[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Liquid Phase Photochlorination and Sulfuryl Chloride Chlorination of Branched-chain Hydrocarbons; the Effect of Structure on the Relative Reactivities of Tertiary Hydrogen in Free Radical Chlorinations[1,2]

BY GLEN A. RUSSELL AND HERBERT C. BROWN

RECEIVED DECEMBER 1, 1954

The photochlorination of isobutane, 2,3-dimethylbutane, 2,2,3-trimethylbutane and 2,3,4-trimethylpentane was investigated in order to determine the rate of attack of the tertiary hydrogens relative to the primary. Assuming that the reactivities of the primary hydrogens in these compounds do not vary significantly, it appears that the reactivities of the tertiary hydrogen atoms in these aliphatic hydrocarbons are remarkably constant, with the variation no greater than the experimental uncertainty of 10%. At 25° the tertiary hydrogens are 3.4 times as reactive as the primary hydrogens in these compounds. The ratio varies with the temperature, with the following ratios observed for 2,2,3-trimethylbutane: 4.5 at −15°, 3.7 at 0°, 3.4 at 25° and 3.2 at 80°. The presence of the phenyl group in cumene increases the reactivity of the tertiary hydrogen atom to 18.0 at 25° and 12.8 at 80°. The observation that the reactivity of tertiary hydrogen toward chlorine atom attack is not altered appreciably by the accumulation of bulky groups raises a question as to the configuration of the transition state in chlorination reactions. Two explanations appear possible. Either the transition state ($R_3C{-}{-}{-}H{-}{-}{-}Cl$) is one in which the carbon–hydrogen bond is only slightly broken so that the geometrical arrangement is still essentially tetrahedral, or alkyl free radicals possess an essentially tetrahedral configuration rather than the planar structure commonly accepted. Chlorine and sulfuryl chloride exhibit different selectivity in the chlorination of 2,3-dimethylbutane and 2,3,3-trimethylbutane. It is probable that the altered selectivity results from the difference in the hydrogen abstracting species in the two reactions—chlorine atoms in the photochlorination reaction and $\cdot SO_2Cl$ free radicals in the sulfuryl chloride reaction.

Rearrangement of radicals or exchange between radicals and hydrocarbons does not appear to be significant in photochlorinations.[3] Consequently, the distribution of isomeric alkyl chlorides in chlorination should constitute a direct measure of the relative reactivities of the hydrogen atoms undergoing substitution.

Such data could have a number of interesting applications in organic theory. Unfortunately, since the classical studies of Hass and his co-workers[4] there have been relatively few quantitative data of this kind. In particular, liquid phase data are lacking. In order to obtain data on the effect of the structure of hydrocarbons on the relative reactivity of carbon–hydrogen bonds toward free radical attack, we have chlorinated a series of hydrocarbons in the liquid phase, analyzing by chemical methods the mixture of isomeric chlorides produced in the reaction. To minimize the analytical difficulties, the study was restricted to hydrocarbons containing only primary and tertiary carbon atoms.

It appeared that some information might be gained as to the nature of the transition state by examining both the effect of bulky alkyl groups on the reactivity of the tertiary hydrogen, as well as the effect of the phenyl group. Accordingly, isobutane, 2,3-dimethylbutane, 2,2,3-trimethylbutane (triptane) and 2,3,4-trimethylpentane, as well as cumene were included in the study.

Sulfuryl chloride chlorinations of triptane and 2,3-dimethylbutane were performed to allow a comparison of the relative selectivity of this mode of chlorination with the photochlorination reaction. If the same hydrogen abstracting species were involved in both reactions, the selectivity should be the same, whereas a different intermediate in the sulfuryl chloride reaction should lead to a different ratio of reactivity for the primary and tertiary hydrogen atoms.

Results

A series of photochlorinations of branched-chain hydrocarbons was performed at controlled temperatures and the products were analyzed for tertiary chloride by solvolysis in 50–80% ethanol at 25–40°. The quantity of primary chloride formed was taken as the difference between total and hydrolyzable chlorine. Since the hydrocarbons were free of olefins, as evidenced by the absence of reaction with bromine in the dark, and the chlorinations were allowed to proceed only to an extent of approximately 5 mole %, it is believed that dichloride formation is negligible. The results obtained are summarized in Table I, wherein the reactivity of each tertiary hydrogen relative to a primary hydrogen in the same molecule has been calculated from the analytical data by making a statistical correction for the number of primary and tertiary hydrogens present in each molecule.

