Free-radical Addition Reactions of Some Olefins related to Bicyclo-[2,2,2]octane

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The products of the addition of benzenethiol to bicyclo[2,2,2]oct-2-ene, 2-methylenebicyclo[2,2,2]octane, 5-methylenebicyclo[2,2,2]oct-2-ene, 2,3-dimethylenebicyclo[2,2,2]octane, 5,6-dimethylenebicyclo[2,2,2]oct-2-ene, and 8,9-dimethylenebicyclo[3,2,2]non-6-ene have been investigated. The additions of methanethiol to 2,3-dimethylenebicyclo[2,2,2]octane, of *p*-thiocresol to 5,6-dimethylenebicyclo[2,2,2]oct-2-ene, and of bromotrichloromethane and methylene dibromide to bicyclo[2,2,2]oct-2-ene have also been studied. In the additions to mono-olefins, products of 1,2-addition to the double bond result, whereas with conjugated dienes products of 1,4-addition to the diene systems are formed. Only a few per cent, at most, of products of homoconjugative addition were isolated in the addition of benzenethiol to 5-methylenebicyclo[2,2,2]oct-2-ene. No such product was detected in additions to 5,6-dimethylenebicyclo[2,2,2]oct-2-ene and 8,9-dimethylenebicyclo[3,2,2]non-6-ene. The double bonds and diene systems in these compounds react independently of each other to a large extent. The reactivities (relative to oct-1-ene) of the olefins and dienes in the bicyclo[2,2,2]octane series towards benzenethiol, and towards methyl thioglycollate have been obtained. Apart from the conjugated dienes, which have high reactivities, the olefins and non-conjugated diene are less reactive than the corresponding compounds related to norbornene. This may indicate the smaller degree of strain in olefins in the bicyclo[2,2,2]octane series.

THE free-radical addition of reagents to olefins and dienes in the bicyclo[2,2,1]heptane series [1,2] has received much greater attention than the additions to comparable compounds in the bicyclo[2,2,2]octane series.[3-5] The total ground state strain in bicyclo[2,2,2]octane is very much less than that in norbornane,[6] and a similar

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[1] See D. I. Davies and S. J. Cristol, *Adv. in Free Radical Chem.*, 1966, **1**, 155, for a review.

[2] J. A. Claisse and D. I. Davies, *J. Chem. Soc.* (*C*), 1966, 1045.

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

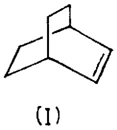
[4] N. A. LeBel, J. E. Huber, and L. H. Zalkow, *J. Amer. Chem. Soc.*, 1962, **84**, 2226.

[5] H. M. Walborsky, *Experientia*, 1953, **9**, 209.

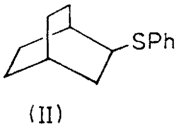
[6] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582, and references therein.

difference in strain probably exists between unsaturated compounds in the two series. We therefore studied additions to unsaturated bicyclo[2,2,2]octanes, so that a comparison could be made with the bicyclo[2,2,1]heptane series, and some estimate could be made of the effect of strain in such additions.

The addition of benzenethiol to bicyclo[2,2,2]oct-2-ene (I) requires more vigorous conditions than in the addition of the related *p*-thiocresol[7] to norbornene. The earlier assignment[4] of the product as bicyclo[2,2,2]oct-2-yl phenyl sulphide (II) is consistent[8] with our observation that H(2) gives rise to a poorly resolved quartet at τ 6·63 (*J* 6 and 10 c./sec.) in the n.m.r. spectrum.

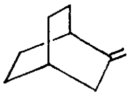


(I)

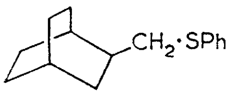


(II)

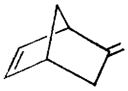
Benzenethiol adds to 2-methylenebicyclo[2,2,2]octane (III), under conditions similar to those for the addition to bicyclo[2,2,2]oct-2-ene (I), and affords bicyclo[2,2,2]oct-2-ylmethyl phenyl sulphide (IV) as sole product [τ 7·15 (d, *J* 7 c./sec., CH_2·SPh); any rearrangement would put CH_2·SPh at a bridgehead, which would give a singlet in the n.m.r. spectrum].



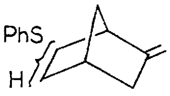
(III)



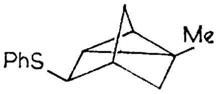
(IV)



(V)



(VI)



(VII)

In the addition of benzenethiol[9] to 5-methylenenorborn-2-ene (V), the products (VI) and (VII) are formed from radical attack on the endocyclic double bond, whereas in polyhalogenomethane[10] additions radical attack can occur on both double bonds. The reaction between equimolar quantities of benzenethiol and 5-methylenebicyclo[2,2,2]oct-2-ene (VIII) affords 20—25% of unchanged diene and a mixture of 1 : 1 and 2 : 1 adducts in the ratio *ca.* 2 : 1. The attack of phenylthio-radicals on (VIII) could lead to intermediates (IX)—(XI) of which (IX) and (XI) can undergo internal homoconjugative addition (see Scheme) to form (XII) and (XIII). Chain transfer of the intermediates (IX)—(XIII) can then lead to the 1 : 1 adducts (XIV)—(XVIII). Of these, (XV)—(XVII) still possess a double bond, and further addition of benzenethiol should produce the 2 : 1 adduct mixture (XIXa)—(XXIIb). The observation of appreciable quantities of 2 : 1 adducts implies that the reactivity of (XV)—(XVII) is not appreciably different from that of starting diene (VIII), which suggests that the double bonds of (VIII) react independently to a large extent and have little homoconjugative interaction. The n.m.r. spectrum of the 1 : 1 adduct mixture shows endocyclic olefinic protons [τ 3·62 (q, *J* 3·5 and 4 c./sec.)] and exocyclic olefinic protons [5·10 and 5·30 (each q, *J* 4 and 2 c./sec.)] in the ratio 1·67 : 1·25, which suggests that (XVII) and (XV + XVI) are present in these proportions, and that the two different types of double bond in (VIII) have therefore comparable reactivity towards addition of phenylthio-radicals. In an effort to isolate any tricyclic products, (XIV) and (XVIII), formed by homoconjugative addition, the reaction was repeated, and then excess of mercaptoacetic acid was added. This reacts with unsaturated 1 : 1 adducts (XV)—(XVII) to afford 2 : 1 adducts (XIXb)—(XXIIb), which contain a carboxy-group, and which were extracted with alkali to leave any tricyclic products, (XIV) and (XVIII), together with 2 : 1 adducts (XIXa)—(XXIIa), from the original benzenethiol addition, which we attempted to separate by distillation. This allowed us to estimate that the original 1 : 1 adduct (XIV)—(XVIII) mixture contains less than 5% of the tricyclic adducts (XIV) and (XVIII). The addition of excess of benzenethiol to 5-methylenebicyclo[2,2,2]oct-2-ene (VIII) affords a mixture of 2 : 1 adducts (XIXa)—(XXIIa), together with the tricyclic 1 : 1 adducts (XIV) and (XVIII), which cannot react further. The ratio of aromatic to aliphatic protons in these 2 : 1 adducts is about twice that in the tricyclic 1 : 1 adducts. In the n.m.r. spectrum of the product mixture, the integral ratio of aromatic to aliphatic protons fitted very well for the 2 : 1 adduct, indicating that not more than a few per cent of the tricyclic 1 : 1 adducts (XIV) and (XVIII) could be present. The absence of appreciable quantities of (XIV) and (XVIII) suggests that there is little homoconjugative interaction between the double bonds of (VIII).

