Effect of Remotely Positioned Groups on the Reactivities of Olefins toward Radical Addition[1]

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Competition reactions show that the reactivities of terminal olefins toward free radical addition by mercaptans are influenced by the extent of substitution on the 4-carbon of the olefin. An order of reactivity of 2-methyl-1-pentene > 2,4-dimethyl-1-pentene > 2,4,4-trimethyl-1-pentene toward addition by *n*-amyl mercaptan at 80° has been demonstrated. This order of reactivity is parallel to that predicted by Newman's empirical "rule of six." Addition of methyl mercaptan is not so markedly influenced by substitution on the 4-carbon of the olefin as are additions of *n*-amyl and *n*-dodecyl mercaptans. There are no appreciable differences in the reactivities of these olefins toward addition of bromotrichloromethane. An explanation is proposed for the anomalous behavior of these olefins toward addition of these reagents and an explanation of the nature of the effect of these remotely positioned groups on the reactivities of these olefins toward addition of mercaptans is suggested.

The generally accepted mechanism for the free radical addition of a reagent XY across the double bond of an olefin involves the following two free radical chain propagating reactions.[2]

$$Y\cdot + CH_2{=}CHR \longrightarrow YCH_2\dot{C}HR \qquad (1)$$

$$YCH_2\dot{C}HR + XY \longrightarrow YCH_2CXHR + Y\cdot \qquad (2)$$

Relative reactivities of olefins toward addition by free radicals can be determined by competition reactions of two or more olefins with an adding reagent. Removal of olefin by reaction of the adduct radical with olefin rather than with the adding reagent (reaction 2) can be eliminated as a complicating factor by using very reactive adding reagents such as bromotrichloromethane or mercaptans. Such studies have been reported by Kharasch and co-workers who used bromotrichloromethane[3] to determine the relative reactivities of various olefins toward addition by trichloromethyl radicals ($Y\cdot = Cl_3C\cdot$) and by Walling and Helmreich who used mercaptans[4] to obtain the relative reactivities of olefins toward addition by thiyl radicals ($Y\cdot = RS\cdot$). Reversibility of the addition of thiyl radicals to olefins, a possible complicating factor as far as reactivities toward addition by thiyl radicals are concerned, has been demonstrated by the rapid isomerization of unchanged olefin in the addition of methyl mercaptan to *cis*- and to *trans*-2-butene.[4] Walling and Helmreich have, however, demonstrated that reliable ratios of reactivities of various olefins toward mercaptan addition can be obtained by maintaining a constant mercaptan:olefin concentration ratio. Their values for the relative reactivities of several olefins toward addition by thiyl radicals are in general agreement with those found by Kharasch and co-workers for the trichloromethyl radicals.

We have employed the method of competition reactions to determine the effect of groups remotely positioned from the reaction center on the reactivities of terminal olefins toward free radical addition of various mercaptans and bromotrichloromethane. The olefins used in our investigation were 2-methyl-1-pentene (I), 2,4-dimethyl-1-pentene (II), 2,4,4-trimethyl-1-pentene (III), and 2,3,3-trimethyl-1-butene (IV).

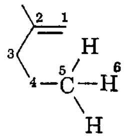
$$\underset{\text{I}}{CH_3CH_2CH_2C(CH_3){=}CH_2} + XY \xrightarrow{k_{I}} CH_3CH_2CH_2CX(CH_3)CH_2Y \qquad (3)$$

$$\underset{\text{II}}{(CH_3)_2CHCH_2C(CH_3){=}CH_2} + XY \xrightarrow{k_{II}} (CH_3)_2CHCH_2CX(CH_3)CH_2Y \qquad (4)$$

$$\underset{\text{III}}{(CH_3)_3CCH_2C(CH_3){=}CH_2} + XY \xrightarrow{k_{III}} (CH_3)_3CCH_2CX(CH_3)CH_2Y \qquad (5)$$

$$\underset{\text{IV}}{(CH_3)_3CC(CH_3){=}CH_2} + XY \xrightarrow{k_{IV}} (CH_3)_3CCX(CH_3)CH_2Y \qquad (6)$$

These particular olefins were chosen because they could involve the type of steric effect suggested by Newman's "rule of six," namely that reaction at an unsaturated linkage is sterically hindered by the atoms or groups positioned six atoms from the site at which the reaction is taking place.[5] In olefin I, there are three hydrogens in the 6-position. Substitution of a second methyl on the 4-carbon of the olefin would result in a compound with six such hydrogens and substitution of a third methyl on the 4-carbon would result in nine such hydrogens.