TABLE I

RELATIVE REACTIVITIES OF TERTIARY AND PRIMARY HYDROGEN ATOMS IN PHOTOCHLORINATION[a]

	Temperature, °C.			
Compound	−15 ± 0.5	0 ± 1	25 ± 0.1	80 ± 0.1
Isobutane	4.5 ± 0.2			
2,3-Dimethylbutane			3.5 ± 0.2	
Triptane	4.5 ± 0.2	3.7 ± 0.2	3.4 ± 0.2	3.2 ± 0.2
2,3,4-Trimethylpentane			3.4 ± 0.2[b]	
Cumene			18.0 ± 0.6	12.8 ± 0.7

[a] Rel. react. = moles tertiary chloride × no. of primary hydrogens/moles primary chloride × no. of tertiary hydrogens. [b] Both types of tertiary hydrogen atoms have equal reactivity.

The relative reactivity of the tertiary hydrogen atoms of 2,3,4-trimethylpentane at 25° of 3.4 ± 0.2 is in satisfactory agreement with the reactivity ratio of 3.7 previously reported.[5] However, the tertiary/primary hydrogen reactivity in isobutane

---

[1] Directive Effects in Aliphatic Substitution. IV.

[2] This paper is abstracted from a thesis submitted by Glen A. Russell in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] H. C. Brown and G. A. Russell, THIS JOURNAL, **74**, 3995 (1952).

[4] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

[5] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **73**, 1317 (1951).

of 4.5 ± 0.2 at −15° is considerably lower than the reactivity of 7.5 calculated from the data of Hass, McBee and Weber.[4] Because of this discrepancy, the products of a chlorination of isobutane at −15° were isolated and examined for possible dichloride formation.[6] The reaction of 0.0680 mole of chlorine with 1.50 moles of isobutane produced 0.0675 mole of hydrogen chloride, indicating the absence of dichlorides. Moreover, careful distillation of the isobutane from the product gave a residue which did not contain chlorine in excess of that calculated for the formula C_4H_9Cl.

This result excludes the possibility that the relative reactivities observed for the hydrogen atoms of isobutane in our work are in error because of the formation of major amounts of isobutylene dichloride, which would analyze as primary chloride in the hydrolysis procedure, either from the reaction of chlorine with isobutylene that might be present as an impurity or from the reaction of chlorine with the monochloride originally present.[7]

The reactivity of the tertiary hydrogen atom of triptane was noticeably higher, 7.33, when sulfuryl chloride was used as the chlorinating agent at 80°. This compares with the value of 3.2 observed in the photochlorination of this hydrocarbon at the same temperature.

The products of the sulfuryl chloride chlorination gave negative qualitative tests for the presence of sulfur, thus removing the possibility that chlorosulfonation had occurred and had interfered with the analytical method. Furthermore, slow addition of the sulfuryl chloride to the reaction mixture, thus maintaining the instantaneous concentration of sulfuryl chloride at a low value, resulted in a selectivity value of 7.44, essentially identical with that previously obtained. It therefore appears that the difference between photochlorination and sulfuryl chloride chlorination cannot be the result of a rearrangement of the free radical intermediates or of an exchange of these free radicals with the hydrocarbon undergoing chlorination.[3]

Further evidence that hydrogen atom abstraction cannot be occurring by the same process in both types of chlorination reactions was furnished by the sulfuryl chloride chlorination of 2,3-dimethylbutane. At 55°, a tertiary hydrogen atom of 2,3-dimethylbutane was 6.3 times as reactive as a primary hydrogen atom, while in photochlorination a relative reactivity of only 3.5 was observed at the lower temperature of 25°. In addition, the reactivity of the tertiary hydrogen atom of cumene in sulfuryl chloride chlorination[8] is roughly 50 times that of the primary, considerably greater than the 12.8 value observed at 80° for the photochlorination reaction (Table I).

Discussion

In recent years the study of the reactions of methyl free radicals in the gas phase by W. A. Noyes, Jr., G. Kistiakowsky, E. W. R. Steacie and A. F. Trotman-Dickenson and their co-workers has greatly clarified this area of chemistry.[9] The results support the conclusion that primary carbon–hydrogen bonds in the saturated alkanes are relatively insensitive to their environment—only minor differences are observed in the frequency factors and activation energies for the reactions of methyl free radicals with primary hydrogen atoms in ethane, neopentane and hexamethylethane.

