[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF KANSAS]

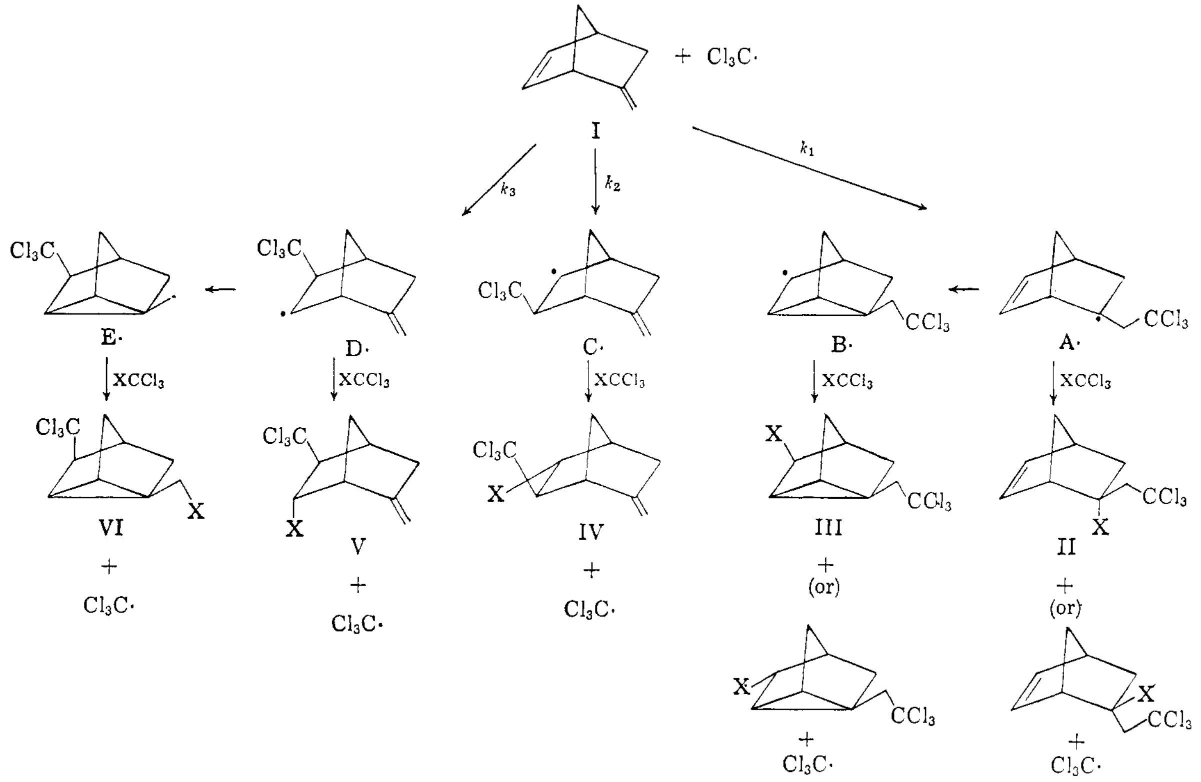
Free Radical Additions to 2-Methylenebicyclo[2.2.1]hept-2-ene[1]

EARL S. HUYSER AND GLORIA ECHEGARAY

Received July 24, 1961

Carbon tetrachloride, chloroform, and bromotrichloromethane have been added to 5-methylenebicyclo[2.2.1]hept-2-ene (I) in benzoyl peroxide–induced reactions. The major addition product in these reactions is a tricyclene derivative. Competitive reactions involving I, norbornene, and 2-methylenenorbornane with the trichloromethyl radical show that the exocyclic double bond in this bicyclic system is about 4.4 times more reactive than an endocyclic double bond toward addition by a free radical and, furthermore, no anchimeric assistance involving a nonclassical free radical is involved in additions of a trichloromethyl radical to this bicyclic system.