The addition of benzenethiol to 2,3-dimethylenebicyclo[2,2,2]octane (XXIII) affords the product (XXVIIa) of 1,4-addition to the diene system, recognised by the absence of olefinic proton signals in the n.m.r. spectrum, and the presence of signals for vinylic methyl protons, and vinylic methylene protons adjacent to sulphur, as singlets at τ 8·52 and 6·52, respectively. Chain transfer with the intermediate allylic radical system (XXIVa) ⟷ (XXVa) apparently leads to (XXVIIa), the more stable of the two possible product olefins (XXVIa) and (XXVIIa). This is analogous to the addition of thiols to 2,3-dimethylenenorbornane.[2,11] To increase the ease

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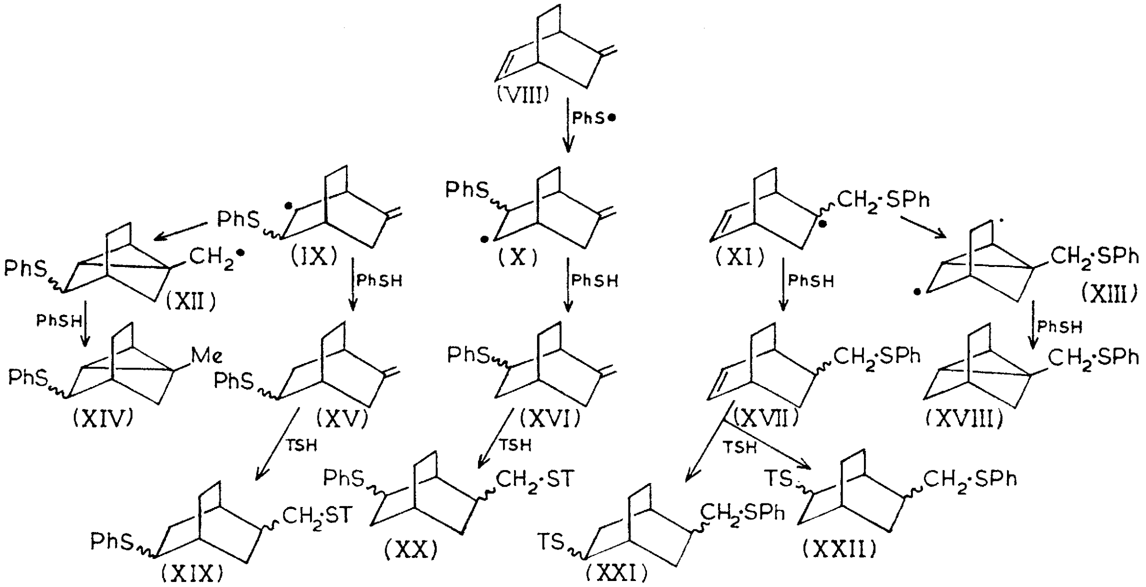
S. J. Cristol and G. D. Brindell, *J. Amer. Chem. Soc.*, 1954, **76**, 5699.

[8] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, 1964, **97**, 2798; D. B. Roll and A. C. Huitric, *J. Pharm. Sci.*, 1965, **54**, 1110.

[9] S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, 1965, **30**, 207.

[10] E. S. Huyser and G. Echegaray, *J. Org. Chem.*, 1962, **27**, 429.

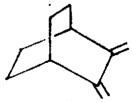
[11] J. A. Claisse and D. I. Davies, *J. Chem. Soc.*, 1965, 4894.

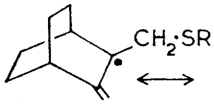


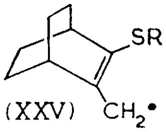
SCHEME

⁓ Indicates stereochemistry unknown at this position. It is likely that both of the two possible epimers are formed. For (XIX)—(XXII): a, T = Ph; b, T = $CH_2{\cdot}CO_2H$.

of access to chain transfer at the tertiary position of the allylic radical, the smaller methanethiol was added, but again the product of 1,4-addition (XXVIIb) was formed [τ 8·3 (MeC:C), 6·81 ($CH_2C{:}C$), and 8·1 (MeS) as singlets].

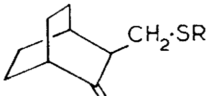

(XXIII)


(XXIV)

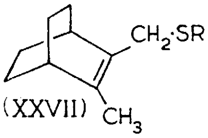


(XXV)

a; R = Ph
b; R = Me



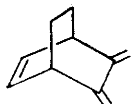
(XXVI)

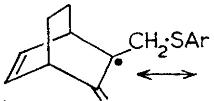


(XXVII)

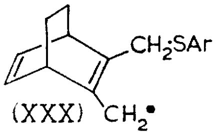
a; Ar = Ph b; Ar = p — MeC_6H_4 —

The reaction between equimolar quantities of benzenethiol and the triene 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII) afforded a 1 : 1 adduct, the n.m.r. spectrum of which showed olefinic proton signals, corresponding to the 2,3-endocyclic double bond, at τ 3·78, but signals due to exocyclic olefinic protons were absent.