In the chlorination studies of the present investigation it was observed that the ratios of attack by chlorine atoms of the tertiary hydrogens relative to that of the primary hydrogen atoms in the paraffin hydrocarbons are remarkably constant. If we make the reasonable assumption that the reactivities of primary hydrogen atoms are essentially constant and assign a value of 1.00 to this quantity, we find that the tertiary hydrogens possess a reactivity of 3.4. Any variations are quite small and well within the estimated uncertainty of 10%. In other words, the reactivity of the tertiary hydrogen atoms appears to be quite insensitive to the accumulation of bulky groups on the tertiary carbon.

It has been demonstrated that the accumulation of large bulky alkyl groups results in an increase in the solvolysis rate of tertiary alkyl chlorides.[10] The increase is believed to be the result of a decrease in steric strain in the transition state as the molecule moves along the reaction path to a planar carbonium ion.[11] Significant increases in rate were observed both for *t*-butyldimethylcarbinyl chloride and for diisopropylmethylcarbinyl chloride.

In the present study a similar enhancement in the rate of attack of a tertiary hydrogen was not observed in the analogous hydrocarbons, triptane and 2,3,4-trimethylpentane. Moreover, it has been established that the attack of chlorine atoms on the two different tertiary hydrogens present in 2,3,4-trimethylpentane is purely statistical, whereas the corresponding tertiary chlorides exhibit markedly different solvolysis rates.[5]

This difference in the effect of bulky alkyl groups in the solvolysis of the tertiary chlorides and in the chlorine atom attack of the tertiary hydrocarbons might arise either from differences in the configurations of the carbonium ion and the free radical, or it might arise from differences in the extent of bond breaking in the transition states.

Both alkyl free radicals[12,13] and carbonium ions[14]

---

[6] It has been noted that the bromination of branched-chain hydrocarbons results in the formation of considerable quantities of dibromides: G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4025 (1955).

[7] The cause of the discrepancy between the reactivities of the hydrogen atoms of isobutane as determined in this work and as previously reported (ref. 4) is not entirely clear. The chlorinations reported by Hass, McBee and Weber produced a considerable amount (14–20% by weight) of polychlorides which were not considered in assigning relative reactivities to the tertiary and primary hydrogen atoms. Since isobutyl chloride should chlorinate more easily than *t*-butyl chloride, there is a possibility that the ratio of primary to tertiary chloride in the product was altered seriously as a result of the further chlorination. Furthermore, the fractional distillation procedure used for the analysis does not offer the precision possible with the analytical procedure utilized in the present study.

[8] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

[9] For a concise review and pertinent references, see A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953).

[10] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[11] H. C. Brown, *Science*, **103**, 385 (1946).

[12] H. C. Brown, M. S. Kharasch and T. H. Chao, THIS JOURNAL, **62**, 3435 (1940).

[13] W. E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, *ibid.*, **74**, 3000 (1952).

[14] P. D. Bartlett and L. H. Knox, *ibid.*, **61**, 3184 (1939); P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).

are generally considered to possess planar configurations. The evidence in favor of a planar carbonium ion is reasonably good, whereas that for the free radical is far less satisfactory.[15] The present result suggests the desirability of a further study of the geometrical configuration of alkyl free radicals.

The existence of a marked difference in the extent of bond breaking in the two transition states provides an alternative explanation. Thus if the bond breaking in the transition state of the solvolysis of the tertiary halides is large, then the tertiary group would be well on the way to a carbonium ion and the relief of steric strain would be large. On the other hand, in the chlorination reaction, a relatively small amount of bond-breaking in the transition state would mean that the incipient free radical was still largely in its original configuration and the steric strain contribution would be negligible.

On the assumption that there will be no important difference in the frequency terms for the attack of a chlorine atom with a primary as compared to a tertiary hydrogen atom, it is possible to calculate from the data in Table I the difference in the energies of activation for the two processes. Treatment of an Arrhenius plot of these data for 2,2,3-trimethylbutane by the method of least squares (no error assumed in $1/T$) gives an energy of activation difference ($E^{\mathrm{P}}_{\mathrm{act}} - E^{\mathrm{T}}_{\mathrm{act}}$) of 0.6 kcal./mole.[16]

The difference in the dissociation energy of primary and tertiary carbon–hydrogen bonds has been estimated as 7 kcal./mole.[9] On this basis, it would appear that in the transition state for the removal of hydrogen by the chlorine atom, the carbon–hydrogen bond must be broken only to the extent of approximately 10%.[17]

It does not appear possible at this time to reach a definite decision between the two possible explanations for the lack of sensitivity of the tertiary hydrogen to the presence of steric strain. It could well be that both factors are involved.

