0.8; ν 3610 w (free OH), 3472 w (assoc. OH), 2732–2704 w (intramolecular OH····O=C), 1602 s (broad chelated C=O-····H—O), 1527 s (asym. NO_2), and 1342 cm.$^{-1}$ s (sym. NO_2); λ^{I}_{max} 327 mμ (ϵ 50,200); n.m.r. τ 7.73 (keto —CH_3), 3.77 (vinyl), 3.5 aromatic quartet (J = 10 c.p.s.), and −5.9 (OH).

Benzalacetone (**11**) had m.p. 42° (lit.[20] m.p. 42°); dibromide m.p. 124–125° (lit.[21] m.p. 124°); ν 1683 s (conj. C=O), and 1254 cm.$^{-1}$ vs (*trans* C=C); λ^{I}_{max} 285 mμ (ϵ 21,500); λ^{H}_{max} 281 mμ (ϵ 24,100); n.m.r. τ 7.77 (CH_3) and 3.77 (vinyl).

p-**Methylbenzalacetone** (**12**) had b.p. 97–98 (7 mm.) [lit.[22] b.p. 142–145 (15 mm.)]; ν 1685 s (conj. C=O) and 1252 cm.$^{-1}$ vs (*trans* C=C); λ^{I}_{max} 296 mμ (ϵ 21,500); λ^{H}_{max} 285 mμ (ϵ 31,800).

p-**Methoxybenzalacetone** (**13**) had m.p. 74–75° (lit.[20] m.p. 72–74°); oxime m.p. 125° (lit.[23] m.p. 123–124°); ν 1682 s (conj. C=O) and 1247 cm.$^{-1}$ vs (*trans* C=C); λ^{I}_{max} 317 mμ (ϵ 24,000); λ^{H}_{max} 307 mμ (ϵ 44,700).

p-**Bromobenzalacetone** (**14**) had m.p. 83–84° (lit.[24] m.p. 83–84°); ν 1686 s (conj. C=O) and 1259 cm.$^{-1}$ vs (*trans* C=C); λ^{I}_{max} 289 mμ (ϵ 48,000); λ^{H}_{max} 288 mμ (ϵ 100,500).

p-**Nitrobenzalacetone** (**15**) had m.p. 107–108° (lit.[24,25] m.p. 110°); ν 1692 m (conj. C=O), 1344 vs (asym. NO_2), and 1247 cm.$^{-1}$ m (sym. NO_2); λ^{I}_{max} 298 mμ (ϵ 15,800); λ^{H}_{max} 295 mμ (ϵ 49,000).

Crotonophenone (**16**) had b.p. 58° (0.14 mm); n^{25}_{D} 1.5567 [lit.[26] b.p. 98.6–98.9 (3.9–4.0 mm.); n^{25}_{D} 1.5586]; ν 1673 cm.$^{-1}$ vs (arom. C=O); λ^{I}_{max} 254 mμ (ϵ 17,000); λ^{H}_{max} 248 mμ (ϵ 46,900); n.m.r. τ 8.1 and 8.2 (CH_3) and 3.22 and 2.87 (vinyl) (J = 21 c.p.s.).

p-**Methylcrotonophenone** (**17**) had b.p. 77–78° (0.2 mm); n^{26}_{D} 1.5549; ν 1674 cm.$^{-1}$ vs (arom. C=O); λ^{I}_{max} 255 mμ (ϵ 31,600); λ^{H}_{max} 254 mμ (ϵ 37,200); n.m.r. τ 8.09 (doublet, CH_3), 7.67 (arom. CH_3), and 3.25 (doublet, vinyl).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.27; H, 7.79.

p-**Methoxycrotonophenone** (**18**) had m.p. 22–23° (lit.[27] m.p. 23°), b.p. 107° (0.2 mm); ν 1670 cm.$^{-1}$ vs (arom. C=O); λ^{I}_{max} 292 mμ (ϵ 18,200); λ^{H}_{max} 283 mμ (ϵ 19,500); n.m.r. τ 8.09 (doublet, CH_3), 6.23 (CH_3O), and 3.85 (doublet, vinyl).

α,α-**Dimethylbenzoylacetone** (**19**) had b.p. 83–84° (11 mm.); $n^{27.5}_{D}$ 1.5151 [lit.[28] b.p. 84° (2 mm.), 125–128 (14 mm.)]; ν 1748 m, 1718 s (aliphatic C=O), and 1677 cm.$^{-1}$ vs (arom. C=O); λ^{I}_{max} 242 mμ (ϵ 15,500); λ^{H}_{max} 253 mμ (ϵ 19,500).