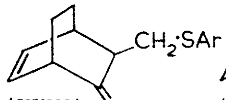

(XXVIII)



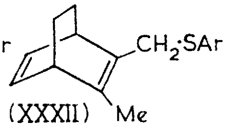
(XXIX)



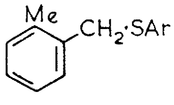
(XXX)



(XXXI)



(XXXII)



(XXXIII)

a; Ar = Ph b; Ar = p — MeC_6H_4

The additional presence of signals for vinylic methyl protons and vinylic methylene protons adjacent to sulphur as singlets at τ 8·51 and 6·52, respectively, leads to the assignment of structure (XXXIIa), further supported by hydrogenation to afford (XXVIIa). Thus chain transfer of the allylic radical system (XXIXa) ⟷ (XXXa) again leads to the thermodynamically more stable system. There appears to be no appreciable interaction between the allylic radical and the endocyclic double bond in (XXIXa) ⟷ (XXXa). In the n.m.r. spectra of both the adduct (XXXIIa) and its hydrogenation product (XXVIIa), two anomalous singlets were present, at τ 6·08 and 7·72, which may be assigned to the methyl and methylene groups of o-methylbenzyl phenyl sulphide (XXXIIIa), presumably formed by thermal decomposition of the adduct (XXXIIa) with loss of the ethano-bridge as ethylene. The addition of p-thiocresol to 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII) similarly affords a product (XXXIIb) of 1,4-addition to the diene system, together with its thermal decomposition product o-methylbenzyl p-tolyl sulphide (XXXIIIb). Analogous decompositions of substituted bicyclo[2,2,2]-octa-2,5-diene systems have been reported by Alder and his co-workers.[12]

In the addition of benzenethiol to 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII), 13% of a 2 : 1 thiol–triene adduct was isolated. It was assumed to be a mixture of (XXXIVa) and (XXXVa) derived by addition of benzenethiol to the 2,3-double bond of the first formed 1 : 1 adduct (XXXIIa), since addition of benzenethiol to the separated 1 : 1 adduct gave an identical product. Since no unchanged triene was recovered, the formation of the 2 : 1 adduct is likely to be due to loss of triene

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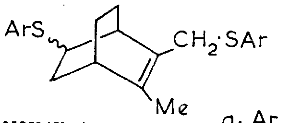
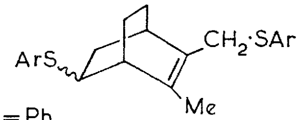
[12] (a) K. Alder, S. Hartung, and O. Netz, *Chem. Ber.*, 1957, **90**, 1; (b) K. Alder and H. F. Rickert, *Ber.*, 1937, **70**, 1364.

(XXVIII) by polymerisation (related compounds polymerise readily [13]), rather than to exceptional reactivity of the 1 : 1 adduct. The analogous 2 : 1 adducts (XXXIVb) and (XXXVb) are formed in the addition of *p*-thiocresol.

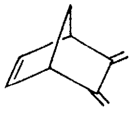


(XXXIV)

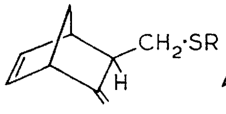


(XXXV)

a; Ar = Ph
b; Ar = p-MeC$_6$H$_4$



(XXXVI)



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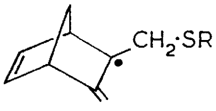
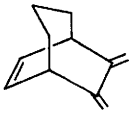
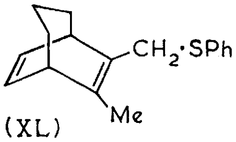


(XXXVIII)

In the addition of thiols to 5,6-dimethylenenorborn-2-ene (XXXVI) [2] the major 1 : 1 adduct isolated was (XXXVII) derived from 1,2-addition to its diene system. This was explained on the basis of homoconjugative interaction between the 2,3-double bond and the radical centre of the canonical species (XXXVIII) of the allylic radical system formed on addition of thio-radicals to the triene (XXXVI). A similar homoconjugative interaction does not appear to be important in the addition of thiols to 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII). Such homoconjugative interaction appears to be restricted to the 5,6-dimethylenenorborn-2-ene system (XXXVI), since benzenethiol addition to 8,9-dimethylenebicyclo[3,2,2]non-6-ene (XXXIX) affords solely (XL), the product of 1,4-addition to the diene system.



(XXXIX)



(XL)

Relative reactivities of unsaturated compounds in the bicyclo[2,2,2]octane and norbornane series [2] towards methyl mercaptoacetate and benzenethiol

	Relative reactivity			Relative reactivity	
Unsaturated compound	$\mathrm{HS{\cdot}CH_2{\cdot}CO_2Me}$	PhSH	Unsaturated compound	$\mathrm{HS{\cdot}CH_2{\cdot}CO_2Me}$	PhSH
Oct-1-ene	1·00	1·00	Oct-1-ene	1·00	1·00
Norbornene	15·5	97	(I)	1·12	3·30
2-Methylenenorbornane	1·5 †	2·6	(III)	2·12	2·02
(V)	22·3	172	(VIII)	3·25	6·00
2,3-Dimethylenenorbornane	55	3078	(XXIII)	29·8 *	4850 *
(XXXVI)	26·7	434	(XXVIII)	18·6 *	4750 *

* Converted from norbornene as standard by use of the values of Claisse and Davies.[11] † Result of Cadogan and Sadler.[14]