Since the primary steric factors (all are terminal olefins), resonance factors, and any polar contributions are essentially the same in I, II, and III, any observed differences in the reactivities of these olefins toward addition must very likely result from the extent of substitution on the 4-carbon. Olefin IV has no hydrogens in the 6-position that might exert a steric influence on the addition reaction. However, IV does have two less allylic hydrogens available to stabilize the adduct radical and might be expected to be lower in reactivity with respect to I, II, and III toward radical addition.

Relative reactivity ratios of these olefins toward free radical addition by various mercaptans and bromotri-

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[1] This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 240.

[3] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949); M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

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

[5] M. S. Newman, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 206.

chloromethane were determined by allowing mixtures of known quantities of two of the olefins to react with the adding reagent. The adding reagent was always present in a large excess to eliminate any polymerization of the olefin. Further, the mole ratio of the adding reagent to the total olefin content was kept constant in all cases. The chain reactions were initiated either chemically with azobisisobutyronitrile (AIBN) or photochemically with a sun lamp and were allowed to proceed until an appreciable amount of each olefin had reacted to allow for the calculation of the reactivity ratio. The amounts of the olefins that had reacted were determined by gas chromatographic analyses of the reaction mixtures. The relative reactivity ratio of two olefins A and B (k_A/k_B) could be found by substituting the values for the amounts of the olefins before and after reaction in the equation

$$k_A/k_B = \frac{\log (A_0/A)}{\log (B_0/B)}$$

where A_0 and B_0 are the amounts of the olefins before reaction and A and B are the amounts after reaction. In our hands, this method gave reactivity ratios of these olefins toward addition that were fairly consistent for two or more runs (see Table I). In the duplicate runs for each reactivity ratio, the initial amount of each olefin was significantly altered. The reliability of the values for the reactivity ratios is further supported by the cross-check experiments.

The relative reactivities of these olefins, using the reactivities of 2-methyl-1-pentene (I) as a standard, to addition by the various reagents serve better to illustrate the following discussion (see Table II).

TABLE I

COMPETITION REACTION STUDIES OF OLEFINS TOWARD FREE RADICAL ADDITION

Adding reagent	Temp., °C.	Init.	Reactivity ratio	Value	No. of runs	Average deviation
n-$C_5H_{11}SH$	80	AIBN	k_I/k_{II}	3.8	4	0.6
n-$C_5H_{11}SH$	80	AIBN	k_I/k_{III}	13.0	4	2.7
n-$C_5H_{11}SH$	80	AIBN	k_I/k_{IV}	2.6	4	0.2
n-$C_5H_{11}SH$	80	AIBN	k_{II}/k_{III}	2.9	2	.3
n-$C_5H_{11}SH$	80	AIBN	k_{IV}/k_{III}	4.2	2	.05
n-$C_{12}H_{25}SH$	80	AIBN	k_I/k_{III}	13.3	4	3.0
CH_3SH	0	$h\nu$	k_I/k_{III}	6.3	2	0.9
$BrCCl_3$	40	$h\nu$	k_I/k_{II}	1.05	8	.11
$BrCCl_3$	40	$h\nu$	k_I/k_{III}	0.99	6	.05
$BrCCl_3$	0	$h\nu$	k_I/k_{III}	1.01	2	.05
$BrCCl_3$	40	$h\nu$	k_{II}/k_{III}	0.96	2	.08
$BrCCl_3$	40	$h\nu$	k_I/k_{IV}	2.4	3	.10

TABLE II

RELATIVE REACTIVITIES OF OLEFINS TO ADDITION BY VARIOUS ADDING REAGENTS

Olefin	n-$C_5H_{11}SH^a$	CH_3SH^b	n-$C_{12}H_{25}SH^a$	$BrCCl_3^c$
$CH_3CH_2CH_2C(CH_3){=}CH_2$	1.00	1.00	1.00	1.00
$(CH_3)_2CHCH_2C(CH_3){=}CH_2$	0.26	..	..	1.05
$(CH_3)_3CCH_2C(CH_3){=}CH_2$	.08	0.16	0.08	0.99
$(CH_3)_3CC(CH_3){=}CH_2$	.39	..	..	.42

[a] Temp., 80°. [b] Temp., 0°. [c] Temp., 40°.