α,α-**Dimethyl**-*p*-**methylbenzoylacetone** (**20**) had b.p. 130° (1 mm.); n^{23}_{D} 1.5228; ν 1735 m, 1705 s (aliphatic C=O), and 1667 cm.$^{-1}$ vs (arom. C=O); λ^{I}_{max} 254.5 mμ (ϵ 13,500); λ^{H}_{max} 253 mμ (ϵ 28,000).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.45; H, 7.90. Found: C, 76.38; H, 8.21.

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Reactivities of Bicycloalkenes toward Free-Radical Addition of Thiols[1]

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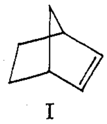
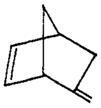
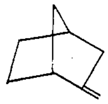
The reactivity ratio of norbornene with respect to methylenenorbornane toward free-radical addition of ethanethiol was shown to vary with both the ethanethiol concentration and temperature. At 40°, norbornene is 2.1 times more reactive than methylenenorbornane when the mole fraction of ethanethiol is 0.87, and 6.7 times more reactive when the mole fraction of ethanethiol is 0.24. At 0°, the relative reactivity ratio was considerably lower and varied between 1.13 and 1.55 as the mole fraction of ethanethiol was decreased from 0.85 to 0.55. These concentration and temperature effects are explained in terms of reversibility of the ethanethiyl radical addition to alkenes, a factor more important with methylenenorbornane than with norbornene.

The relative reactivities of alkenes have been demonstrated to be quite similar toward addition by thiyl radicals[3] and trichloromethyl radicals.[4] One notable exception is the considerably higher reactivity of endocyclic double bonds of bicycloalkenes toward addition by thiyl radicals compared with addition by trichloromethyl radicals. Norbornene (I) was shown to be 45 times more reactive than cyclohexene (II) toward addition of *p*-toluenethiol[5] but only five times more reactive than cyclohexene toward addition by trichloromethyl radicals.[4a] A more striking anomaly was recently pointed out by Cristol and co-workers who found the products formed in the addition of benzenethiol to 5-methylenenorbornene (III) resulted from addition of benzenethiyl radicals only to the endocyclic double bond with complete exclusion of any addition to the exocyclic double bond.[6] A comparison of the reactivity of I with methylenenorbornane (IV) toward addition of the trichloromethyl radical showed that IV, an alkene with an exocyclic double bond, was at least four times more reactive at 78° than I, an alkene with an endocyclic double bond.[7] Cristol and co-workers suggested that the rate of addition to an endocyclic double bond in such a system would be expected to be greater than to an exocyclic double bond


I


II


III


IV

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[2] National Science Foundation Cooperative Fellow, 1963–1965. The work described was taken from the thesis submitted by R. M. K. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1965.

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since there is a greater relief of strain in the former reaction. The slower rate of addition of the trichloromethyl radical was ascribed to the steric hindrance this radical encounters in adding to the endocyclic double bond. Although such steric effects may well play a role in retarding the addition rate of the trichloromethyl radical to endocyclic double bonds, the reversible addition of thiyl radicals to double bonds[3] may be a significant factor in causing what appears to be an enhanced reactivity of an endocyclic double bond to addition by a thiyl radical. Experiments designed to show that this reversibility factor is operative in competition reactions involving bicycloalkenes are described in this paper.

The experimentally determined reactivity ratio, $\bar{P}$, of two alkenes, M_1 and M_2, toward addition by an adding reagent in a competition reaction is generally obtained from the equation

$$\bar{P} = \frac{\log (M_1)_o/(M_1)_f}{\log (M_2)_o/(M_2)_f} \qquad (1)$$

where the subscripts o and f refer to the initial and final amounts of the alkenes, respectively. If the mechanism of a free-radical addition involves a nonreversible addition of the adding radical, as is the case of the trichloromethyl radical ($Cl_3C\cdot$) in the addition of bromotrichloromethane,[8] $\bar{P}$ is the ratio of the reaction

$$Cl_3C\cdot + M_1 \xrightarrow{k_{a_1}} Cl_3CM_1\cdot \xrightarrow[BrCCl_3]{k_{tr_1}} Cl_3CM_1Br + Cl_3C\cdot \qquad (2)$$