In the Table are recorded the relative reactivities of unsaturated compounds in the bicyclo[2,2,2]octane series towards both benzenethiol and methyl thioglycollate obtained by standard procedures.[2,11,14] For comparison the reactivities of the corresponding compounds in the norbornane series are also included.[2,11,14] The results for bicyclo[2,2,2]oct-2-ene (I), 2-methylenebicyclo[2,2,2]octane (III), and 5-methylenebicyclo-[2,2,2]oct-2-ene (VIII) suggest that the two different kinds of double bond have comparable reactivities, which are additive in 5-methylenebicyclo[2,2,2]oct-2-ene (VIII); this suggests that homoconjugative interaction in (VIII) is minimal. When these results are compared with those for corresponding compounds in the norbornane series, an exceptional reactivity for norbornene and 5-methylenenorborn-2-ene (V) is found; this may indicate the greater strain in norbornene compared with bicyclo[2,2,2]-oct-2-ene (I), and additional homoconjugation in (V). The main difference in strain between norbornane and bicyclo[2,2,2]octane is angle strain of about 15 kcal./mole.[6] This difference is likely to be exacerbated as a result of introduction of double bonds. Relief of strain may therefore account, at least in part, for the difference in reactivities between the two sets of olefins.

The diene 2,3-dimethylenebicyclo[2,2,2]octane (XXIII) and the triene 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII) have the enhanced reactivity expected [2,11] for conjugated diene systems. When the dienes 2,3-dimethylenenorbornane and 2,3-dimethylenebicyclo[2,2,2]octane (XXIII) are compared with the corresponding trienes 5,6-dimethylenenorborn-2-ene (XXXVI) and 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII), it is found that, particularly towards methyl thioglycollate, the trienes are less reactive than the dienes. This may be a measure of the less effective conjugation in the diene systems of the trienes owing to increased strain in the molecules as a result of the introduction of the endocyclic double bond. Stabilisation of the allylic radical systems formed on thio-radical attack may therefore be reduced.

Although the unsaturated compounds are in approximately the same order of reactivity with both thiols, there is a much greater range of reactivity with benzenethiol. This may be due to reversibility of thiol addition, which occurs in the addition of ethanethiol to some bicycloalkenes,[15] and that of benzenethiol to some conjugated dienes for which methanethiol addition is not reversible.[16] Also in the addition of benzenethiol to the

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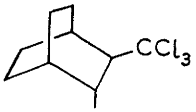
[13] M. A. P. Bowe, R. G. J. Miller, J. B. Rose, and D. G. M. Wood, *J. Chem. Soc.*, 1960, 1541.

[14] J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc.* (*B*), 1966, 1191.

[15] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, 1965, **30**, 3003.

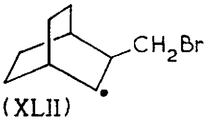
[16] W. A. Thaler, A. A. Oswald, and B. E. Hudson, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 310.

dienes and trienes, both the attacking phenylthio-radical and the intermediate allylic radical are resonance stabilised. Therefore the assumption made in the derivation of the kinetics [11,14,17] on which relative reactivities in the Table are based, that the initial step involving attack of phenylthio-radicals is much slower than the chain transfer step, may not hold for conjugated systems, and these rates may become more nearly comparable.

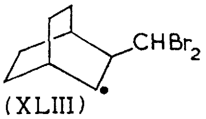


(XLI)

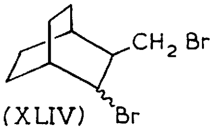
The additions of bromotrichloromethane and of methylene bromide to bicyclo[2,2,2]oct-2-ene (I) are of some interest. The former forms a 1 : 1 adduct [3] for which the structure *endo*-3-bromo-*exo*-2-trichloromethylbicyclo[2,2,2]octane (XLI) has been suggested.[18] This is confirmed by the n.m.r. spectrum which shows signals for both H(2) and H(3) as quartets at τ 6·93 and 5·62, each displaying a *trans*-coupling of 5 c./sec.; the additional couplings with adjacent bridgeheads, or possibly ethano-bridge protons were different and had the surprisingly large values [8] of 3 and 4 c./sec. each, respectively. Such values probably indicate some distortion of the molecule. This is supported by the size of the *trans*-coupling constant, which corresponds to a dihedral angle of 130° rather than 120°,[19,20] which would be expected in the D_{3h} eclipsed conformation,[21] and therefore indicates a staggered conformation [22] for (XLI).



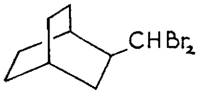
(XLII)



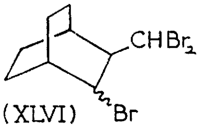
(XLIII)



(XLIV)



(XLV)



(XLVI)

The addition of methylene bromide to bicyclo[2,2,2]-oct-2-ene (I) affords a product, the n.m.r. spectrum of which shows a doublet (J 9 c./sec.) at τ 4·36, characteristic of $>$CH·C*H*Br$_2$, and indicates (XLV) as a possible product; the remaining low field peaks were multiplets of integral ratio 1 : 2 at τ 5·95 ($W_{\frac{1}{2}}$ 10·5 c./sec.) and 7·25 ($W_{\frac{1}{2}}$ 18 c./sec.). These are consistent [8] with $>$CHBr and CH$_2$Br in the *cis*- and *trans*-isomer mixture (XLIV). The rather high τ value for C*H*$_2$Br we ascribe to shielding by the 1,7 carbon–carbon bond.[23]

Methylene bromide can provide both bromomethyl and dibromomethyl radicals,[24] which on addition to bicyclo[2,2,2]oct-2-ene (I) should provide intermediates (XLII) and (XLIII). Previous work [24] on methylene bromide addition to olefins suggests that these radicals should abstract bromine from methylene bromide; however for steric reasons it is likely that for radical (XLIII) abstraction of hydrogen to give (XLV) will be easier. When the smaller bromomethyl group is present (XLII), chain transfer by bromine abstraction occurs leading to (XLIV). Integral ratios in the n.m.r. suggest that (XLIV) and (XLV) are formed in the ratio 3 : 2. Elemental analysis, and size of the CHBr integral rule out the formation of (XLVI), the potential product of bromine abstraction by (XLIII).

