TABLE VI

DECOMPOSITION OF HA IN A METHANOLIC PYRIDINE BUFFER AT 25°

[HA] = 1.385×10^{-4} *M*, [C_5H_5N] = [$C_5H_5NH^+$] = 4.144×10^{-3} *M*, [$NaClO_4$] = 0.100 *M*

Time, sec.	Optical density[a]	$\log \frac{D_\infty}{D_\infty - D}$	10^5k, sec.$^{-1}$
3960	0.151	0.0614	3.57
4560	.173	.0715	3.62
12360	.411	.1931	3.60
13560	.441	.2111	3.58
14760	.468	.2281	3.57
15960	.496	.2465	3.55
16560	.510	.2560	3.57
		Av.	3.58 ± 0.02

[a] $D_\infty = 1.150$, the calculated value is 1.140.

anolic hydrogen chloride to weighed samples of HA and then adding enough 1.00 *M* sodium perchlorate to bring the ionic strength to 0.100. At given times samples were pipetted from the reaction flask in a 40 ± 0.1° bath into a spectrophotometer cell at 25° and the optical density at 3100 and 3500 Å. determined. From these measurements and the ionization constants of nitroform under these conditions, the concentrations of β-nitrostyrene and nitroform were calculated and substituted into the integrated form of the first-order rate equation. The reaction was relatively slow and was only followed to about 20% of completion since β-nitrostyrene was found to decompose in methanol at a rate sufficient to have produced significant errors if we had tried to follow the reaction much further. Calculations based on K_e show that the reaction should proceed to more than 99% completion under the conditions used in these experiments.

Kinetics of the Addition of Nitroform to β-Nitrostyrene and Determination of K_e.—To 1.0518 g. of β-nitrostyrene in a 50-ml. low-actinic volumetric flask were added 20 ml. of 1.0380 *M* nitroform, 5 ml. of 1.00 *M* sodium perchlorate and 25 ml. of methanol. The flask was shaken, placed in a thermostated bath at 40 ± 0.1°, and at measured times 5-ml. samples were transferred into 45 ml. of ~ 0.5 *M* methanolic hydrogen chloride, to quench the reaction. A 5-ml. aliquot of this solution was then diluted to 100 ml. with methanol to give a solution of which 5 ml. was removed and diluted to 50 ml. Optical density measurements were made at 3100 and 3500 Å. on this final solution which was 2000 times as dilute as the reaction mixture. From these measurements, the concentrations of reactants and products were calculated. The resultant data are listed in Table VII and plotted (open circles) in Fig. 2. Also plotted in Fig. 2 is a run made with [HNF]$_0$ = 0.0909, [NS] = 0.0713, [$NaClO_4$] = 0.000.

TABLE VII

ADDITION OF NITROFORM TO β-NITROSTYRENE IN METHANOL AT 40°

Time, hr.	Optical density 3100 Å.	Optical density 3500 Å.	[NS][a]
0.0	0.583	0.135	0.1402
2.5	.538	.113	.1340
4.5	.503	.119	.1208
21.5	.366	.081	.0884
24.5	.356	.076	.0860

[a] Initial value of [HNF]$_{\text{formal}}$ = 0.4152 *M*.

Runs used to determine the value of K_e were carried out similarly except that no sodium perchlorate was used, and in some cases HA was used as the reactant. The data obtained are plotted in Fig. 2.

Acknowledgments.—We acknowledge with gratitude the support of this investigation by the Department of the Navy, Bureau of Ordnance.

ATLANTA, GA.

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

Phenyl Migration during Decomposition of Peroxides in Alkylbenzenes[1a,b]

BY HERMAN PINES AND C. N. PILLAI

RECEIVED JUNE 26, 1959

The decomposition of peroxides in alkylbenzenes was studied. Decomposition of di-*t*-butyl peroxide in cumene and *t*-butylbenzene yielded, in addition to the products previously reported in the literature, *n*-propylbenzene in small yield and isobutylbenzene, respectively. *t*-Amylbenzene under similar conditions yielded 2-phenyl-3-methylbutane and 1-phenyl-2-methylbutane. Peroxides giving rise to more reactive free radicals, namely, benzoyl peroxide and acetyl peroxide, also caused similar isomerizations, but to a lesser extent. With the latter peroxides, reactions with the aromatic nucleus became more important than side-chain hydrogen abstraction. The decomposition of di-*t*-butyl peroxide in cumene at higher temperature is accompanied by side-chain methylation resulting in the formation of *t*-butylbenzene.