Examination of the relative reactivities shown in Table II shows that: (1) increasing the number of methyl groups on the 4-carbon of the olefin (and hence increasing the number of hydrogens in the 6-position relative to the terminal carbon of the double bond) does markedly lower the reactivity of an olefin toward addition by mercaptans; (2) this effect is not observed in the addition of bromotrichloromethane; and (3) the reactivity of an olefin with no hydrogens in the 6-position but with two less allylic hydrogens (olefin IV) is the same to addition by mercaptans and bromotrichloromethane. If these reactivity ratios are to be taken as the relative reactivities of the olefins to addition by thiyl radicals and trichloromethyl radicals, one might conclude that thiyl radical additions are sterically hindered by remotely positioned groups whereas trichloromethyl radical additions are not. Such a conclusion would be surprising in light of the similar effects of other factors (primary steric, resonance, and polar) on the reactivities of various other unsaturates to addition by these radicals. We find in our own work that a structure change that decreases the resonance factor has the same effect on the reactivity of the olefin to addition by both mercaptans and bromotrichloromethane.

One explanation for these anomalous results is that reversibility of the thiyl radical addition to olefins may be an important factor in our work in spite of our efforts to minimize this factor by maintaining a constant mercaptan:olefin ratio. Examination of the kinetic aspects of the chain sequences for the additions of mercaptans (reactions 7 and 8) and for the additions of bromotrichloromethane (reactions 9 and 10) show

$$RS\cdot + CH_2{=}CR'CH_3 \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} RSCH_2\dot{C}R'CH_3 \qquad (7)$$

$$RSCH_2\dot{C}R'CH_3 + RSH \xrightarrow{k_{tr}} RSCH_2CHR'CH_3 + RS\cdot \qquad (8)$$

$$Cl_3C\cdot + CH_2{=}CRCH_3 \xrightarrow{k_a} Cl_3CCH_2\dot{C}RCH_3 \qquad (9)$$

$$Cl_3CCH_2\dot{C}RCH_3 + BrCCl_3 \xrightarrow{k_{tr}} Cl_3CCH_2CBrRCH_3 + Cl_3C\cdot \qquad (10)$$

that the reversibility of the thiyl radical addition is the only kinetic factor that is significantly different.[6] In the bromotrichloromethane reactions, it follows that the relative rates of removal of the olefins from the reaction mixture (what we are actually measuring in our competition reactions) is dependent only on the relative rates of addition of the trichloromethyl radical to the olefins. In the mercaptan additions, the relative rates of removal of the olefins are equal to the relative rates of addition of the thiyl radicals only if the rates of elimination (k_{-a}) are the same for all of the adduct radicals and the rates of chain transfer are the same (reaction 8). This latter requirement is met by maintaining a mercaptan:olefin ratio that is significantly greater than one and essentially constant for various runs. Since there is no difference in the reactivities of olefins I, II, and III to addition by trichloromethyl radicals, we might conclude that the rates of addition of thiyl radicals to these olefins is also the same. This leaves only the elimination of the thiyl radicals from the

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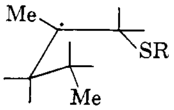
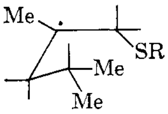
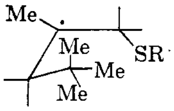
[6] Skell and Woodworth found that there was no isomerization of the unchanged olefins in the addition of bromotrichloromethane to *cis*-2-butene and to *trans*-2-butene. P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **77**, 4638 (1955).

adduct radicals to explain the reactivities of olefins I, II, and III to addition by mercaptans.

The order of reactivity I > II > III toward mercaptan addition is consistent with this conclusion that the elimination of the thiyl radical is the determining factor for their different reactivities. The adduct radicals A·, B·, and C· resulting from addition of a thiyl radical to I, II, and III, respectively, can assume (among many others) the cyclic conformations shown.

$\mathrm{RS}\cdot + \mathrm{I} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}}$  A· (11)

$\mathrm{RS}\cdot + \mathrm{II} \underset{k'_{-a}}{\overset{k'_a}{\rightleftharpoons}}$  B· (12)

$\mathrm{RS}\cdot + \mathrm{III} \underset{k''_{-a}}{\overset{k''_a}{\rightleftharpoons}}$  C· (13)

The reaction rate constants for formation of these adduct radicals may well be the same, that is $k_a = k_a' = k_a''$. Relief of strain caused by steric crowding that results when the adduct radical is in a cyclic conformation may well accelerate the elimination of the thiyl radical. Since the extent of crowding would depend on the number of methyl groups on the 4-carbon (and presumably on the number of hydrogens in the 6-position), the predicted order of the rate constants for the elimination reactions would be $k_{-a}'' > k_{-a}' > k_{-a}$. The elimination reaction of the adduct radical must be faster than its chain transfer reaction with the mercaptan as evidenced by the isomerization of the 2-butenes.[4] Thus, the concentration of a crowded adduct radical would be lower than that of a less crowded one in a competition reaction and its rate of removal, and consequently that of the olefin from which it was formed, would be slower.