EXPERIMENTAL

The n.m.r. spectra (60 Mc./sec.) were obtained with a Perkin-Elmer R.10 instrument. Column chromatography was performed with Laporte activated alumina, grade H, 100—120 mesh. Light petroleum had b.p. 60—80°. Analytical g.l.c. was carried out with a Griffin D6 density balance chromatograph, with nitrogen as carrier gas and the following columns (6 ft. × 0·25 in.): A, 10% silicon oil on Silocel (40—60 mesh); B, 20% Carbowax 20M on Celite (40—60 mesh); C, 10% NPGA on Celite (40—60 mesh); and D, 10% APL on Celite (40—60 mesh).

Purification of Reagents and Preparation of Compounds.—Bromotrichloromethane (Eastman) was distilled and stored over a molecular sieve (4—8 mesh); b.p. 103—104° (lit.,[25] 104·3°); methylene bromide (Koch Light) was distilled prior to use; b.p. 97—98° (lit.,[25] 96·9°).

5,6-Dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII) and 8,9-dimethylenebicyclo[3,2,2]non-6-ene (XXXIX) were prepared by the method of Alder, Hartung, and Netz,[12a] and had, respectively, b.p. 77—84°/20 mm., n_D^{25} 1·5290 (lit.,[12a] b.p. 68°/12 mm., n_D^{20} 1·5289), and b.p. 88—91°/20—22 mm., n_D^{25} 1·5270 (lit.,[12a] b.p. 88°/20 mm., n_D^{20} 1·5307).

Bicyclo[2,2,2]*oct-2-ene* (I) (*cf.* ref. 26). Cyclohexa-1,3-diene (30 ml.), pyridine (1·0 ml.), and hydroquinone (0·05 g.), were mixed in a steel-lined autoclave (1 l.), which was then charged with ethylene at 60 atmos. The autoclave was rocked continuously and heated at 200 ± 10° for 24 hr., then cooled. The excess of ethylene was then released, and the residue was extracted with hexane (4 × 50 ml.). The combined extracts were fractionated and the distillate b.p. 120—140° was retained. The crude product was sublimed to afford bicyclo[2,2,2]oct-2-ene (I) as a white crystalline solid, m.p. 111° (lit.,[26] 111—112°; lit.,[27] 112—113°).

5-*Methylenebicyclo*[2,2,2]*oct*-2-ene (VIII). Cyclohexa-1,3-diene (20 g.) and allyl bromide (40 g.) were heated together in a Carius tube at 160° for 20 hr., then cooled. The excess of allyl bromide was then evaporated off and the residue was partially purified by column chromatography with benzene as eluant to afford 5-bromomethylbicyclo[2,2,2]oct-2-ene

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[17] C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144.

[18] F. S. Fawcett, *Chem. Rev.*, 1950, **47**, 219.

[19] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

[20] F. A. L. Anet, *Canad. J. Chem.*, 1961, **39**, 789.

[21] O. Ermer and J. D. Dunitz, *Chem. Comm.*, 1968, 567.

[22] A. F. Cameron, G. Ferguson, and D. G. Morris, *Chem. Comm.*, 1968, 316.

[23] J. A. Claisse and D. I. Davies, *J. Chem. Soc.* (*B*), 1967, 679.

[24] J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 1965, 3949.

[25] I. Heilbron, ' Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswode, London, 1965.

[26] H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, 1954, **76**, 5396.

[27] A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, 1960, **9**, 230.

(20 g.). This crude bromide was added dropwise during 1 hr. to a solution of sodium hydroxide (20 g.) in ethylene glycol (100 ml.) under reflux; the product diene (b.p. 124—136°) distilled out as it formed. Redistillation afforded 5-methylenebicyclo[2,2,2]oct-2-ene (VIII) (9·4 g.), b.p. 128°, $n_{\mathrm{D}}^{23\cdot5}$ 1·4914 (lit.,[12a] b.p. 80°/80 mm., n_{D}^{20} 1·500) (Found: C, 89·9; H, 10·2. Calc. for C_9H_{12}: C, 89·9; H, 10·1%).

2-Methylenebicyclo[2,2,2]*octane* (III). Crude 5-bromomethylbicyclo[2,2,2]oct-2-ene (14 g.), prepared as above, was dissolved in absolute ethanol (60 ml.) and the solution was shaken with hydrogen at 1 atmos. in the presence of 10% palladium–charcoal (1 g.) until uptake of hydrogen had ceased. The catalyst filtered off through Celite (200 mesh), and ethanol was evaporated from the filtrate. The product, 2-bromomethylbicyclo[2,2,2]octane (13 g.), was added dropwise during 1 hr. to a solutian of sodium hydroxide (20 g.) in ethylene glycol (100 ml.) under reflux; the olefin, b.p. 120—125°, distilled out as it formed. Redistillation gave 2-methylenebicyclo[2,2,2]octane (III) (5·8 g.), b.p. 125—126°/100 mm. (lit.,[28] 154—155°; lit.[29] 157—158°) n_{D}^{25} 1·4870 (Found: C, 88·3; H, 11·6. Calc. for C_9H_{14}: C, 88·45; H, 11·55%).

2,3-Dimethylenebicyclo[2,2,2]*octane* (XXIII). The method of synthesis was analogous to that used by Alder [12a] for 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII), with the exception that after preparation of *NNN′N′*-tetramethylbicyclo[2,2,2]oct-5-ene-2,3-dicarboxamide, the endocyclic 5,6-double bond was reduced as follows. The amide (48 g.) was dissolved in absolute ethanol (300 ml.) and the solution was shaken with hydrogen at 1 atmos. in the presence of 10% palladium–charcoal (2 g.) until hydrogen uptake had ceased (*ca.* 35 min.). The catalyst was filtered off through Celite (200 mesh), and the ethanol was evaporated off to leave crude *NNN′N′*-tetramethylbicyclo-[2,2,2]octane-2,3-dicarboxamide (40 g.), which was converted into 2,3-dimethylenebicyclo[2,2,2]octane (XXIII) (6·0 g.), b.p. 78—80°/20—21 mm., $n_{\mathrm{D}}^{21\cdot5}$ 1·5120 (lit.,[30] b.p. 93—95°/50 mm., n_{D}^{20} 1·5106).

o-*Methylbenzyl phenyl sulphide* (XXXIIIa). *o*-Toluic acid (6 g.) in ether (20 ml.) was added dropwise (during 5 min.) to a vigorously stirred suspension of lithium aluminium hydride (2 g.) in ether, so that the solution was maintained at reflux. Excess of hydride was decomposed by the careful addition of moist ether, and the resultant mixture was poured into 2N-sulphuric acid (100 ml.) to decompose aluminium complexes. The ether layer was separated and the aqueous layer was extracted with ether (3 × 50 ml.); the combined ethereal extracts were dried ($MgSO_4$). Evaporation left crude *o*-methylbenzyl alcohol (5·1 g.).