Recently[1,2] it was observed in this Laboratory that during the thermal reaction of alkylbenzenes with olefins 1,2-aryl migrations took place readily. In all the cases studied, the migration was that of a phenyl group to an adjacent terminal carbon atom. For example, during the thermal reaction of cumene with propylene, in addition to the normal side-chain alkylation products, the rearranged product 2-methyl-1-phenylpentane was also detected. This product was evidently formed by the migration of the phenyl group of 2-methyl-2-phenylpentane to the adjacent terminal carbon atom. The alternate type of migration, namely, to the adjacent non-terminal carbon atom, would have led to 2-methyl-3-phenylpentane. However, this product was not detected. In view of this it was of interest to see if the radical produced by the removal of a β-hydrogen atom of an alkylbenzene under less severe conditions will rearrange. Specifically, it was of interest to see what type of rearrangement, if any, will take place as a result of hydrogen abstraction from *t*-amylbenzene. With these ends in mind the decompositions of peroxides in isopropylbenzene, *t*-butylbenzene and *t*-amylbenzene were studied.

Several instances of 1,2-phenyl migration during free radical reactions are to be found in the literature. Among the most well-known of these are

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[1] (a) Paper III of the series, "Thermal Alkylation Reactions." For paper II, see H. Pines and C. N. Pillai, THIS JOURNAL, **81**, 3629 (1959). (b) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Fund.

[2] H. Pines and J. T. Arrigo, THIS JOURNAL, **79**, 4957 (1957).

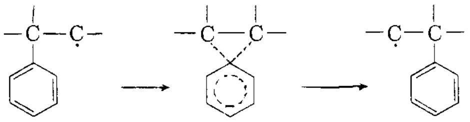
the rearrangements of the 2,2,2-triarylethyl radicals[3] and the rearrangement of the neophyl radical.

β-Aryl radicals produced in a variety of reactions have been found to rearrange by phenyl migration. Among these are the peroxide induced decomposition of aldehydes,[4,5a,b,6] Grignard reactions in the presence of certain metal ions,[7a,b] thermal decomposition of azo compounds,[8] oxidation of certain diarylethanes[9] and pyrolysis of alkylbenzenes.[10]

However, no rearrangement was observed during the side-chain halogenation of *t*-butylbenzene.[11a–c]

In certain cases where spacial requirements are satisfied, an aryl group can move several atoms away from its original position.[12a,b]

In all these cases the migrating group is aryl. Migration of alkyl groups is relatively unfamiliar. There are a few reports in the literature where methyl group migrations have been claimed.[13a–c] The relative ease of migration of the aryl group is generally considered to be due to the participation of the aryl group in the transition state

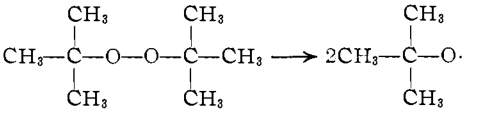


In all the instances discussed here, the initial radical which leads to rearrangement is formed by a dissociation rather than by hydrogen abstraction by another radical. Previous workers in the field who studied the decomposition of peroxides in alkylbenzenes failed to detect any rearrangement during these reactions.[14a–g]

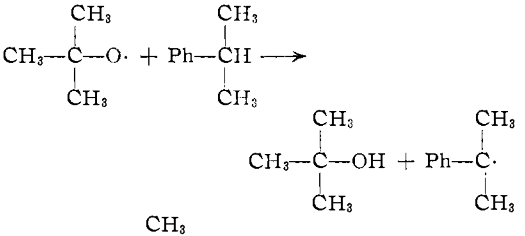
We now report the isomerization of radicals formed by the abstraction of a non-benzylic hydrogen atom of the alkylbenzene during the decomposition of peroxides.

