min. The mixture was stirred at 60° for 5 hr, cooled to room temp. and 20 ml water was added. The phases were separated, and the aqueous phase was extracted with ether (3 × 30 ml). The organic solns were combined, washed successively with water (2 × 50 ml), sat NaCl aq (2 × 50 ml), dried (Na_2SO_4), and concentrated by distillation. Analysis by VPC and NMR indicated that the only product formed in *ca.* 100% VPC yield was *trans*- **11**.[12]

Standard VPC *curves for determination of product ratios from competition reactions* were prepared as described in the accompanying paper[1]

Competition reactions. The following is representative. To a rapidly stirred mixture of mg (0·3 g; 12 mg atom), styrene, (0·95 g; 9·1 mmole) 2,3-dimethylbutadiene, (0·75 g; 9·1 mole) and 10 ml THF at 60° **5** (0·30 g; 1·8 mmole) was added in 20 min. The mixture was stirred for 5 hr at 60°, cooled to room temp. and 7 ml water was added. The phases were separated, and the aqueous phase was washed with ether (3 × 15 ml). The organic solns were combined, washed successively with water (10 ml) and sat NaCl aq (2 × 15 ml), dried (Na_2SO_4) and analyzed by VPC on a 500′ × 0·03″ Carbowax 20M column. The results of the various competition experiments are summarized in Tables 2 and 3, and the corresponding relative reactivities of the various trapping reagents are included in Table 1.

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