The reactivity of the tertiary hydrogen atom of cumene relative to a tertiary hydrogen atom of a purely aliphatic molecule corresponds to an energy of activation difference of approximately 1 kcal./mole, a quantity that is quite small compared to the resonance energy of benzyl free radicals.[18] This result also argues for a relatively minor amount of bond breaking in the transition state.

The observation that photochemical and sulfuryl chloride chlorinations do not give the same distribution of isomeric alkyl chlorides suggests that the original mechanism proposed for the sulfuryl chloride chlorination reaction[8,19] should be altered slightly with the chain reaction involving the following propagation steps.

$$\mathrm{R\cdot + SO_2Cl_2 \longrightarrow RCl + SO_2Cl\cdot} \qquad (1)$$

$$\mathrm{SO_2Cl\cdot \rightleftharpoons SO_2 + Cl\cdot} \qquad (2)$$

$$\mathrm{RH + SO_2Cl\cdot \longrightarrow R\cdot + HCl + SO_2} \qquad (3)$$

$$\mathrm{RH + Cl\cdot \longrightarrow R\cdot + HCl} \qquad (4)$$

Evidence that equilibrium 2 exists has been furnished by Schumacher,[20] while reaction 3 is related to the hydrogen abstraction step proposed for the decomposition of acetyl peroxide in hydrocarbon solvents[21] and to one of the possible mechanisms for the reaction of benzoate radicals with allyl acetate.[22] In addition there is evidence that some of

$$\mathrm{RH + CH_3CO_2\cdot \longrightarrow R\cdot + CH_4 + CO_2}$$

the products formed in the peroxide-catalyzed reaction of sulfuryl chloride with olefins results from the addition of a $\mathrm{SO_2Cl\cdot}$ radical to the olefin.[23–25]

The relative amounts of chlorination proceeding by reactions 3 and 4 should depend upon both the concentration of sulfur dioxide and the reactivity of the material being chlorinated. Since the $\mathrm{SO_2Cl\cdot}$ free radical must have a lower reactivity and a greater selectivity than a chlorine atom, a very reactive substrate should favor reaction 3 and an unreactive substrate reaction 4. Moreover, a high concentration of sulfur dioxide should create a relatively high concentration of $\mathrm{SO_2Cl\cdot}$ and thus favor reaction 3.

These predictions have been confirmed by observations on the sulfuryl chloride chlorinations of *t*-butylbenzene. When the chlorination is performed in refluxing carbon tetrachloride (80°), reaction occurs to give neophyl chloride. However, in the absence of a volatile solvent, the reaction does not proceed at 80° and the reaction mixture must be heated to reflux in order for chlorination to occur. If a reaction which has been initiated in this way is cooled to 80°, the reaction ceases and neither chlorination nor chlorosulfonation proceeds at an appreciable rate.

These observations are interpreted to mean that in refluxing carbon tetrachloride the concentration of sulfur dioxide is maintained at a low level and the chlorination reaction proceeds *via* reaction 4. In the absence of a low-boiling solvent, the sulfur dioxide accumulates and equilibrium 2 is favored. The reaction of the relatively stable $\mathrm{SO_2Cl\cdot}$ radical with the relatively inert carbon–hydrogen bonds in *t*-butylbenzene must be sufficiently slow so that the hydrogen atom abstraction stage cannot com-

---

(15) The observation that the chlorination of a tertiary hydrogen at the asymmetric center leads to an inactive tertiary chloride is incompatible with a pyramidal free radical which retains its configuration. The experimental result is compatible with either a planar free radical or a pyramidal free radical which undergoes rapid oscillation through the plane of the three substituents.

(16) Similar treatment of the data of Hass, McBee and Weber (ref. 4) for the liquid phase chlorination of isobutane from −55 to 100° gives the value 1.3 kcal./mole. From data for the vapor phase chlorination (ref. 4), the value 0.9 kcal./mole results.

(17) For discussion and pertinent references see H. Steiner and H. R. Watson, *Disc. Faraday Soc.*, **2**, 88 (1947).