Free radical additions to certain bicyclic dienes have been shown to yield considerable amounts of saturated tricyclene derivatives. The addition of arylthiols to norbornadiene in a free radical chain reaction has been studied by Cristol and co-workers, who report the presence of saturated tricyclene derivatives in the simple addition product.[2] The work described in this report is concerned with the free radical additions of polyhalomethanes to 5-methylenebicyclo[2.2.1]hept-2-ene (I), a homoconjugated bicyclic diene readily obtained by the Diels-Alder reaction of cyclopentadiene and allene.[3] Additions to this diene, which has nonequivalent double bonds, one exocyclic and one endocyclic, result in the formation of complex mixtures of addition products consisting of one molecule of diene and one of the polyhalomethane. This bicyclic diene does, however, lend itself readily to certain mechanistic studies of free radical addition reactions.



The benzoyl peroxide–induced reactions of carbon tetrachloride, chloroform, and bromotrichloromethane to I yielded products which gave analyses corresponding to material resulting from the addition of one molecule of the polyhalomethane to I (see Table I). However, as the following reaction scheme indicates, several different products, both saturated tricyclene derivatives (III and VI) and unsaturated bicyclic derivatives, could be formed as addition products. Although the investigations described below do not lead to a complete analysis of the product distribution, they do suggest that

---

(1) Abstracted from the thesis submitted by G. Echegaray in partial fulfillment of the requirements for the M.S. degree at The University of Kansas.

(2) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

(3) H. Pledger, Jr., *J. Org. Chem.*, **25**, 278 (1960).

TABLE I

ADDITION PRODUCTS OF POLYHALOMETHANES TO 5-METHYLENEBICYCLO[2.2.1]HEPT-2-ENE

Addition Product	Mol. Wt. Calc.	Mol. Wt. Found	C Calc.	C Found	H Calc.	H Found	Cl Calc.	Cl Found	% Unsat.
I: CCl_4	260	268	41.58	41.31	3.88	3.71	54.55	54.58	9–10
I: $HCCl_3$	225	229	47.93	48.22	4.92	4.94	47.16	46.80	13–15
I: $BrCCl_3$	304	320	35.50	35.77	3.31	3.23	—	—	2–4

the tricyclene derivative III is the major addition product in these reactions.

The stereochemistry of X and the 2,2,2-trichloroethyl group in II and of X in III has not been determined and either or both isomers could be present in the product. The trans addition of bromotrichloromethane to norbornene[4] with the trichloromethyl radical entering *exo* would lend validity to the stereochemical assignments of X and the trichloromethyl groups in IV, V, and VI.

The relative amounts of II and III produced with respect to IV, V, and VI should be dependent only on the ratio $\frac{k_1}{k_2 + k_3}$ and independent of the polyhalomethane. This relative reactivity ratio of the exocyclic double bond with respect to the endocyclic double bond was determined from competition reactions of the model compounds 2-methyl-endnorbornane (VII) and norbornene (VIII) toward the trichloromethyl radical.

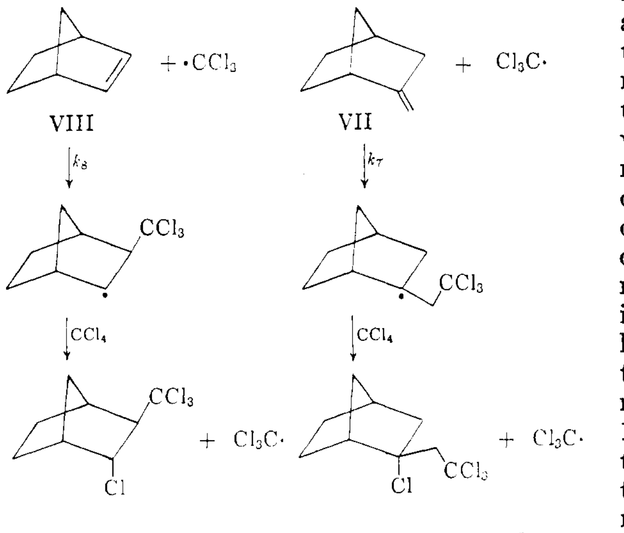


TABLE II

COMPETITION REACTIONS OF 2-METHYLENENORBORNANE AND NORBORNENE WITH CCl_4 AT 78°

	VII Int. Conc.[a]	VII Final Conc.	VIII Int. Conc.	VIII Final Conc.	k_7/k_8
1	2.59	0.99	2.83	2.23	4.0
2	2.79	1.37	3.06	2.64	4.8
3	2.63	1.20	2.98	2.46	4.3

[a] Concentrations in moles.