The lower reactivity of IV with respect to I toward addition by *n*-amyl mercaptan very likely results from its lower reactivity to addition by the thiyl radicals themselves. This conclusion appears valid in light of the very similar relative reactivity ratio of these two olefins to addition by trichloromethyl radicals. Further, the alkyl chain in the adduct radical obtained from IV is not long enough to permit the type of crowding that is encountered in the adduct radicals obtained from the pentenes. The lower reactivities of II and III compared to that of IV indicate that the elimination reaction is accelerated to a much greater extent when there are two or three methyls on the 4-carbon than when there is only one.

The smaller difference in the reactivities of I and III toward addition of methyl mercaptan compared to the larger differences noted with *n*-amyl and dodecyl mercaptans is also consistent with the above explanation. Cyclic conformations of the *n*-amyl and *n*-dodecyl groups may be responsible for some of the crowding in the adduct radicals making elimination of *n*-amyl and *n*-dodecyl thiyl radicals more favorable than the elimination of methyl thiyl radicals.

In summary, it appears that β-elimination of thiyl radicals is markedly accelerated if the radical, which is undergoing fragmentation, can assume conformations which involve crowding near the reaction site. The addition of the radical is not, however, sterically hindered by remotely positioned groups.

Experimental

Materials.—*n*-Amyl mercaptan, *n*-dodecyl mercaptan (both from Aldrich Chemical Co., Inc.), and methyl mercaptan (Matheson) were used without further purification. Bromotrichloromethane (Dow Chemical Co.) was redistilled under vacuum until it gave a single peak on gas chromatographic analysis. 2-Methyl-1-pentene and 2,4,4-trimethyl-1-pentene (both from Phillips, Pure Grade) were redistilled and each gave a single peak on gas chromatographic analysis. 2,4-Dimethyl-1-pentene (b.p. 80°) was prepared by the acetate pyrolysis of 2,4-dimethyl-1-acetoxypentane which was obtained from an authentic sample of 2,4-dimethyl-1-pentanol (K and K Laboratories). 2,3,3-Trimethyl-1-butene (b.p. 77°) was prepared by the dehydration of 2,3,3-trimethyl-2-butanol over alumina at 550°. This alcohol was prepared by a standard Grignard reaction of methyl magnesium iodide with pinacolone.

The azobisisobutyronitrile (Matheson Coleman and Bell) was used without further purification. The photochemical reactions were induced with a 275-watt Sylvania Sunlamp.

Experimental Procedure.—The reactivity ratios reported in Table I were all determined in the following manner. A mixture consisting of 0.1 to 0.3 g. each of the two olefins, the amount of each accurately determined on an analytical balance, was diluted with an excess of the adding reagent. In the case of the mercaptans, the initial mole ratio of the adding reagent to the total amount of the olefins was 4:1 in all runs. A sample of the mixture (0.01 ml.) was removed by means of a pipet and injected on the gas chromatographic column through a Fisher sample injection valve. The areas of the two olefin peaks (and in some cases the adding reagent peak) were determined. In the AIBN induced reactions, about 5 mg. of this initiator was added to the reaction mixture. The reaction mixtures were sealed in Pyrex tubes and the tubes immersed in a constant temperature oil bath set at 80° for the chemically initiated reactions. The photochemically induced reactions were performed by immersing the tube in constant temperature water baths set at either 40° or 0°. The reaction mixture was then illuminated by a sun lamp which was placed about 6 in. from the side of the bath. The reactions were stopped in all cases before either of the two olefins was completely consumed. The tube was removed from the constant temperature bath and allowed to come to room temperature before another 0.01-ml. sample was removed by means of a pipet and subjected to gas chromatographic analysis under the same conditions used for the first sample. Determination of the amounts of each of the olefins remaining in the reaction mixture was made by comparison of the olefin peak areas with those obtained before reaction. The data were treated in the manner described previously.