$$Cl_3C\cdot + M_2 \xrightarrow{k_{a_2}} Cl_3CM_2\cdot \xrightarrow[BrCCl_3]{k_{tr_2}} Cl_3CM_2Br + Cl_3C\cdot \qquad (3)$$

$$\bar{P} = k_{a_1}/k_{a_2} \qquad (4)$$

rate constants for the addition of $Cl_3C\cdot$ to M_1 and M_2, respectively, provided there are no other reactions, *i.e.*, telomerization, of the alkenes. If addition of the adding radical to the alkenes is reversible, as it is in the case of alkylthiyl radicals ($RS\cdot$) in alkanethiol additions

$$RS\cdot + M_1 \underset{k_{-a_1}}{\overset{k_{a_1}}{\rightleftarrows}} RSM_1\cdot \xrightarrow[RSH]{k_{tr_1}} RSM_1H + RS\cdot \qquad (5)$$

$$RS\cdot + M_2 \underset{k_{-a_2}}{\overset{k_{a_2}}{\rightleftarrows}} RSM_2\cdot \xrightarrow[RSH]{k_{tr_2}} RSM_2H + RS\cdot \qquad (6)$$

$$\bar{P} = \frac{k_{a_1}k_{tr_1}(k_{-a_2} + k_{tr_2}[RSH])}{k_{a_2}k_{tr_2}(k_{-a_1} + k_{tr_1}[RSH])} \qquad (7)$$ [9]

In this case, the observed value of $\bar{P}$ depends not only on the reactivities of M_1 and M_2 toward addition, but also on the rates of elimination of $RS\cdot$ from the adduct radicals and on the rates of reaction of the adduct radicals with the alkanethiol as well as the concentration of the alkanethiol. If $k_{-a_1} \ll k_{tr_1}$ and $k_{-a_2} \ll k_{tr_2}$, eq. 7 reduces to eq. 4 and $\bar{P}$ is independent of [RSH]. Conversely, if $k_{-a_1} \gg k_{tr_1}$, and $k_{-a_2} \gg k_{tr_2}$, eq. 7 reduces to

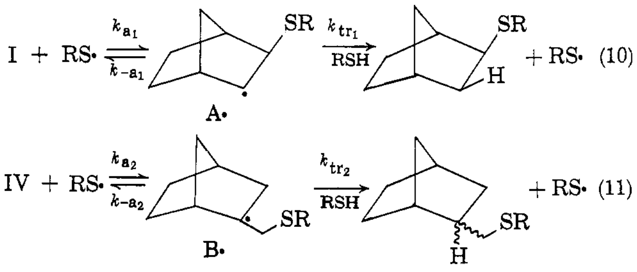
$$\bar{P} = \frac{k_{a_1}k_{-a_2}k_{tr_1}}{k_{-a_1}k_{a_2}k_{tr_2}} \qquad (8)$$

and $\bar{P}$ is again independent of [RSH]. If $k_{-a_1} \simeq k_{-a_2}$ and $k_{tr_1} \simeq k_{tr_2}$, a situation that may exist for similar alkenes, changes in [RSH] would not significantly alter $\bar{P}$. In such a situation, the value of $\bar{P}$ is very nearly that shown in eq. 4, and the determination of reliable reactivity ratios of such alkenes toward attack by alkylthiyl radicals is possible as shown by Walling and Helmreich.[3] On the other hand, if the above requirements are not met, $\bar{P}$ will become [RSH] dependent. Of particular interest is the situation where k_{-a_1} and k_{-a_2} differ to significant extent. In an extreme case, one where $k_{-a_1} = 0$ and k_{-a_2} is finite

$$\bar{P} = \frac{k_{a_1}k_{-a_2}}{k_{a_2}k_{tr_2}[RSH]} + \frac{k_{a_1}}{k_{a_2}} \qquad (9)$$

In this case, $\bar{P}$ becomes a linear function of $[RSH]^{-1}$ and at infinite concentration of the alkanethiol would equal the reactivity ratio, k_{a_1}/k_{a_2}, for M_1 and M_2 toward addition by the alkylthiyl radical.