Discussion

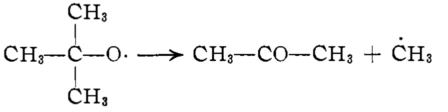
The results of the experiments with cumene and di-*t*-butyl peroxide (DTBP) are given in Table I. Experiment 1 was carried out by slowly distilling the reaction mixture from a short column. The major product of the reaction was 2,3-dimethyl-2,3-diphenylbutane ("bicumyl"), as was expected. However a small amount of *n*-propylbenzene was also detected; traces of olefins were formed. The products arising from DTBP were methane, acetone and *t*-butyl alcohol. These facts suggest the reaction scheme



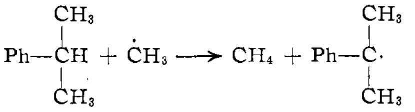
$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3} \longrightarrow 2\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}\cdot \quad (1)$$



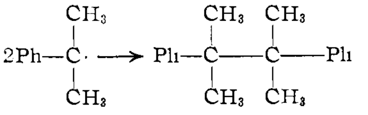
$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}\cdot + \mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{CH}}} \longrightarrow \mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{OH} + \mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdot \quad (2)$$



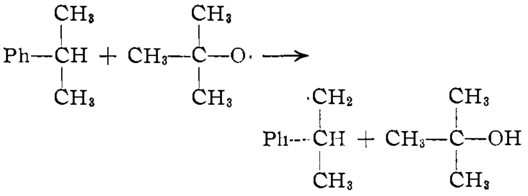
$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}\cdot \longrightarrow \mathrm{CH_3-CO-CH_3} + \dot{\mathrm{C}}\mathrm{H_3} \quad (3)$$



$$\mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{CH}}} + \dot{\mathrm{C}}\mathrm{H_3} \longrightarrow \mathrm{CH_4} + \mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdot \quad (4)$$



$$2\mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdot \longrightarrow \mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{Ph} \quad (5)$$



$$\mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{CH}}} + \mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}\cdot \longrightarrow \mathrm{Ph}-\underset{\mathrm{CH_3}}{\overset{\cdot\mathrm{CH_2}}{\mathrm{CH}}} + \mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{OH} \quad (6)$$

TABLE I

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN CUMENE

Experiment	1[a]	2[b]	3[c]
Reactants, mole			
Cumene	0.1	0.69	0.34
DTBP	0.05	0.14	0.052
Mole % of DTBP decomposed	63	100	100
Yields based on *t*-butoxy radicals produced, mole %			
Methane	27	33.4	. .
Ethane[d]	0	59.3	. .
Acetone	27.2	100	33.1
t-Butyl alcohol	68.3	0	50.6
n-Propylbenzene	1.3	. .	1.6
t-Butylbenzene	. .	5.3	2.2
α-Methylstyrene	Traces	9	Traces
Cymenes	0	0	2.2
Bicumyl[e]	87.4	9.0	96.6

[a] Mixture distilled through a 6″ column over a period of 24 hours; flask temperature 128–135°. [b] Mixture was passed down a glass-packed column at the rate of 25 cc./hour; atmospheric pressure; gas phase 320°. [c] Pressure-flow reaction; glass-packed column; 210°; 50 atm.; flow rate 25 cc./hour. [d] Ethane value as methyl radicals. [e] Bicumyl as cumyl radicals.

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(5) (a) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952); (b) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

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(7) (a) W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944); (b) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

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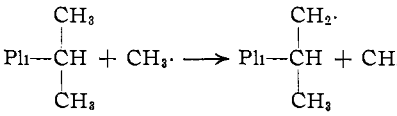
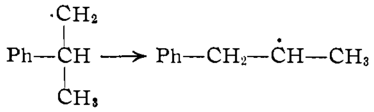
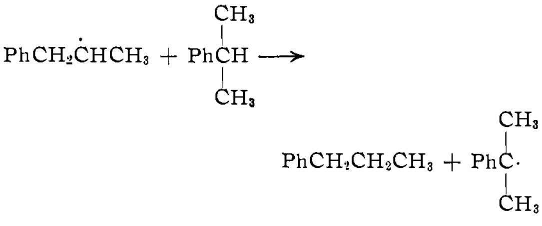
(14) (a) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948); (b) A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956); (c) J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957); (d) K. M. Johnson and G. H. Williams, *Chemistry & Industry*, 328 (1958); (e) M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945); (f) J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 3352 (1954); (g) R. L. Dannley and B. Zaremsky, THIS JOURNAL, **77**, 1588 (1955).