Phosphorus tribromide (5 g.) was added dropwise to the *o*-methylbenzyl alcohol (5·1 g.) during 10 min. The mixture was then warmed to 100° for 30 min., cooled, and diluted with chloroform (50 ml.). The chloroform solution was washed with water (2 × 50 ml.), saturated sodium hydrogen carbonate (2 × 50 ml.) and water (2 × 50 ml.), and dried ($MgSO_4$). Evaporation afforded *o*-methylbenzyl bromide (3·8 g.), which was added dropwise during 5 min. to a stirred solution of sodium benzenethiolate (2·7 g.) in absolute ethanol (25 ml.). The solution was stirred for a further 1 hr., water (50 ml.) was added, and the mixture was extracted with ether (3 × 50 ml.). The combined extracts were then washed with water (2 × 100 ml.) and dried ($MgSO_4$). Evaporation followed by recrystallisation from ether–light petroleum gave o-*methylbenzyl phenyl sulphide* (XXXIIIa) (3·4 g.), b.p. 172—178°/21 mm., $n_{\mathrm{D}}^{23\cdot5}$ 1·5987 (Found: C, 78·2; H, 6·4. $C_{14}H_{14}S$ requires C, 78·6; H, 6·15%). o-*Methylbenzyl* p-*tolyl sulphide* (XXXIIIb). This was synthesised like *o*-methylbenzyl phenyl sulphide (XXXIIIa), except that sodium benzenethiolate was replaced by sodium toluene-*p*-thiolate. Redistillation of crude product afforded the *sulphide* (XXXIIIb) (2·2 g.), b.p. 185—187°/20 mm., $n_{\mathrm{D}}^{23\cdot5}$ 1·6035 (Found: C, 78·6; H, 7·2. $C_{15}H_{16}S$ requires C, 78·9; H, 7·05%).

Addition of Benzenethiol to Olefins: General Method.—The olefin and benzenethiol were mixed in a glass vial, which was then sealed and heated (usually at 75°) for a fixed period. The vial was cooled and the products were diluted with ether (10—20 ml.), washed with sodium hydroxide (10% w/v; 3 × 10 ml.) and water (3 × 25 ml.), and dried ($MgSO_4$). After removal of ether, the product was distilled *in vacuo*.

Bicyclo[2,2,2]*oct-2-ene* (I). A mixture of olefin (I) (100 mg.) and benzenethiol (100 mg.) was kept at 75° for 24 hr. Bicyclo[2,2,2]oct-2-yl phenyl sulphide (II) (80 mg.) had b.p. 90—99°/0·11 mm., n_{D}^{25} 1·5830 (Found: C, 76·9; H, 8·3. Calc. for $C_{14}H_{18}S$: C, 77·05; H, 8·3%). LeBel, Huber, and Zalkow [4] report b.p. 118—122°/0·8 mm., n_{D}^{25} 1·5859.

2-Methylenebicyclo[2,2,2]*octane* (III). Olefin (III) (0·5 g.) and benzenethiol (0·5 g.) were heated at 80° for 24 hr. *Bicyclo*[2,2,2]*oct-2-ylmethyl phenyl sulphide* (IV) (0·47 g.) had b.p. 100°/0·1 mm., n_{D}^{25} 1·5567 (Found: C, 77·3; H, 8·25. $C_{15}H_{20}S$ requires C, 77·55; H, 8·7%).

5-Methylenebicyclo[2,2,2]*oct-2-ene* (VIII). Diene (VIII) (1 g.) and benzenethiol (1 g.) were heated at 80° for 48 hr. Unchanged diene (VIII) was removed by column chromatography with light petroleum as eluant. Distillation of the residue afforded a mixture of 1 : 1 adducts, presumably (XIV)—(XVIII) (0·7 g.), b.p. 125—140°/0·1—0·2 mm., n_{D}^{25} 1·5788 (Found: C, 77·3; H, 7·6. Calc. for $C_{15}H_{18}S$: C, 78·25; H, 7·9%). Analytical g.l.c. on column C at 150° indicated the presence of at least five products. Further distillation gave a mixture of 2 : 1 adducts, presumably (XIXa—XXIIa) (0·38 g.), b.p. 210—220°/0·05 mm., n_{D}^{25} 1·5523 (Found: C, 74·5; H, 7·25. Calc. for $C_{21}H_{24}S_2$: C, 74·1; H, 7·1%). A further reaction between 5-methylenebicyclo[2,2,2]oct-2-ene (VIII) but with a large excess of benezenethiol produced a mixture of 2 : 1 adducts with identical properties.

In a further experiment, mercaptoacetic acid (2 g.) was added to the crude reaction product [from equimolar amounts of diene (VIII) and benzenethiol], after removal of unchanged diene, and heating was continued at 80° for a further 8 hr. The mixture was cooled, diluted with ether (25 ml.), washed with sodium hydroxide solution (10% w/v; 3 × 25 ml.) and dried ($MgSO_4$). Solvents evaporated off; the n.m.r. spectrum of the crude product showed a complete loss of olefinic protons. The product was distilled, and the first drop (15 mg.), b.p. *ca.* 150°/0·1 mm. was assumed to consist largely of tricyclic 1 : 1 adducts (XIV + XVIII) (Found: C, 77·3; H, 7·4. Calc. for $C_{15}H_{18}S$: C, 78·25; H, 7·9%). This was followed by the 2 : 1 adducts (XIXa—XXIIa) (0·32 g.), b.p. 210—220°/0·05 mm., n_{D}^{25} 1·5523.

