ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Kinetics of Carbanion-catalyzed Isomerization of Butenes and 1-Pentene[1-3]

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RECEIVED JUNE 22, 1959

The catalytic isomerization of olefins was studied kinetically between 30° and 195°. It was found that *n*-butenes isomerize reversibly in the presence of base catalysts such as sodium–anthracene, sodium deposited on alumina, silica or sodium carbonate, lithium-on-alumina, and sodium dispersion. 1-Pentene similarly was isomerized to an equilibrium mixture of the *n*-pentenes over sodium-on-alumina. From the kinetic data the individual relative rate constants were determined for the sodium on alumina catalyzed isomerization of the *n*-butenes. The rate expression for the kinetic system consisting of competitive reversible reactions between each of three components was set up. The experimental data indicate that kinetic control of the products is operating. For instance, in the isomerization of 1-butene the thermodynamically less stable *cis*-2-butene is produced four times faster than the *trans* isomer. The mechanisms of the base-catalyzed isomerizations are discussed in the light of the kinetic data.

Olefinic hydrocarbons possessing allylic hydrogen atoms can undergo isomerization under the catalytic influence of strong bases. The ease of such isomerizations can be correlated with the acidity of the allylic hydrogen atoms and with the strength of the bases, which include potassium amide,[5] the lithium–ethylenediamine system[6] and organosodium compounds.[7-9] Detailed investigations[7,8] have established the fact that in contact with base catalysts monoölefins undergo a reversible shift of the double bond, while in cyclic diolefins the isomerization is accompanied by a slower dehydrogenation.

The double bond shift is visualized as occurring by a chain mechanism involving allylic carbanion intermediates.[7] In contrast to the well known acid-catalyzed isomerizations proceeding through carbonium ions, no rearrangement of the carbon skeleton has been observed in the base-catalyzed reactions. This is a further support for the anionic nature of the intermediates, since no electrophilic rearrangement from carbon to carbon is known in aliphatic hydrocarbons.[10,11]

Alkali metals were found by Ziegler and co-workers[12] to have no effect on either *cis*- or *trans*-2-butene. However, it was reported recently[13] that sodium dispersed on alumina is an active catalyst for the gas phase isomerization of 1-butene and that the reaction proceeds in a stereoselective way.

We have now investigated the activity and stereoselectivity of sodium on several different supports and of lithium-on-alumina. The reaction was further extended to the liquid phase isomerization of 1-pentene. Since no information as to the relative rates of *cis–trans* interconversion *versus* double bond shift was available, the three-component system consisting of 1-, *cis*-2- and *trans*-2-butene was studied kinetically in detail. The results of such studies are important for the mechanism of the base-catalyzed olefin isomerization and quite general for the reactions of allylic anions.[14]

Experimental

The three *n*-butenes and 1-pentene were Phillips Research Grade. The butenes were dried before use by passage through a Drierite tube; 1-pentene was used without further purification.

High surface sodium catalysts were prepared by adding sodium to the dry solids which were stirred with a sweep-type stirrer in a glass flask at 150° in a nitrogen atmosphere.[15] Catalysts prepared in this way were considerably more active than those made *in situ* in a rotating autoclave.[13] The material was transferred under dry nitrogen into small glass ampules and sealed.

Most of the reactions were carried out at 30° and at 800 mm. in a 2-liter glass flask which could be attached to a rotating wheel immersed in thermostated water. The reaction flask was dried by evacuating and flaming, filled with dry nitrogen and the solid catalyst added. The flask was then placed in the thermostat, evacuated and the reactant gas admitted. Gas samples were withdrawn periodically through a rubber serum cap with a hypodermic syringe and charged directly into the vapor fractometer for analysis.

The isomerization of 1-pentene was performed in a 25-ml. flask fitted with a Dry Ice condenser at reflux temperature under a nitrogen blanket. Samples were withdrawn from the liquid with a precooled syringe.