Table II lists the data from gas chromatographic analysis of reaction mixtures in which VII and VIII react with carbon tetrachloride in a benzoyl peroxide induced addition reaction at 78°. An excess amount of carbon tetrachloride was used to minimize polymerization of the olefins. The relative reactivity ratio k_7/k_8 was determined by the use of the data in Table II *via* the usual kinetic expression

$$k_7/k_8 = \frac{\log (VII)_0/(VII)}{\log (VIII)_0/(VIII)}$$

where $(VII)_0$ and (VII) are the initial and final concentrations respectively of VII, and $(VIII)_0$ and (VIII) are the initial and final concentrations of VIII. The three determinations performed with this system lead to an average value of 4.4 for k_7/k_8. This value is consistent with other previously determined relative reactivities for somewhat similar systems. Kharasch[5] reports the terminal olefin 1-octene to be 4.2 times more reactive than the endocyclic olefin cyclohexene toward trichloromethyl radicals. Walling reports a relative reactivity of about 4.0 for 1-octene with respect to cyclohexene toward thiyl radicals.[6] However, comparing the reactivity of the double bond in norbornene with that in cyclohexene toward radical addition is not valid. Kharasch and Friedlander[5] report that the reactivity of norbornene is about five times that of cyclohexene in reactions with trichloromethyl radicals and Cristol and Brindell report the bicyclic olefin to be 45 times more reactive toward thiyl radicals.[7] The suggestion has been made that strain in the bicyclic system is responsible for the enhanced reactivity in norbornene. The correlation of the relative reactivity of VII and VIII with that reported for nonstrained olefins (cyclohexene and 1-octene) suggests that whatever factors increase the reactivity of the endocyclic double bonds in these systems are also operative in increasing the reactivity of the exocyclic double bond to the same extent.

One cannot conclude *pa riori* that the ratio of reactivity of the exo double bond with respect to the endo double bond in I will necessarily be that found from the experiments with VII and VIII.

---

[4] See ref. 5. Also, E. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

[5] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, 14, 239 (1949).

[6] C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, 81, 1144 (1959).

[7] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, 76, 5699 (1954).

The homoconjugative nature of the double bonds suggests the possibility of nonclassical radical stabilization in the transition state which might change the reactivity of this diene toward radical addition as shown for addition to the exocyclic double bond in I. Similar nonclassical stabilization could be postulated for addition of the free radical at the 2-carbon of the endocyclic double bond. All previous reports[8] tend to deny the existence of a nonclassical free radical analogous to the well founded nonclassical carbonium ion. Competitive reactions of I and VII with the trichloromethyl radical (see Table III) show about 28% enhancement in the reactivity of the homoconjugated diene. From the previous data described for the endo and exo cyclic double bonds, these results indicate that the two double bonds in I react independently, the total reactivity being almost additive.[9]

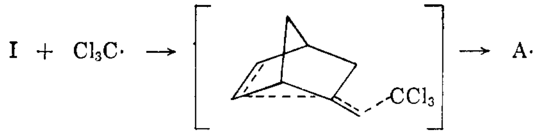


TABLE III

Competitive Reactions of 2-Methylenebicyclo [2.2.1] hept-2-ene and 2-methylenenorbornane with $Cl_3C\cdot$ at 78°

	I		VII		
	Int. conc.	Fin. conc.	Int. conc.	Fin. conc.	$\frac{k_1 + k_2 + k_3}{k_7}$
1	2.75	1.55	2.74	1.72	1.23
2	2.68	1.90	2.66	2.01	1.28
3	2.76	2.12	2.86	2.01	1.33

Our competitive studies indicate that 75–80% of the trichloromethyl radicals add to the exocyclic double bond of I. This suggests that II and III are very likely the predominant addition products one might expect in addition of polyhalomethanes which involve the trichloromethyl radical as the adding species. As about 20–25% of the radicals can add to the endocyclic double bond, part of the addition product almost certainly consists of IV, V, and VI. The amount of addition involving bonding at the 2-carbon with respect to that involving the 3-carbon cannot be deduced from our experiments. However, the apparent lack of any anchimeric assistance in these reactions would tend to indicate equal amounts. Further, previous work has shown that both in radical and nonchain processes,[10] the entering species forms an *exo* bond with the bicyclic system. This would tend to eliminate the possibility of any steric consideration rendering the 3-carbon less reactive than the 2-carbon toward attack by the trichloromethyl radical.