(18) The carbon-hydrogen bond energy in toluene is estimated to be 77.5 kcal./mole as compared to 98 kcal./mole in ethane; M. Szwarc, *J. Chem. Phys.*, **16**, 138 (1948); *Chem. Revs.*, **47**, 75 (1950).

(19) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 3433 (1939); **62**, 925 (1940).

(20) H. J. Schumacher and C. Schott, *Z. physik. Chem.*, **193**, 343 (1944).

(21) F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).

(22) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 812 (1945).

(23) M. S. Kharasch and A. F. Zavist, *ibid.*, **73**, 964 (1951).

(24) A. Y. Yakubovich and Y. M. Zinov'ev, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 2028 (1947); *C. A.*, **43**, 1248 (1949).

(25) Our observations of different selectivities for the photochlorination and sulfuryl chloride chlorination reactions appear to exclude conclusively the possibility that sulfuryl chloride chlorinations proceed *via* dissociation of sulfuryl chloride into sulfur dioxide and molecular chlorine as advanced by Schumacher: H. J. Schumacher and J. Stauff, *Die Chemie*, **55**, 341 (1942).

TABLE II

SUMMARY OF CHLORINATION EXPERIMENTS[a]

Hydrocarbon	Temp., °C.	Reactants			Mole % chlorination	Products	
		Hydrocarbon	Chlorinating agent Cl_2[b]	SO_2Cl_2[c]		Alkyl chlorides	*t*-Chloride
Cumene	25.0 ± 0.1	0.60	0.034		5.7	0.0312	0.0236
Cumene	25.0 ± .1	.70	.056		9.3	.0542	.0403
Cumene	80.0 ± .1	.87	.050		5.7	.0465	.0310
Cumene	80.0 ± .1	.71	.043		6.0	.0430	.0298
2,3-Dimethylbutane	25.0 ± .1	.90	.044		4.9	.0469	.0173
2,3-Dimethylbutane	25.0 ± .1	.88	.048		5.4	.0482	.0183
2,3-Dimethylbutane	55.0 ± 2	1.05		0.140	13.3	.1324	.0679
Triptane	−15.0 ± 0.2	0.90	.049		5.3	.0508	.0113
Triptane	−15.0 ± 0.2	.85	.045		5.3	.0518	.0123
Triptane	0.0 ± 2	1.17	.130		11.1	.1250	.0409
Triptane	0 ± 0.5	1.00	.030		3.0	.0283	.0092
Triptane	25.0 ± .1	0.71	.026		3.4	.0257	.00455
Triptane	25.0 ± .1	.70	.021		3.1	.0213	.0037
Triptane	80.0 ± .1	.53	.031		5.8	.0342	.0062
Triptane	80 ± 2	1.02		.070	14.6	.0695	.1131
Triptane[d]	80 ± 2	1.23		.120	10.3	.0228	.0341
Isobutane	−15.0 ± 0.5	1.5	.115		7.8	.1173	.0389
Isobutane	−15.0 ± 0.5	1.5	.111		7.4	.1043	.0341
2,3,4-Trimethylbutane	25.0 ± 0.1	0.13	.011		8.3	.0093	.0036[e]

[a] All quantities in moles. [b] ±0.003 mole. [c] 1% by wt. benzoyl peroxide. [d] Sulfuryl chloride added dropwise over reaction period. [e] Analysis of the hydrolysis data indicated the presence of 0.0012 mole of a tertiary chloride which hydrolyzed rapidly (presumably 3-chloro-2,3,4-trimethylpentane) and 0.0024 mole of a slower solvolyzing tertiary chloride (presumably 2-chloro-2,3,4-trimethylpentane).

pete with the termination reaction

$$2SO_2Cl\cdot \longrightarrow SO_2Cl_2 + SO_2$$

On the other hand, a relative reactive hydrocarbon such as cyclohexane apparently can react with the $SO_2Cl\cdot$ radical, and chlorination becomes quite vigorous at temperatures considerably below the boiling point of the hydrocarbon.

This difference between the active species involved in photochlorinations and sulfuryl chloride chlorinations also is evident in recent data on the competitive chlorinations of nuclear substituted toluenes. Sulfuryl chloride chlorination gives a linear Hammett ρ–σ-relationship with $\rho = -1.5$.[26] On the other hand, the competitive photochlorination gives a similar linear ρ–σ plot, but with $\rho = -0.76$.[27]

The observation that the sulfuryl chloride chlorinations exhibit a significantly different activity and selectivity as compared to photochemical chlorinations opens up the possibility that the selectivity of such chlorinations can be varied within wide limits by adding small amounts of materials with which chlorine atoms will be associated. Thus photochemical chlorinations in the presence of sulfur dioxide should lead to the formation of the $SO_2Cl\cdot$ intermediate and the photochemical reaction should then exhibit the selectivity of the sulfuryl chloride chlorination.