In the kinetic runs, the reaction velocities were adjusted by selecting the proper amount of catalyst. Two to four determinations were made with each isomer.

The chromatographic columns have been described previously.[13] For the quantitative evaluation the peak areas were measured by the method of Cremer and Müller,[16,17] employing the product of peak height and half-band width. Calibrating showed that this procedure gave the correct composition within 1–2%.

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[1] Paper XVII of the series of Base-catalyzed Reactions. For paper XVI see H. Pines and D. Wunderlich, THIS JOURNAL, **81**, 2568 (1959).

[2] Taken in part from a dissertation submitted by W. O. H. in partial fulfillment of the requirements for the Ph.D. degree, June, 1959.

[3] Presented before the Division of Petroleum Chemistry, American Chemical Society Meeting, April 5–10, 1959, Boston, Mass.

[4] Predoctoral Fellow Universal Oil Products Co., 1956–1957; Toni Co., Chicago, Ill., 1957–1958.

[5] A. I. Shatenstein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izrailevich, *Doklady Akad. Nauk, S.S.S.R.*, **85**, 381 (1952); *C. A.*, **46**, 9954 (1952).

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Results

Isomerization of 1-Pentene.—The results in Table I demonstrate the powerful activity of sodium-on-alumina for the double bond isomerization of olefins. In experiment 1, over 65% of 1-pentene was converted in six minutes at about 30°. After one hour the mixture was equilibrated. No compounds other than the three *n*-pentenes could be detected by gas chromatography. The lack of side reactions which are frequently encountered in acid-catalyzed isomerizations, and the high activity make the sodium catalyst the preferred reagent in equilibrium studies of double bond isomers. The rate of reaction was slowed down in expt. 2 by using only 0.002 g. of sodium in order to observe the primary reaction products. A stereoselectivity factor of >10 in favor of the *cis* isomer was found at about 1% conversion.

TABLE I

ISOMERIZATION OF 1-PENTENE OVER SODIUM–ALUMINA

Time, min.	Pentene, % 1-	2-*trans*	2-*cis*	Ratio *cis*/*trans*
		Experiment 1[a]		
0	100	..	..	..
6	34.8	26.3	38.9	1.5
60	1.5	73.5	25.0	0.34
Calcd.[c]	1.6	72.0	26.4	0.37
		Experiment 2[b]		
0	100	..	..	..
3	99.1	Trace	0.9	>10
27	97.5	0.4	2.1	5.3
64	97.0	0.80	2.2	2.8

[a] 10 ml. of 1-pentene and 2.7 g. of 8% sodium-on-alumina. [b] 10 ml. of 1-pentene and 0.40 g. of 0.5% sodium-on-alumina. [c] Calculated from the thermodynamic data[18] for 27°.

Screening of Catalysts.—It was of interest to see whether the excellent isomerization activity of sodium-on-alumina was also exhibited by other catalysts. These catalysts were tested with 1-butene at 30°: alumina prepared from aluminum isopropoxide, sodium-on-silica, sodium-on-sodium carbonate, lithium-on-alumina, and sodium dispersed in *n*-octane. The results are shown in Table II. It becomes apparent that alumina *per se* is not a catalyst at the temperature used. Sodium-on-silica and sodium-on-sodium carbonate both show much lower activity than sodium-on-alumina.[13] However, *cis*-2-butene is the only product obtained, although 0.1% of the *trans* isomer easily could be detected. Lithium-on-alumina has a similar activity to sodium-on-alumina, but seems to exhibit a lower selectivity. Experiment 6 demonstrates that finely dispersed sodium alone shows activity as well as selectivity.

Isomerization of *cis*-2-Butene.—Although the reversibility of the sodium-catalyzed isomerization reaction was strongly suggested by the fact that in the isomerization of 1-butene[13] and 1-pentene equilibrium mixtures were obtained, it was felt necessary to demonstrate this in view of contradictory observations in a related system.[9] In experiment 8 *cis*-2-butene (4.5 g.) was isomerized over 40 mg. of sodium deposited on 8.0 g. of alumina (0.5% sodium). The results are presented in Fig. 1. It is evident that the same equilibrium mixture was obtained from 1- and from *cis*-2-butene. At very low conversion the amount of 1-butene produced exceeds that of the *trans* isomer, although the latter is thermodynamically favored by a factor of 25.