$$\mathrm{Ph{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}} + CH_3\cdot \longrightarrow Ph{-}\overset{\displaystyle CH_2\cdot}{\underset{\displaystyle CH_3}{CH}} + CH_4} \qquad (7)$$

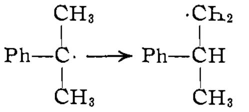


$$\mathrm{Ph{-}\overset{\displaystyle \cdot CH_2}{\underset{\displaystyle CH_3}{CH}} \longrightarrow Ph{-}CH_2{-}\dot{C}H{-}CH_3} \qquad (8)$$



$$\mathrm{PhCH_2\dot{C}HCH_3 + Ph\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}} \longrightarrow PhCH_2CH_2CH_3 + Ph\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot} \qquad (9)$$

Steps 1–4 are the generally accepted steps for the decomposition of DTBP in cumene. At a given temperature the relative rates of 2 and 3 will depend upon the ease with which a hydrogen is removed from the alkylbenzene by the *t*-butoxy radical. This fact has been extensively made use of to study the relative ease of hydrogen abstraction from various hydrocarbons.[14,b–d] As the temperature increases, reaction 3 becomes more important than 2. We consider that reactions 6 and 7 are the sources of the 2-phenyl-1-propyl radical. The other possible step by which this radical could be formed is

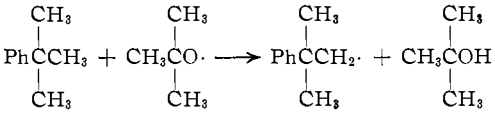


$$\mathrm{Ph{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot \longrightarrow Ph{-}\overset{\displaystyle \cdot CH_2}{\underset{\displaystyle CH_3}{CH}}} \qquad (10)$$

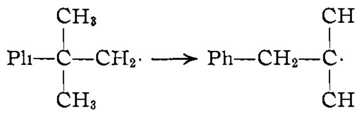
The hydrogen migration represented by step 10 may be considered unlikely in view of the unfavorable energetics of such a reaction. The following experiment supports this view. When "bicumyl" is distilled at 230°, it dissociates into cumene and α-methylstyrene. The primary step in this reaction is evidently the dissociation of dicumyl into two cumyl radicals. This is followed by disproportionation to yield the observed products. Now, if the isomerization corresponding to 10 took place and significant quantities of the 2-phenyl-1-propyl radical were present, one would reasonably expect this to isomerize according to 8 and yield products having the *n*-propylbenzene skeleton. However, no such product was detected. This shows that migration of a β-hydrogen atom to the α-position in the cumyl radical is not a reaction to be considered.[15]

Experiment 2 was carried out in a flow system in the vapor phase at 320°. No significant amount of isomerization was observed under these conditions. Evidently at this high temperature methyl radicals are formed at a fast rate and radical recombination reactions, as exemplified by the formation of ethane and *t*-butylbenzene, predominate over hydrogen abstraction.

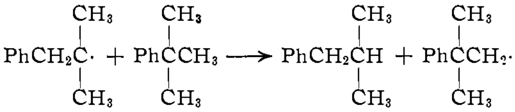
Experiment 3 of Table I was carried out in a pressure-flow system at 50 atm. pressure and a temperature of 210°. Here, both side-chain and nuclear methylations take place. While homolytic nuclear arylation is a well-known reaction, nuclear alkylation by free-radicals is relatively unfamiliar.[16] Eliel and co-workers[17a,b] have obtained nuclear as well as side-chain methylation during the decomposition of acetyl peroxide in toluene. Beckwith and Waters[18] already have reported the formation of chlorotoluenes and methylated dichlorobiphenyls during the decomposition of DTBP in chlorobenzene. It is interesting to notice that in the reaction of phenyl radicals with toluene in the vapor phase, side-chain hydrogen abstraction takes place, whereas in the liquid phase, biphenyls are formed.[19] It has been proposed that this difference is due to the formation of a complex between the attacking radical and toluene in the liquid phase.[19,20] For the methyl radical which is a comparatively nucleophilic radical,[21] the tendency for this complex formation will be low with an electron-rich nucleus like an alkylbenzene. This may also be one of the reasons why the tendency for nuclear methylation decreases in the series toluene, ethylbenzene, cumene as reported by Wilen and Eliel.[17b] In view of these, we may conclude that at the higher temperature the nuclear methylation observed in experiment 3 takes place in the liquid phase. That side-chain methylation also takes place shows that we are dealing with mixed phase reactions here. In Table II, experiment 4, the results of decomposing DTBP in *t*-butylbenzene are given. Again we notice that in the liquid phase no ethane is formed. Isomerization of *t*-butylbenzene to isobutylbenzene takes place to an appreciable extent. No olefins are formed. The following reaction scheme may be written for the isomerization