Arguments can be presented to support the conclusion that chlorine atoms and free radicals should be considered generally as electrophilic reagents. Consequently, such intermediates should associate strongly with the π-electrons of the aromatic ring. It is probable that photochlorinations carried out in the presence of aromatic rings involve attack, not by chlorine atoms, but by a chlorine atom–aromatic π-complex. It may be that the reactivity ratio of 12.8 observed for cumene at 80° (Table I) is due partly to the fact that the hydrogen abstraction is accomplished not by chlorine atoms, but by the more selective chlorine atom–cumene π-complex.

Experimental Part

Materials.—Purification and physical constants of the 2,3-dimethylbutane, triptane and cumene have been described previously.[28] Isobutane (Phillips Petroleum Co.), specified to be 99 mole % minimum purity, was passed through sulfuric acid and over calcium hydride before use. 2,3,4-Trimethylpentane was obtained from the American Institute Research Project No. 44 and was certified to have a purity of 99.35 ± 0.1%, $n^{20}{}_D$ 1.4043. A technical grade of sulfuryl chloride was distilled through a Vigreux column and a constant boiling middle fraction used.

Chlorination Procedures.—The procedures used for the chlorination studies were similar to the following, except in the case of isobutane. A three-necked 200-ml. flask was immersed in a water-bath maintained at the appropriate temperature so that only the necks of the flask projected above the surface of the water. The hydrocarbon was placed in the flask and brought to the reaction temperature. A stream of prepurified nitrogen was passed through the apparatus and the hydrocarbon to remove oxygen. Chlorine was liquefied in a calibrated tube and measured as a liquid. In general the mole ratio of hydrocarbon to chlorine was maintained at approximately 20/1. The chlorine was carried by a stream of nitrogen through a sintered glass disk slowly into the stirred hydrocarbon, under illumination provided by a 150-watt bulb in a photoflash reflector. After the desired amount of chlorine had been added, as determined by the decrease in volume of the liquid chlorine in the calibrated tube, the dissolved hydrogen chloride was removed in a stream of the nitrogen.

With the exception of isobutane, the chlorination products were analyzed, after complete removal of hydrogen chloride, by diluting the entire product to a known volume with pure hydrocarbon and subjecting aliquots to a total chlorine

---

(26) R. van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).

(27) C. Walling and B. Miller, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., Sept., 1954, p. 15R.

(28) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4025 (1955).

analysis and to analysis for tertiary chloride by hydrolysis in 50% ethanol. In the case of isobutane, the excess hydrocarbon was removed, after chlorination was complete, by fractional distillation at a 10:1 reflux ratio in a 40 cm. × 12 mm. vacuum-jacketed column packed with glass helices and fitted with a low temperature head. When reflux no longer occurred, 75 ml. of chlorine-free, neutral dioxane was added to the flask carefully washing the head and column into the flask. The contents of the flask were diluted to 100 ml. with dioxane and aliquots of this solution analyzed as above.

The chlorination products of isobutane were tested for polychloride formation in the following manner. The reaction of 0.068 mole of chlorine with 1.5 mole of isobutane at −15° produced 0.066 mole of alkyl chloride and liberated 0.067 mole of hydrogen chloride. The chlorination product was fractionally distilled until all of the isobutane and most of the *t*-butyl chloride had been removed. The residue containing some of the monochlorides and all of the polychlorides formed in the reaction was analyzed for total chlorine content. The 38.40% chlorine found compares with 38.34% calculated for C_4H_9Cl, indicating the absence of significant amounts of higher chlorinated products.

The results of the chlorination experiments are summarized in Table II.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

p-Methylbenzyl Hydroperoxide

BY E. J. LORAND AND E. I. EDWARDS

RECEIVED FEBRUARY 14, 1955

p-Methylbenzyl hydroperoxide was prepared by the free radical-induced oxidation of *p*-xylene with molecular oxygen at 120–130°. Because of a competing reaction consisting in the fusion of two *p*-methylbenzyl radicals to form a crystalline hydrocarbon, the oxidation does not proceed by a chain mechanism. Isolation of the hydroperoxide was based on its solubility in dilute alkali. By-products of oxidation are *p*-methylbenzaldehyde, toluic acid and *p*-methylbenzyl alcohol. The hydroperoxide in a neutral solution is thermally stable up to almost 130°; in alkaline solution only at or below °C. Its acid-catalyzed decomposition yields mainly *p*-cresol (55%) and tolualdehyde (40%). A high melting, but still impure, trihydroperoxide related to the condensed (crystalline) hydrocarbon is also described.