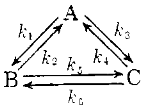
TABLE II

ISOMERIZATION OF 1-BUTENE OVER VARIOUS CATALYSTS[a]

Expt.	Catalyst[a]	Reaction time, min.	Butene, % 1-	*trans*-2	*cis*-2	*cis*/*trans*[b]
3	Al_2O_3	1440	100	0	0	..
4	$Na-SiO_2$	191	100	0	Trace	..
		2865	99	0	1.0	>10
		4080	98.8	0	1.2	>12
5	$Na-Na_2CO_3$	100	99.1	0	0.9	> 9
		3908	95.4	0	4.6	>46
		4440	94.5	0	5.5	>55
6	Na-Disp.	180	98.6	0.3	1.1	3.7
		1500	92.0	1.8	6.2	3.4
		5600	86.6	3.3	10.1	3.1
7	$Li-Al_2O_3$	110	59.4	20.4	20.2	1.0
		255	34.9	31.5	33.6	1.1

[a] Expt. 3–6 were performed at 30.0° in a rotated glass flask; 4.5 g. of 1-butene was used. The amounts of catalysts taken were: expt. 3, 2.9 g. of alumina freshly calcined at 500° for 12 hours; expt. 4, 8.3 g. of sodium (2%) on silica; expt. 5, 8.3 g. of sodium (2%) on sodium carbonate; expt. 6, 5.0 ml. of a sodium dispersion (50%) in *n*-octane; expt. 7 was performed at 40° in a rotating autoclave. The catalyst was prepared *in situ* from 1.04 g. of lithium and 13.0 g. of alumina which had been heated for 3 hours at 300°. After cooling and evacuating, 10 g. of 1-butene was charged. [b] Calculated on the basis that 0.1% *trans*-2-butene could be detected.

Kinetics of the Isomerization of *n*-Butenes.—The data obtained previously indicate that the isomerization of butene is a reversible, parallel reaction of the type



A = 1-butene B = *trans*-2-butene C = *cis*-2-butene

It was desirable to obtain the individual six rate constants in order to gain more insight into the mechanism of the base-catalyzed reaction. The evaluation of the absolute rate constants proved to be rather difficult since the reaction is reversible and the equilibrium concentration of one of the isomers (1-butene) is only 3%; furthermore, absolute rates were difficult to reproduce with sufficient accuracy since the catalyst reacts with traces of water or oxygen. However, the ratio of two rate constants could be reproducibly obtained. For example, starting with A, the ratio k_1/k_3 was obtained from the concentrations of B and C formed

$$dB/dt = k_1[A]^n - k_2[B]^{n'} - k_5[B]^{n''} + k_6[C]^{n'''}$$

$$dC/dt = k_3[A]^m - k_4[C]^{m'} - k_6[C]^{m''} + k_5[B]^{m'''}$$

At very low conversions [B] and [C] are small and the corresponding terms can be neglected. The equations then simplify to

$$(dB/dt)_{t \to 0} = k_1[A]^n \qquad (1)$$

$$(dC/dt)_{t \to 0} = k_3[A]^m \qquad (2)$$

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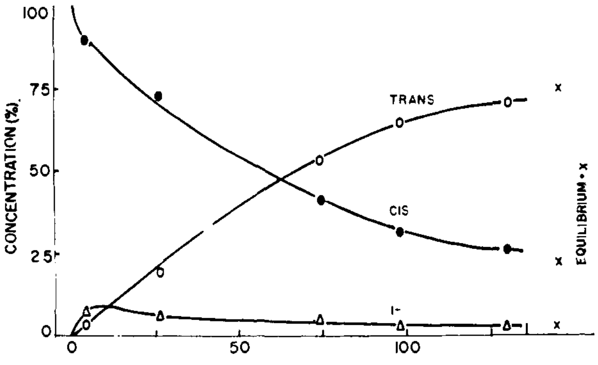

Fig. 1.—Isomerization of *cis*-2-butene over Na-Al_2O_3 at 30°.