Competition reactions of I and IV toward free-radical addition by an alkanethiol may approach the situation described in eq. 9 (I and IV equal M_1 and M_2, respectively). The two sp^2-hybridized carbons in I render a considerable amount of strain to this bicyclic system because of bond angle deformation. The amount of strain in I is reflected in its heat of hydrogenation, −33.1 kcal./mole, compared to −27.1 kcal./mole for cyclohexene.[10] The amount of strain due to bond angle deformation in IV would be expected to be



(10)

(11)

less since there is only one sp^2 carbon in the bicyclic ring system. Support for this assumption is found in that 5-methyl-2-norbornene is isomerized over an acid catalyst to IV in addition to other products resulting from polymerizations and alkyl shifts.[11] Addition of $RS\cdot$ to I producing the adduct radical A·, a species with only one sp^2 carbon in the bicyclic system, might be expected to be fast since relief of strain is involved in the process. Conversely, the fragmentation of A· to $RS\cdot$ and I would be slow because this reaction requires the formation of a strained species. Addition of $RS\cdot$ to IV does not involve any appreciable amount of relief of strain since both IV and the adduct radical B· each have one sp^2 carbon in the bicyclic ring system. Even though the rate of addition of $RS\cdot$ to IV might be expected to be slower than to I, it is also reasonable to expect that the rate of elimination of $RS\cdot$ from B· would be considerably faster than from A· because no increase in strain is encountered when B· eliminates $RS\cdot$ to yield IV.

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[8] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **77**, 4638 (1955).

[9] The same kinetic equation in different form can be found in ref. 3.

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Even though it cannot be assumed that $k_{-a_1} = 0$ in eq. 10, it should be expected that $k_{-a_1} < k_{-a_2}$. It is also possible that k_{tr_2} may be somewhat smaller than k_{tr_1} because B· is a tertiary radical whereas A· is secondary and hydrogen atom abstraction by B· could encounter greater steric hindrance. Both conditions suggest that $\bar{P}$ would increase with decreasing concentration of the alkanethiol if the reversibility of the alkylthiyl radical addition is a significant factor. The data in Table I show that at both 40 and 0° an increase in $\bar{P}$ is observed in the competition reactions of I and IV toward addition by ethanethiol as the ethanethiol concentration is decreased. A sufficient ethanethiol concentration was maintained in these competition studies to minimize any consumption of I and IV in telomerization reactions. The initial ratio of ethanethiol to the sum of the two alkenes was greater than one in the reactions performed at 30 and 0°. In items 2–6 of Table I, the ratio of ethanethiol to the sum of the two alkenes was maintained at 1.3–1.4. The ethanethiol concentration was modified by diluting the reaction mixture with bromobenzene making possible the attainment of comparatively low concentrations of ethanethiol without enhancing the possibility of telomerization.

TABLE I

COMPETITION REACTIONS OF NORBORNENE (I) AND METHYLENENORBORNANE (IV) WITH ETHANETHIOL

	Initial mole fractions					
No.	Ethanethiol	I + IV	Bromobenzene	Temp., °C.	$\bar{P}$	No. of runs
1	0.87	0.13	0.00	40	2.1 ± 0.2	3
2	0.53	0.39	0.08	40	3.1 ± 0.1	2
3	0.46	0.33	0.21	40	5.3 ± 0.3	3
4	0.39	0.27	0.37	40	6.3 ± 0.1	3
5	0.29	0.22	0.49	40	6.2 ± 0.1	3
6	0.24	0.18	0.58	40	6.7 ± 0.3	2
7	0.85	0.15	0.00	30	1.7 ± 0.1	3
8	0.85	0.15	0.00	0	1.13 ± 0.01	3
9	0.70	0.30	0.00	0	1.22 ± 0.03	3
10	0.55	0.45	0.00	0	1.55 ± 0.03	3

Comparison of items 1, 7, and 8, reactions which have essentially the same initial ratios of ethanethiol to alkene, shows that $\bar{P}$ decreases as the temperature is lowered. If there were no reversible addition ($\bar{P} = k_{a_1}/k_{a_2}$), finding $\bar{P} > 1$ would mean that the activation energy requirement for the addition of $C_2H_5S\cdot$ to IV was greater than for the addition to I. Decreasing the temperature of the competition reaction would be expected to raise the value of $\bar{P}$ (increase the difference in the reactivities of I and IV), since the reaction with the higher activation energy would be slowed to a greater extent at a lower temperature than one with a smaller activation energy. The decrease in $\bar{P}$ as the temperature is lowered is, however, consistent with an addition of $C_2H_5S\cdot$ to IV that is significantly reversible, whereas addition to I is essentially irreversible. The rates of fragmentation reactions of radicals generally decrease with decreasing temperature.[12] A decrease in temperature might therefore be expected to cause a significant decrease in the rate of elimination of $C_2H_5S\cdot$ from B· but have no effect on the fragmentation of A· if its rate of elimination of $C_2H_5S\cdot$ is too small to be of any consequence. Examination of eq. 9 shows that lowering the value of k_{-a_2} would result in a decrease in $\bar{P}$.