2,3-Dimethylenebicyclo[2,2,2]*octane* (XXIII). Diene

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[29] M. Blanchard, G. Jochimsmann, and G. Jochimsmann, *Compt. rend.*, 1965, **260**, 5532.

[30] K. Alder and H. Molls, *Chem. Ber.*, 1956, **89**, 1960.

(XXIII) (0·5 g.) and benzenethiol (0·5 g.) reacted completely during 1 hr. at 25° to give 3-*methylbicyclo*[2,2,2]*oct-2-en-2-ylmethyl phenyl sulphide* (XXVIIa) (0·6 g.), b.p. 115—120°/0·2 mm., $n_{\rm D}^{21\cdot5}$ 1·5741 (Found: C, 78·2; H, 7·9. $C_{16}H_{20}S$ requires C, 78·65; H, 8·25%).

5,6-*Dimethylenebicyclo*[2,2,2]*oct*-2-ene (XXVIII). Triene (XXVIII) (1·0 g.) and benzenethiol (0·9 g.) were mixed at room temperature (14°) and shaken vigorously. The internal temperature rose to 25° in 5 min., then fell slowly to reach room temperature in 20 min. The mixture was then kept at room temperature for 1 hr. This gave a mixture (0·96 g.) b.p. 116—130°/0·2 mm. of 3-methylbicyclo[2,2,2]octa-2,5-dien-2-ylmethyl phenyl sulphide (XXXIIa) and *o*-methylbenzyl phenyl sulphide (XXXIIIa). The distillate was collected in three successive fractions shown to contain respectively 8·0, 20, and 34% of *o*-methylbenzyl phenyl sulphide (XXXIIIa) on the basis of integral comparisons of the n.m.r. singlets due to the vinylic methyl groups [τ 7·72 and 8·5 respectively, for (XXXIII) and (XXXIIa)]. Analysis of the first fraction: Found: C, 79·1; H, 7.1. Calc. for $C_{16}H_{18}S$: C, 79·3; H, 7·5%. Calc. for $C_{14}H_{14}S$: C, 78·6; H, 6·15%. After distillation, the residual gum was extracted with chloroform (10 ml.) and purified by column chromatography with light petroleum–benzene (1 : 1) as eluant. Distillation afforded a mixture (0·4 g.) of 2 : 1 adducts, 3-methyl-6-phenylthiobicyclo[2,2,2]oct-2-en-2-ylmethyl phenyl sulphide (XXXIVa) and 3-methyl-5-phenylthiobicyclo[2,2,2]oct-2-en-2-ylmethyl phenyl sulphide (XXXVa), b.p. 210—215°/0·03—0·05 mm. as a colourless viscous gum (Found: C, 75·2; H, 7·05. Calc. for $C_{22}H_{24}S_2$: C, 74·95; H, 6·85%). A 2 : 1 adduct with the same properties, apart from contamination with *o*-methylbenzyl phenyl sulphide, was prepared by the addition of benzenethiol to 3-methylbicyclo[2,2,2]octa-2,5-dien-2-ylmethyl phenyl sulphide (XXXIIa) containing *o*-methylbenzyl phenyl sulphide (XXXIIIa). Catalytic hydrogenation of 3-methylbicyclo[2,2,2]octa-2,5-dien-2-ylmethyl phenyl sulphide (XXXIIa) (0·1 g.) dissolved in benzene (10 ml.) over 10% palladium–charcoal (0·01 g.) afforded 3-methylbicyclo[2,2,2]oct-2-en-2-ylmethyl phenyl sulphide (XXVII) (0·1 g.), identical with that prepared by the addition of benzenethiol to 2,3-dimethylenebicyclo[2,2,2]-octane (XXIII).

8,9-*Dimethylenebicyclo*[3,2,2]*non-6-ene* (XXXIX). The triene (XXXIX) (0·2 g.) and benzenethiol (0·15 g.) were mixed at room temperature and shaken vigorously. An elevation of temperature (2—3°) took place over 5—6 min., and the mixture was then kept at room temperature for a further 1 hr. This afforded 7-*methylbicyclo*[3,2,2]*nona-6,8-dien-6-ylmethyl phenyl sulphide* (XL) (0·13 g.), b.p. 110°/0·05 mm., $n_{\rm D}^{21\cdot5}$ 1·5912 (Found: C, 80·3; H, 8·15. $C_{18}H_{22}S$ requires C, 79·95; H, 8·2%). The residue after distillation was extracted with chloroform (15 ml.) and purified by column chromatography with light petroleum–benzene (1 : 1) as eluant. Distillation afforded a mixture (0·08 g.), b.p. 210—220°/0·4 mm., $n_{\rm D}^{20}$ 1·5440, of 7-methyl-8-phenylthiobicyclo[3,2,2]non-6-en-6-ylmethyl phenyl sulphide and 7-methyl-9-phenylthiobicyclo[3,2,2]non-6-en-6-ylmethyl phenyl sulphide (Found: C, 76·3; H, 7·8. Calc. for $C_{25}H_{30}S_2$: C, 76·1; H, 7·65%). The n.m.r. spectrum of the product mixture showed a complete absence of olefinic protons.

Addition of Bromotrichloromethane to Bicyclo[2,2,2]*oct-2-ene* (I).—Bicyclo[2,2,2]oct-2-ene (I) (100 mg.), bromotrichloromethane (1 ml.), and azobisisobutyronitrile (10 mg.) were heated in a sealed glass vial at 75° for 6 hr. The products were cooled, diluted with ether (25 ml.), washed with saturated sodium hydrogen carbonate solution (3 × 25 ml.) and water (3 × 25 ml.), and dried ($MgSO_4$). Distillation of the crude product afforded 3-*endo*-bromo-2-*exo*-trichloromethylbicyclo[2,2,2]octane (XLI) (68 mg.) b.p. 85°/0·12 mm., $n_{\rm D}^{25}$ 1·5610 (Found: C, 35·8; H, 3·85. Calc. for $C_9H_{12}BrCl_3$: C, 35·45; H, 3·65%). Analytical g.l.c. on column B at 180° indicated the presence of one product only. Kharasch and Friedlander [3] report b.p. 80—85°/0·1 mm., $n_{\rm D}^{20}$ 1·5632.