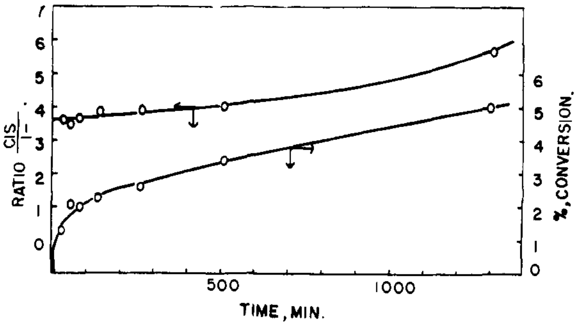

Fig. 2.—Isomerization of *trans*-2-butene.

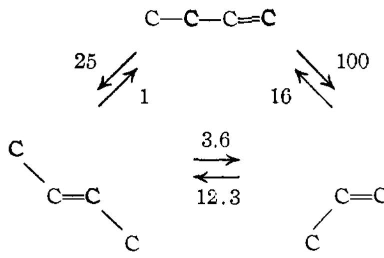

Fig. 3.—Relative rate constants: catalyst, Na-Al_2O_3, 30°.

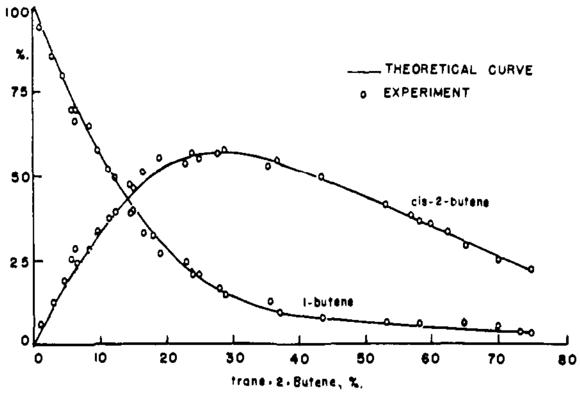

Fig. 4.—Isomerization of 1-butene, sodium–alumina, 30°.

Making the reasonable assumption that $n = m$ and dividing (1) by (2) one obtains

$$\lim_{t \to 0} \left(\frac{B_t}{C_t}\right) = \frac{k_1}{k_3}$$

Thus, determining the ratio B/C at low total conversion and extrapolating back to zero time gives the ratio k_1/k_3. An example is given in Fig. 2. Starting with each of the three isomers, these ratios were obtained

$$k_3/k_1 = 4.0;\ k_4/k_6 = 1.3;\ k_5/k_2 = 3.6 \qquad (3)$$

Since at equilibrium the forward and reverse rates must be equal, a set of relations can be obtained consistent with the thermodynamic equilibrium constant expression, if one assumes that the isomerization is a kinetically simple reaction.[19]

From the equilibrium concentrations[18] of 1-butene (3%), *trans*-2-butene (75%) and *cis*-2-butene (22%) one obtains

$$\frac{k_1}{k_2} = \frac{75}{3};\ \frac{k_2}{k_4} = \frac{22}{3};\ \frac{k_5}{k_6} = \frac{22}{75} \qquad (4)$$

For the six rate constants, (3) and (4) provide six equations, while only five are actually required since the equations are not independent of each other. Setting $k_2 = 1$, the results in Fig. 3 are obtained.