$$\mathrm{Ph\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3 + CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}O\cdot \longrightarrow Ph\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2\cdot + CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}OH} \qquad (11)$$



$$\mathrm{Ph{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2\cdot \longrightarrow Ph{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot} \qquad (12)$$



$$\mathrm{PhCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot + Ph\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3 \longrightarrow PhCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}H + Ph\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2\cdot} \qquad (13)$$

The chain-length is evidently small and the terminating step is a dimerization. The nature of the dimer was not ascertained. This rearrangement is in agreement with the several reported cases of the isomerization of the neophyl radical.[4,5,7] It is likely that part of the isobutylbenzene thus formed has undergone dimerization and consequently the actual extent of isomerization may be more than the 7.1% shown in Table II.

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(15) L. H. Slaugh, ref. 6, gives evidence for the absence of 1,2-hydrogen shift in the 2-phenylethyl radical.

(16) The work of Szwerc and co-workers may be recalled here: M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955), and other papers.

(17) (a) E. L. Eliel, K. Rabindran and S. H. Wilen, *J. Org. Chem.*, **22**, 859 (1957); (b) S. H. Wilen and E. L. Eliel, THIS JOURNAL, **80**, 3309 (1958).

(18) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1665 (1957).

(19) M. T. Jacquiss and M. Szwarc, *Nature*, **170**, 312 (1952).

(20) G. A. Russell, THIS JOURNAL, **80**, 4987 (1958).

(21) The electron affinity of a methyl radical is low and is comparable to that of a sodium atom; for values, see H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

TABLE II

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN *t*-BUTYLBENZENE AND IN *t*-AMYLBENZENE

Experiment	4[a]	5[b]
Reactants, mole		
Alkylbenzene	0.2	0.28
DTBP	0.1	0.29
Mole % of DTBP decomposed	31.5	20.5
Yields based on *t*-butoxy radicals produced, Mole %		
Methane	30	36
Acetone	50	33
t-Butyl alcohol	50	47
Isobutylbenzene	7.1	
2-Phenyl-3-methylbutane	..	10.4
1-Phenyl-2-methylbutane	..	1.8
Higher boiling materials	23.8[c]	14.5[d]

[a] *t*-Butylbenzene experiment; the mixture was refluxed for 27 hours. During this time the flask temperature dropped from 133 to 102°. [b] *t*-amylbenzene experiment; refluxed for 24 hours; temperature dropped from 135 to 120°. [c] Calculated on the basis of $C_{10}H_{13}$ materials. [d] Calculated on the basis of $C_{11}H_{15}$ materials.

In Table II, experiment 5, the results obtained with *t*-amylbenzene are given. The direction of phenyl migration is that expected from considerations of the stability of the intermediate radicals formed. The initiating radical abstracts a hydrogen from a secondary carbon atom in preference to one from a primary carbon atom. This results in the preferential isomerization to 2-phenyl-3-methylbutane over 1-phenyl-2-methylbutane. It may be recalled that during the thermal reactions at 430° with similar molecules[1,2] the phenyl group migrated preferentially to terminal carbon atoms. The reason for this may be that at the high temperature the molecule is so activated that carbon-hydrogen bond-breaking, which precedes phenyl migration, takes place without discrimination and hence follows the statistical course. In the case of *t*-amylbenzene, considerable quantities of olefins were formed. No attempt was made to analyze or identify these. The values given in Table II were obtained after selective hydrogenation. As in the case of *t*-butylbenzene, here also the "polymeric" materials may have units having isomerized carbon skeletons in which case the actual extent of isomerization may be larger than that shown in the table.