Quantitative determination of the amount of unsaturation in the addition product was ascertained by hydrogenation of the material over platinum oxide in ethyl acetate at atmospheric pressure. Under these conditions, no detectable amounts of hydrogenolysis of the halide were observed. The data in Table I shows that for the most part, the addition product is saturated.[11] The very high degree of saturation in each case suggests that III and VI are the major addition products, III predominating over VI for the reasons explained above.

One might expect the product to contain a minimum of about 12% unsaturation due to IV, a product which results from radical C·, which cannot undergo a transannular addition to form a saturated product. The fact that the amount of unsaturation is lower than this minimum value in two cases may be due to removal of IV (and V) by further reaction of the reactive exocyclic double bonds in this 1:1 addition product.

The fact that the saturated tricyclene derivatives predominate is not surprising. It has been previously demonstrated that tricyclene itself is more stable than norbornene.[12] Further, the proximity of the double bond to the free radical site should encourage the transannular addition reaction.

EXPERIMENTAL[13]

Reagents. Carbon tetrachloride; Matheson, Coleman and Bell Spectroquality Reagent. Chloroform; Matheson, Coleman and Bell; Spectroquality Reagent. Bromotrichloromethane; The Dow Chemical Co. Redistilled under vacuum to remove any residual amounts of carbon tetrachloride.

---

[8] For example, see ref. 2. Also J. A. Berson and W. M. Jones, *J. Am. Chem. Soc.*, **78**, 6045 (1956); E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); N. A. Le Bel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

[9] A similar competitive experiment between norbornene and norbornadiene for thiyl radicals showed the diene to be far more reactive (see ref. 2). However, as Cristol points out, this very likely results from destabilization of the highly strained bicyclic diene system.

[10] For example, see ref. 6. Also K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); **515**, 185 (1935); R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948); G. Stork, E. E. van Tamelen, L. J. Friedman, and A. W. Burgstahler, *J. Am. Chem. Soc.*, **75**, 384 (1953).

[11] The variance in the amount of unsaturation in the addition products observed for the different polyhalomethanes is opposite of what might be expected as a first approximation. The data in Table I suggest that the transannular additions occuring in the adduct radicals A· and D· compete more favorably with the abstraction reactions on the good chain transfer agent, bromotrichloromethane, than with the poor chain transfer agent, chloroform. These results may be due to a change in experimental conditions, particularly in the bromotrichloromethane case (see Experimental) or possibly certain kinetic or steric factors present in these bicyclic free radicals. Further experiments designed to study these factors with the system described in this paper and with other bicyclic dienes are presently in progress and will be described in a future publication.

[12] P. von Schlyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

[13] Molecular weights were found by freezing point depression of benzene. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. All boiling points are uncorrected.

Benzoyl peroxide; Matheson, Coleman and Bell. Recrystallized from chloroform and methanol. Norbornene; Matheson, Coleman and Bell.

5-Methylenebicyclo[2.2.1]hept-2-ene[14] was redistilled before using (b.p. 67°/170 mm., n_D^{25} 1.4835) and was 99.5% pure by gas chromatographic analysis.

2-Methylenenorbornane (b.p. 121–122°; n_D^{25} 1.4727) was prepared in the manner described by Diels and Alder,[15] which consisted of a Chugaev elimination on 2-norcamphanemethanol. This alcohol was prepared by catalytic hydrogenation of the olefinic linkage and sodium borohydride reduction of aldehydic function of bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde, the Diels-Alder adduct obtained from acrolein and cyclopentadiene.

The gas chromatographic analyses were performed on a 10 ft. by $^1/_4$ in. column packed with 15% Oronite 16 (Oronite Chem. Co.) on Chromosorb W. Column temperature was maintained at 99° and helium (head pressure 10 p.s.i.g.) was used as the carrier gas.