The rate expression for the system can be derived if one assumes that the reaction is first order in each of the three isomers. If one starts with pure 1-butene, for example, using the designations

concentration of	1-	*trans*-	*cis*-
at time $t = 0$	a	0	0
at time t	$a - x - y$	x	y

one obtains

$$\mathrm{d}x/\mathrm{d}t = k_1(a - x - y) + k_6y - k_2x - k_5x$$

By proper substitution one arrives at the expression

$$\frac{\mathrm{d}_2x}{\mathrm{d}t^2} + m\frac{\mathrm{d}x}{\mathrm{d}t} + nx = p_1a \qquad (5)$$

where

x = concentration of *trans*-2-butene at time t
a = starting concentration of 1-butene
$m = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$
$n = k_1k_4 + k_1k_5 + k_1k_6 + k_2k_3 + k_2k_4 + k_2k_6 + k_3k_5 + k_3k_6 + k_4k_5$
$p_1 = k_1k_4 + k_1k_6 + k_3k_6$

Integration of (5) gives

$$x = \frac{a}{\sqrt{m^2 - 4n}}\left[k_1 - \frac{p_1}{2n}(m + \sqrt{m^2 - 4n}\right]\exp\left[-(m - \sqrt{m^2 - 4n})\frac{t}{2}\right] - \frac{a}{\sqrt{m^2 - 4n}}\left[k_1 - \frac{p_1}{2n}(m - \sqrt{m^2 - 4n}\right]\exp\left[(m + \sqrt{m^2 - 4n})\frac{t}{2}\right] + \frac{p_1a}{n}$$

An analogous expression can be derived for the concentration of the *cis* isomer, y. By selecting arbitrary values for t and using the relative values of the rate constants (Fig. 3), the concentration of *trans*- and *cis*-2-butene and—by differences—of 1-butene can be calculated as a function of time. The resulting data are presented in Fig. 4. In order to eliminate the arbitrarily chosen time parameter, the concentrations of 1- and of *cis*-2-butene are plotted against that of *trans*-2-butene. Included in the graph are the experimentally determined points. The satisfactory agreement between the theoretical and experimental curves seems to justify the assumptions of first-order kinetics.

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Discussion

The data presented above are in accord with the mechanism suggested previously[7] for organosodium-catalyzed isomerizations. The isomerization of 1-butene can be pictured as

initiation:

$$\mathrm{R^-Na^+ = CH_3CH_2CH{=}CH_2 \rightleftarrows RH + [CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^-Na^+}$$

propagation:

$$\begin{array}{l} \mathrm{[CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^-Na^+ + CH_3CH_2CH{=}CH_2} \\ \qquad\qquad\qquad\qquad \downarrow\uparrow \\ \begin{array}{c}\mathrm{CH_3CH{=}CHCH_3} \\ + \\ \mathrm{CH_3CH_2CH{=}CH_2}\end{array} \quad \mathrm{+ [CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^-Na^+} \end{array}$$

Initiator in the sodium-on-alumina-catalyzed reaction might be an organosodium compound formed from sodium and a trace impurity in the butene, or a hydride or a hydroxide ion formed on the surface by reaction of sodium with the hydroxyl groups of the alumina.[20] However, a direct metalation of butene by the finely divided alkali metal is also possible.[21] In the latter case the accelerating effect of alumina as a support could be due to a greater surface polarity as compared to silica or sodium carbonate, which would aid the formation of charged species in a similar way as a polar solvent does.

The relative rate constants (Fig. 3) indicate that *trans*-2-butene undergoes *trans–cis* conversion at a faster rate than double bond shift, while the reverse is true for *cis*-butene.