Changing the concentration of $BrCCl_3$ has no appreciable effect on the reactivity ratios of I with respect to IV toward addition of this reagent (Table II). In this case, $\bar{P}$ is most likely a good measure of the relative reactivities of the two alkenes toward addition of the trichloromethyl radical as would be predicted from eq. 4 because the reaction involves a nonreversible addition of the trichloromethyl radical. Furthermore, the temperature effect, namely the difference in reactivities being greater at the lower temperature, is consistent with a competition reaction where $\bar{P}$ is dependent on the activation energies of the addition of the radical to the double bonds and is independent of any reversible steps in the chain sequence.

TABLE II

COMPETITION REACTIONS OF NORBORNENE (I) AND METHYLENENORBORNANE (IV) TOWARD ADDITION OF $Cl_3C\cdot$

Initial mole fractions					
Adding reagent	I + IV	Bromobenzene	Temp., °C.	$\bar{P}$	No. of runs
0.84 (Cl_4C)	0.16	0.00	78	0.23 ± 0.1	3
0.53 ($BrCCl_3$)	0.47	0.00	35	0.13 ± 0.1	3
0.26 ($BrCCl_3$)	0.25	0.49	35	0.15 ± 0.1	3
0.17 ($BrCCl_3$)	0.17	0.65	35	0.16 ± 0.1	2

Although the data in Table I do not show the linear relationship between $\bar{P}$ and the concentration of ethanethiol predicted by eq. 9, possibly because k_{-a_1} has a finite value, a rough extrapolation to infinite concentration of the thiol indicates that $k_{a_1}/k_{a_2} \cong 1$. The same conclusion can be reached from the temperature effect. This value is still somewhat higher than that found for the reactivity ratio of I with respect to IV toward addition by the trichloromethyl radical. The steric effect encountered in the addition of trichloromethyl radicals to I suggested by Cristol and co-workers may be operative. However, our experiments show that the relief of strain in the addition of the thiyl radical to endocyclic double bonds of bicycloalkenes is not solely responsible for their high reactivity in competition reactions involving addition of thiols. The slow rate of elimination of the thiyl radical from an adduct radical less strained than the parent alkene may be an important factor in causing endocyclic double bonds of bicycloalkenes to display a high reactivity in such competition studies.

Experimental

Ethanethiol (Matheson Coleman and Bell) was used without further purification. Bromotrichloromethane (The Dow Chemical Co.) and norbornene (Aldrich Chemical Co.) were redistilled before use. Methylenenorbornane (b.p. 119–123°) was prepared in the manner previously described.[13]

Competition Reactions of I and IV with Ethanethiol.—Accurately weighed amounts of norbornene (I) and methylenenorbornane (IV), approximately 40 and 80 mg., respectively, were introduced into Pyrex tubes along with accurately determined amounts of ethanethiol and, when required, bromo-

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[12] For a discussion of reversibility of free-radical polymerization reactions, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 212–228.

[13] O. Diels and K. Alder, *Ann.*, **470**, 79 (1929).

benzene. A few milligrams of benzene, which served as an internal standard for the gas chromatographic analyses, was also added to the mixture. During any storage periods, the tubes were immersed in a −80° bath to prevent reaction or evaporation of the components. After warming to room temperature, a 5-μl. sample was withdrawn by a Fisher pipet; the sample was analyzed on a gas chromatographic column packed with Oronite 20 on Chromosorb W. The components were eluted on this column in the order ethanethiol, benzene, norbornene, methylenenorbornane, and bromobenzene. The tubes were again cooled to −80°, sealed with tight-fitting serum caps, and placed in a water bath thermostated at the appropriate temperature. The reaction mixtures were illuminated for 10 to 12 min. with a 275-w. General Electric sun lamp placed 6 to 8 in. from the bath. The tubes were withdrawn from the bath and the reaction immediately quenched by cooling to −80°. After warming to room temperature, another 5-μl. sample was withdrawn and subjected to gas chromatographic analysis. The amounts of the two alkenes remaining after reaction were determined by comparing their peak areas with those obtained before illumination using the peak area of benzene to correct for any differences in the sizes of the samples injected on the gas chromatographic column. Duplicate chromatograms were made in all cases. Knowing the amounts of the two alkenes before and after reaction, the relative reactivity ratios of the two alkenes toward addition of ethanethiol were calculated using eq. 1. The results of these competition reactions are given in Table I.