The remarkable susceptibility to attack by oxygen of tertiary carbons adjacent to an aromatic ring, and even of secondary carbons in some cases (*e.g.*, in tetralin), is in sharp contrast to the inertness of the primary carbon under similar conditions. Hock[1] was the first to prepare a primary benzenoid hydroperoxide by the liquid-phase oxidation of *p*-xylene with molecular oxygen. The very low conversions obtained (0.2 to 0.3%), however, were not suitable for the preparation of substantial amounts of *p*-methylbenzyl hydroperoxide. Attempts to prepare this by the acid-catalyzed reaction of hydrogen peroxide and benzyl alcohol were unsuccessful, and a new approach to the oxidation of the methyl group was tried.[2] Free radicals should be able to remove a primary hydrogen, leaving a free *p*-methylbenzyl radical susceptible to the attack of molecular oxygen.

$$CH_3C_6H_4CH_3 + R\cdot \longrightarrow RH + CH_3C_6H_4CH_2\cdot \xrightarrow{O_2} CH_3C_6H_4CH_2OO\cdot$$

It soon became evident that removal of a primary hydrogen from xylene, even by the action of a free radical, required relatively high temperatures and more than catalytic amounts of an initiator to supply the free radicals. In most experiments *t*-butyl peroxide was used, although its relatively low boiling point (109°) limits the temperature of reaction to about 130°, which, in the course of the reaction, is gradually lowered to 120° by increasing amounts of low boiling decomposition products of the peroxide. The hydroperoxide content rises to a maximum of 4–4.5 g./100 cc. (or approximately 4.5–5.0% by weight) in about 2.5–3.0 hours and then drops. About half of the above maximum is reached in less than one hour; the limiting factor, as will be shown, is the autocatalytic decomposition of the hydroperoxide. The following reactions appear to be involved

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \quad (1)$$

$$CH_3C_6H_4CH_3 + (CH_3)_3CO\cdot\ (\text{or } CH_3\cdot) \longrightarrow (CH_3)_3COH\ (\text{or } CH_4) + CH_3C_6H_4CH_2\cdot \quad (2)$$

$$CH_3C_6H_4CH_2\cdot \xrightarrow{O_2} CH_3C_6H_4CH_2OO\cdot + CH_3C_6H_4CH_3 \longrightarrow CH_3C_6H_4CH_2OOH + CH_3C_6H_4CH_2\cdot \quad (3)$$

$$CH_3C_6H_4CH_2\cdot + \cdot H_2CC_6H_4CH_3 \longrightarrow CH_3C_6H_4CH_2CH_2C_6H_4CH_3 \quad (4)$$

Under the given conditions the *t*-butoxy radical seems to react quite readily with xylene as indicated by the relatively small amount of acetone (reaction 1) found in the reaction mixture and in the Dry Ice trap through which the exit gases passed. It is also to be noted that large amounts of *t*-butyl peroxide are consumed and that much crystalline hydrocarbon is formed according to reaction 4. These facts are inconsistent with the assumption of an oxidation chain of appreciable length which would start by the attack of the peroxy radical (arising from reaction 3) on a xylene molecule.

The free *p*-methylbenzyl radical can react either with oxygen or with another radical to form 4,4′-dimethylbibenzyl. This is apparent from the results of an experiment in which accidental inhibition prevented oxidation. The amount of the crystalline residue per 1000 g. of xylene input was more than 60% higher than in an uninhibited oxidation. The relatively low yield of the pure hydrocarbon "dimer" is accounted for by the further attack of free radicals on the condensed hydrocarbon, thus allowing for "trimer," and perhaps further

---

(1) H. Hock and C. Lang, *Ber.*, **76**, 169 (1943).

(2) Since the work reported in this paper was completed, C. Walling and J. A. Buckler (THIS JOURNAL, **75**, 4372 (1953)) have reported the preparation of benzyl hydroperoxide by the oxidation of benzylmagnesium chloride.