Addition of Methylene Bromide to Bicyclo[2,2,2]*oct-2-ene* (I).—A solution of bicyclo[2,2,2]oct-2-ene (I) (0·5 g.), methylene bromide (5 ml.), and benzoyl peroxide (0·05 g.) was added dropwise during 3 hr. to methylene bromide (20 g.) under reflux. The solution was heated under reflux for a further 18 hr., with addition of benzoyl peroxide (0·05 g.) every 4 hr. The mixture was cooled, diluted with methylene chloride (20 ml.), washed with saturated sodium hydrogen carbonate solution (3 × 50 ml.) and water (3 × 50 ml.), and dried ($MgSO_4$). After evaporation of solvents and excess of reagents, the crude product (brown gum) was purified by column chromatography on alumina with light petroleum as eluant. The n.m.r. spectrum of the purified product indicated the presence of starting olefin (I) (*ca.* 10%), which was removed by further column chromatography. Distillation of the residual product then afforded a mixture of 3-*endo*- and 3-*exo*-bromo-2-*exo*-bromomethylbicyclo[2,2,2]octane (XLIV) and 2-dibromomethylbicyclo[2,2,2]octane (XLV) (0·3 g.), b.p. 92—94°/0·2—0·3 mm., $n_{\rm D}^{25}$ 1·5597 (Found: C, 38·65; H, 4·85. Calc. for $C_9H_{14}Br_2$: C, 38·3; H, 5·0%). Analytical g.l.c. on column A at 180° indicated two peaks, probably corresponding to (XLIV) and (XLV) in the ratio 3 : 2.

Addition of Methanethiol to 2,3-*Dimethylenebicyclo*[2,2,2]-*octane* (XXIII).—The diene (XXIII) (0·2 g.) was cooled to −70° and methanethiol (*ca.* 0·15 g.) similarly cooled was added dropwise. The vial was sealed and allowed to warm to room temperature during 2 hr.; it was then held at room temperature for 2 weeks. The opened vial was then heated at 50° to remove any excess of methanethiol, and the products were purified by distillation to yield 3-*methylbicyclo*[2,2,2]*oct-2-en-2-ylmethyl methyl sulphide* (XXVIIb) (0·12 g.), b.p. 90—95°/0·5 mm., $n_{\rm D}^{21\cdot5}$ 1·5282 (Found: C, 72·2; H, 9·45. $C_{11}H_{18}S$ requires C, 72·5; H, 9·95%).

Addition of p-*Thiocresol to* 5,6-*Dimethylenebicyclo*[2,2,2]-*oct-2-ene* (XXVIII).—The triene (XXVIII) (0·7 g.) and *p*-thiocresol (0·65 g.) were mixed at room temperature (15°) and shaken vigorously; the internal temperature rose to 23° during 5 min., and then dropped to room temperature during 20 min. The mixture was set aside for a further 1 hr., and after work-up as in the benzenethiol addition, it was distilled (in three fractions) to afford a mixture (0·6 g.) of 3-methylbicyclo[2,2,2]octa-2,5-dien-2-ylmethyl *p*-tolyl sulphide (XXXIIb) and *o*-methylbenzyl *p*-tolyl sulphide (XXXIIIb). Three successive fractions were shown to contain 45, 50, and 45% of (XXXIIIb) on the basis of integration in the n.m.r. spectrum of the vinylic methyl resonance peaks [τ 8·56 and 7·72 for (XXXIIb) and (XXXIIIb) respectively]; b.p. 127—140°/0·2 mm., $n_{\rm D}^{21\cdot5}$ 1·5939 (Found: C, 79·2; H, 7·45. Calc. for $C_{17}H_{20}S$: C, 79·45; H, 7·85%. Calc. for $C_{15}H_{16}S$: C, 78·9; H, 7·05%). The residual gum after distillation was extracted with chloroform (10 ml.) and purified by column chromatography and light petroleum–benzene (1 : 1) as eluant. Distillation afforded a mixture (0·12 g.) of 3-methyl-6-*p*-tolylthiobicyclo[2,2,2]oct-2-en-2-ylmethyl *p*-tolyl sulphide (XXXIVb) and 3-methyl-5-*p*-tolylthiobicyclo[2,2,2]oct-2-en-2-ylmethyl *p*-tolyl sulphide (XXXVb) b.p. 220°/0·02 mm., as a pale yellow viscous gum (Found: C, 75·5; H, 7·2. Calc. for $C_{24}H_{28}S_2$: C, 75·75; H, 7·4%). An identical product was prepared by the addition of *p*-thiocresol to 3-methylbicyclo[2,2,2]octa-2,5-dien-2-ylmethyl *p*-tolyl sulphide (XXXIIb).

Determination of the Relative Reactivities of Olefins in the Bicyclo[2,2,2]*octane System toward Benzenethiol* [2,11] *and Methyl Mercaptoacetate*.[14]—The general theory of the competitive method is well documented.[2,11,14,17] By use of oct-1-ene as standard, the relative reactivities of bicyclo-[2,2,2]oct-2-ene (I), 2-methylenebicyclo[2,2,2]octane (III), and 5-methylenebicyclo[2,2,2]oct-2-ene (VIII) were determined. For 2,3-dimethylenebicyclo[2,2,2]octane (XXIII) and 5,6-dimethylenebicyclo[2,2,2]oct-2-ene (XXVIII) it was necessary to use norbornene as standard, and to compute reactivities relative to oct-1-ene by use of the known relative reactivities of norbornene.[2,11,14] Approximately equimolar quantities of olefins under test, together with a standard marker hydrocarbon (benzene or ethylbenzene) were mixed in a glass vial. The initial concentrations of the two olefins relative to the marker were then determined by analytical g.l.c. on column A at 100° (oct-1-ene as standard) or 130° (norbornene as standard). Sufficient thiol was then added to bring about the consumption of approximately 30% of the olefins present, and the mixture was left at 20° for 1 hr. The final concentrations of the olefins relative to the marker were again measured by g.l.c. and the relative reactivities were computed according to the usual theory (see Table).[2,11,14,17]

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