The most striking feature is the observed stereoselectivity which can be considered as a kinetically controlled attack at various positions of the intermediate allylic anions by butene molecules. Since allylic anions should have a considerable energy barrier to rotation about the allylic carbon–carbon bonds, 2 distinct isomers, T and C, can exist[22] (Fig. 5). Protonation by chain propagating butene molecules at positions (a) and (c) produces *trans*- and *cis*-2-butene, respectively, whereas attack at (b) and (d) both give 1-butene. According to the rate data, protonation at (c) occurs four times more frequently than at (a). One of two reasons is responsible for this fact. First, preferred attack at (c) as compared to (a) might result from a greater reactivity of the *cis*-butenyl carbanion. This would require an interconversion T $\rightleftarrows$ C faster than the protonation reaction. Alternatively, C could be present in a greater concentration than T. The latter possibility seems more attractive at the present. There is evidence that the butenyl Grignard reagent is actually present in the *cis* form.[23] Although Grignard reagents are considered essentially covalent,[14,24] they can be compared with organosodium compounds in view of the similarity of the spectra of allylic magnesium compounds with those of allylic organoalkali reagents.[22] The higher concentration of the *cis*-butenyl–sodium reagent could result from stabilization by an additional resonance structure.

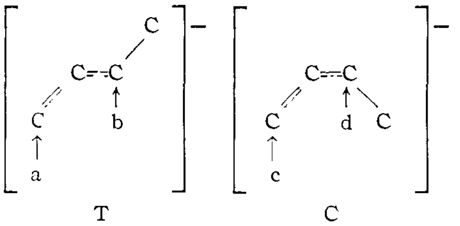
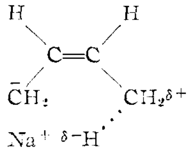


Fig. 5.—Relative rates of protonation.

a = 16 *trans*-2-butene
c = 64 *cis*-2-butene
$b + d$ = 20 1-butene



It is reasonable to assume that the hydrogens in the methyl group of the butenyl anion have some anionic mobility due to the high electron density of the carbon chain. A similar hydride character of the hydrogens on the carbon atoms adjacent to the center of a negative charge has been postulated by Wittig.[25,26] There is spectral evidence for anionic mobility of hydrogen atoms in the related alkoxide ions.[27] Models indicate that a sodium ion fits just in between the two terminal groups of the *cis*-butenyl anion, while lithium does not have complete contact. This might account for the somewhat lower stereoselectivity observed in the lithium-catalyzed reaction.

The preferred formation of *cis*-2-butene as compared to the *trans* isomer is not believed to result from a selective adsorption by the alumina support since a similar selectivity was observed with sodium dispersion and with sodium–anthracene.[13]

A second question concerns the rate of protonation at positions (b) + (d) to give 1-butene relative to that at (a) and (c). The problem of the position of reaction of allylic anions is a very general one and has been discussed extensively in the literature.[14,28] The nature of the solvent[29,30] has a deciding influence as does the steric requirement of the attacking species.[31] It is interesting to note that in the isomerization reaction the anions react at the less nucleophilic primary carbons (a) and (c) four times faster than at the secondary (b + d), whereas in the carbonation of the butenyl–sodium reagent the corresponding acids are isolated in equal amounts.[32,33] The factors influencing the

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position of reaction in the isomerization might be related to those responsible for the formation of 1,2- or 1,4-polymers in the polymerization of dienes.

Acknowledgment.—The authors wish to express their thanks to Mr. E. M. Lewicki for technical assistance.

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[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

The Photochemically Induced Reactions of Bromotrichloromethane with Alkyl Aromatics

BY EARL S. HUYSER[1]

RECEIVED JULY 6, 1959

The photochemically induced reaction of bromotrichloromethane and certain alkyl aromatics yielded the α-bromoalkyl aromatic and an equivalent amount of chloroform through a free radical chain process. Alkyl aromatics having at least one benzylic hydrogen such as toluene, ethylbenzene and cumene, as well as a number of substituted toluenes have been successfully brominated in this manner.

The use of polyhalomethanes as halogenating agents has been known for some time.[2] The reaction presumably involves a free radical chain sequence which results in the halogenated substrate and a haloform.