Addition of carbon tetrachloride to 5-methylenebicyclo[2.2.1]hept-2-ene. Carbon tetrachloride (308 g., 2.0 moles), 5-methylenebicyclo [2.2.1] hept-2-ene (26.5 g., 0.25 mole), and benzoyl peroxide (2.4 g., 0.01 mole) were heated at reflux (86–87°) for eighteen hours. Removal of the excess carbon tetrachloride by distillation at atmospheric pressure left a high boiling residue which on vacuum distillation yielded 47.7 g. (73% based on diene present) of crude 1:1 addition product (b.p. 91–100° at 3 mm.).

The material gave an analysis of $C_9H_{10}Cl_4$: Calc. C, 41.58; H, 3.88; Cl, 54.55. Found: C, 41.31; H, 3.71; C, 54.88. Calculated molecular weight 260; found 260 ± 5. Quantitative hydrogenation over platinum oxide in ethyl acetate indicated about 9–10% unsaturation.

After removal of the 1:1 addition product by vacuum distillation of the reaction mixture, a higher boiling residue amounting to 15.9 g. with an average molecular weight of 413 ± 5 remained.

Addition of chloroform to 5-methylenebicyclo[2.2.1]hept-2-ene. Chloroform (239 g., 2.0 mole), 5-methylenebicyclo[2.2.1] hept-2-ene (26.5 g., 0.25 mole), and benzoyl peroxide (2.4 g., 0.01 mole) were heated at reflux (69–70°) for 24 hours. After removal of the unchanged chloroform by distillation at atmospheric pressure, 23.4 g. (42% based on diene present) of crude 1:1 addition product were distilled over a range of 62–75° at 3 mm. from the remaining residue.

This material gave an analysis corresponding to $C_9H_{11}Cl_3$: Calc. C, 47.93; H, 4.92; Cl, 47.16. Found: C, 48.22; H, 4.94; Cl, 46.80. Calc. molecular weight, 225.6; found, 229 ± 6. Quantitative hydrogenation over platinum oxide in ethyl acetate indicated 13–15% unsaturation.

A residue with a molecular weight of 349 ± 5 amounting to 15.1 g. remained after distillation of the 1:1 addition product from the reaction mixture.

Addition of bromotrichloromethane to 5-methylenebicyclo[2.2.1]hept-2-ene. Over a period of three hours, a mixture consisting of 5-methylenebicyclo[2.2.1]hept-2-ene (13.25 g., 0.125 mole) and benzoyl peroxide (0.5 g., 0.002 mole) was added to 99 g. (0.50 mole) of bromotrichloromethane heated at 75–80° in an oil bath. Vacuum distillation of the reaction mixture yielded 28.6 g. (61.2% based on diene present) of crude 1:1 addition product (b.p. 119–123° at 3 mm.).

Anal. Calcd. for $C_9H_{10}Cl_3Br$: C, 35.50; H, 3.31; Found: C, 35.77; H, 3.23. Calc. molecular weight, 304.5; found 321 ± 6. Quantitative hydrogenation shows 2–4% unsaturation in this material.

A high boiling residue amounting to 9.0 g. with a molecular weight of 412 ± 5 remained after distillation of the 1:1 addition product from the reaction mixture.

Determination of relative reactivity ratios. The data in Tables II and III used to calculate the relative reactivity ratios of the olefins toward trichloromethyl radicals were obtained in the following manner: About 0.2 to 0.3 g. of the two olefins was accurately weighed out to the nearest milligram and added to an excess of carbon tetrachloride (mole ratio of carbon tetrachloride to olefins was about 5:1). An amount of chlorobenzene very nearly equivalent to the individual olefins present was added to serve as an internal standard for the gas chromatographic analysis. The peak areas of the two olefins and the chlorobenzene in the gas chromatogram of this reaction mixture before heating were measured with a planar compensating planimeter. The reaction mixture was then sealed in a Pyrex tube with 5–10 mg. of benzoyl peroxide and heated for several hours in an ethanol vapor bath. The concentrations of the two olefins remaining after this heating period was determined from the peak areas of the gas chromatogram of this reaction mixture. The area of the internal standard was used to correct for any difference in the sample size used for the gas chromatographic analysis.

Lawrence, Kan.

---

[14] Kindly supplied to us by Dr. H. Pledger, Jr., The Dow Chemical Co., Texas Division, Freeport, Tex.

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