Competition Reactions of I and IV with Bromotrichloromethane.—Solutions consisting of accurately weighed amounts of norbornene, methylenenorbornane, bromotrichloromethane, bromobenzene, and benzene were prepared and placed in Pyrex tubes. Samples of the mixtures were subjected to gas chromatographic analysis on a column packed with S.E.-30 on Chromosorb W. The mixtures were placed in a water bath thermostated at 35° and illuminated with a 275-w. General Electric sun lamp for about 1 hr. Samples were again chromatographed, and the amounts of the two alkenes remaining were determined from their peak areas using the area of the benzene to correct for any differences in sample size. The relative reactivity ratios were calculated using eq. 1, and the results are shown in Table II.

The Isomerization of Cyclooctadienes to *cis*-Bicyclo[3.3.0]oct-2-ene

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Treatment of either 1,5- or 1,3-cyclooctadiene with phenylpotassium or other strong bases has been shown to give *cis*-bicyclo[3.3.0]oct-2-ene as the major product in 50–65% yield. The use of elemental potassium as a catalyst for the rearrangement of 1,3-cyclooctadiene provides a very useful synthesis of this hitherto difficultly obtainable olefin. Investigation of dimeric by-products in the isomerization of 1,3-cyclooctadiene has shown that a cyclooctenyl-*cis*-bicyclo[3.3.0]octene, a cyclooctenylcyclooctadiene, and an octadienyl-*cis*-bicyclo[3.3.0]-octene were produced.

cis-Bicyclo[3.3.0]oct-2-ene has been reported as a minor product formed by a transannular hydride shift in the solvolysis of *cis*- and *trans*-1,2-cyclooctanediol ditosylate,[1] and in the solvolysis of 4-cycloocten-1-yl brosylate.[2] Blanchard and Germain[3] have shown that *cis*-bicyclo[3.3.0]oct-2-ene is also obtained as one of the products of the isomerization of various eight-carbon cyclic olefins and diolefins over a silicophosphoric acid catalyst at 250°. The compounds that were isomerized include 4-vinylcyclohexene, 2-methylenenorbornane, 5-methyl-2-norbornene, and bicyclo[2.2.2]oct-2-ene. Previously described synthetic routes to this olefin have been based on the difficultly accessible *cis*-bicyclo[3.3.0]octan-2-one.[4] It has now been found that either 1,5- or 1,3-cyclooctadiene undergoes a facile rearrangement when heated with catalytic quantities of strong base to give *cis*-bicyclo[3.3.0]-oct-2-ene in good yield.

1,5-Cyclooctadiene was heated with 15 wt. % of phenylpotassium (from anisole and potassium[5]) in heptane in a stirred autoclave at 175°. Gas chromatographic analysis of the C_8 fraction, obtained in 72% yield, showed it to contain at least six components with the predominant isomer accounting for 70% of the total. This major product was purified by fractionation and was shown to be *cis*-bicyclo[3.3.0]oct-2-ene by its mass spectrum (mol. wt. 108), boiling point, and refractive index, and by comparison of its infrared spectrum with a published spectrum.[3c] Further confirmation was provided by oxidation with potassium permanganate and sodium metaperiodate[6] to the known *cis*-2-carboxycyclopentaneacetic acid.[7]

Four of the remaining five components were identified (see Experimental) as 1,5-cyclooctadiene, cyclooctene, 1,3-cyclooctadiene, and 4-vinylcyclohexene by a combination of gas chromatographic retention times and hydrogenation of different fractions. Two large-scale runs were combined and carefully fractionated to give a forecut enriched in the lower boiling C_8 by-products for characterization. After hydrogenation, analysis with a gas chromatograph–mass spectrometer combination showed that ethylbenzene, *n*-propylcyclopentane (corresponding to the unidentified olefin in the initial run), and *n*-octane were also present in addition to the previously identified compound. Attempts to detect bicyclo[4.2.0]octane in the saturated hydrocarbon mixture were unsuccessful.

A plausible mechanism, consistent with the formation of *cis*-bicyclo[3.3.0]oct-2-ene, involves the well-known base-catalyzed isomerization of 1,5-cyclooctadiene to the 1,3 isomer.[8] Allylic proton abstraction, followed by a transannular addition of the resulting carbanion to the end of the conjugated system, would lead to the observed product. A previous proposal of a transannular attack of a carbanion upon an

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