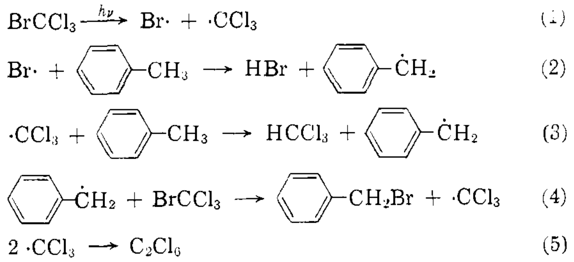
$$\cdot CX_3 + RH \longrightarrow R\cdot + HCX_3$$
$$R\cdot + CX_4 \longrightarrow RX + \cdot CX_3$$

Carbon tetrachloride and carbon tetrabromide have been reported to halogenate various hydrocarbons,[3] and similar hydrogen–halogen exchange reactions involving alcohols[4] and adehydes[5] with polyhalomethanes have been observed. Kooyman and Farenhorst found that in the free radical reaction of carbon tetrachloride and cyclohexene, allylic chlorination had occurred along with the expected addition reaction.[6] More recently Anderson and Heiba made brief mention of the fact that bromotrichloromethane brominated the benzylic position of alkyl aromatics under the influence of high energy radiation.[7] The present report describes the side chain bromination of various alkylbenzenes and substituted toluenes with bromotrichloromethane under relatively mild photochemical conditions.

Results and Discussion

When bromotrichloromethane and certain alkylated aromatic compounds were exposed to near ultraviolet irradiation, a reaction took place in which the bromine of the polyhalomethane and a benzylic hydrogen were interchanged, the products of the reaction being chloroform and the α-brominated alkylated aromatic. These reactions were carried out in ordinary Pyrex equipment with light from a 275-watt General Electric sunlamp. As can be seen in Table I, the amounts of chloroform and the brominated product were essentially equimolar. Along with those products, small amounts of hydrogen bromide were also found and evidence of small amounts of hexachloroethane was detected in the infrared spectra of the reaction mixtures.

These products and their distribution suggest the following reaction sequence illustrated for the photochemically induced reaction of toluene and bromotrichloromethane. The chain sequence



shown in steps 3 and 4 comprises the major portion of the reaction of bromotrichloromethane and toluene. This is evidenced both by the formation of equimolar amounts of the two products of these steps (chloroform and benzyl bromide), and by their relatively high molar ratio to the hydrogen bromide formed. This ratio is of the order of 20:1 under the conditions used in these reactions. According to the above sequence, hydrogen bromide can be formed only from attack of a bromine atom on toluene (2) and the only source of bromine atoms is the photochemical reaction shown in step 1. The formation of chloroform (3), on the other hand, results not only from the trichloromethyl radical produced in (1) but also from (4) which is part of the chain sequence. Since hydrogen bromide formation is equivalent to the amount of photochemical initiation according to this scheme, this suggests a kinetic chain length for the free radical chain sequence shown in (3) and (4) of about 20 under the conditions of these experiments. The dimerization of two trichloromethyl radicals (5) is a chain-terminating reaction.

The brominated products formed in these reactions (Table I) of the various alkylbenzenes are

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(3) J. P. West and L. Schmerling, U. S. Patent 2,553,799 and 2,553,800 (1951); W. H. Hunter and D. E. Edgar, THIS JOURNAL, **54**, 2025 (1932); Y. A. Ol'dekop, *Doklady Akad. Nauk SSSR*, **93**, 75 (1953).

(4) G. A. Razuvaev and N. S. Vasiliesky, *ibid.*, **80**, 69 (1951); G. A. Razuvaev and Y. A. Sorokin, *Zhur. Obshchei. Khim.*, **23**, 1519 (1953); G. A. Razuvaev, B. N. Moryganov and A. S. Volkova, *ibid.*, **25**, 495 (1955); J. W. Heberling, Jr., and W. B. McCormack, THIS JOURNAL, **78**, 5433 (1956).

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(6) E. C. Kooyman and E. Farenhorst, *Rev. trav. chim.*, **70**, 867 (1951).

(7) E. I. Heiba and L. C. Anderson, THIS JOURNAL, **79**, 494 (1957).