Product analysis studies for the reactions of benzoyl peroxide with cumene[14g] and *t*-butylbenzene[14f] have been reported by other workers. These reactions were repeated and products arising from phenyl migration were specifically looked for. Experiment 6 of Table III gives the results obtained from cumene and benzoyl peroxide. No isomerization was detected here. Some α-methylstyrene, unreported by the earlier workers, was formed.

TABLE III

DECOMPOSITION OF BENZOYL PEROXIDE IN CUMENE AND IN *t*-BUTYLBENZENE

Experiment	6	7
Reactants, grams		
Alkylbenzene	48.2[a]	53.6[b]
Benzoyl peroxide	12.0	12.0
Products, grams		
Carbon dioxide	2.2	3.4
Benzene	1.7	Not detected
α-Methylstyrene	0.6	..
n-Propylbenzene	Not detected	..
Isobutylbenzene	..	0.5
Solid residue	12.2	13.0
Mole % isomerization based on benzoyloxy radicals	0	3.5

[a] Cumene. [b] *t*-Butylbenzene.

Data from the decomposition of benzoyl peroxide with *t*-butylbenzene are given in experiment 7 of Table III. Cadogan, Hey and Williams[14f] who studied this reaction had failed to identify any products corresponding to side-chain attack. The solid products formed during this reaction were not analyzed. However, the presence of isobutylbenzene formed during the reaction shows that side-chain hydrogen abstraction does take place. The extent of isomerization is less than that with DTBP. This is evidently due to the fact that attack on the ring is the preferred reaction here.

Data on the reaction of acetyl peroxide in *t*-butylbenzene are given in Table IV.[22]

TABLE IV

DECOMPOSITION OF ACETYL PEROXIDE IN *t*-BUTYLBENZENE

Experiment	8
Reactants, mole	
t-Butylbenzene	0.542
Acetyl peroxide	0.065
Yields based on acetoxy radicals, mole %	
Methane	45.2
Ethane (as CH_3)	9.8
Carbon dioxide	93.0
Acetic acid	6.6
Isobutylbenzene	3.0
Methyl *t*-butylbenzenes	5.0
Residue	[a]

[a] The high boiling residue obtained from 70.9 g. of *t*-butylbenzene and 7.7 g. of acetyl peroxide weighed 3.1 g. It was unsaturated to the extent of 20%, calculated as a "dimeric" product of *t*-butylbenzene.

The formation of the small amount of ethane had been observed by other investigators also. Rembaum and Szwarc[23] have concluded that this results from the recombination of methyl radicals in the initial solvent cage. It seems reasonable to assume that the small amount of acetic acid is formed as a result of hydrogen abstraction by the acetoxy radical before it has time to decompose, though reports in the literature seem to indicate that the acetoxy radical decomposes almost simultaneously as it is formed.[24] It should be stated here that the acetyl peroxide used for the reaction was first carefully washed with sodium bicarbonate solution to remove all traces of acetic acid.

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(22) At first we studied these reactions with a 25% solution of acetyl peroxide in dimethyl phthalate. Under these conditions no isomerization took place. This led us to the erroneous conclusion that methyl radicals do not abstract the side-chain hydrogen of *t*-butylbenzene and cause isomerization. Reinvestigation of this problem showed that the methyl radicals preferentially reacted with the ester leaving the *t*-butylbenzene unchanged. We are thankful to the referee for his helpful suggestions which led us to these findings.

(23) A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 3487 (1955).

(24) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 493.

Isomerization of *t*-butylbenzene to isobutylbenzene took place to the extent of 3% based on acetoxy radicals produced; some ring-methylated *t*-butylbenzene was also formed. The presence, however, of pentylbenzenes or neophyl acetate could not be detected. The volatile fractions were also free of olefins.

The yield of isobutylbenzene is less than that in the case of di-*t*-butyl peroxide. However, it should be remembered that the amount of isobutylbenzene may not be a true measure of the extent of isomerization of the neophyl radical. It is likely that more isobutylbenzene undergoes hydrogen abstraction and dimerization in the presence of acetyl peroxide, which provides the very reactive methyl radicals at a fast rate, than in the presence of di-*t*-butyl peroxide which yields mostly the less reactive *t*-butoxy radicals at a slower rate. The ring-methylated products formed with acetyl peroxide may also compete with the *t*-butylbenzene as hydrogen donors, thus lessening the chance for attack on the side chain of *t*-butylbenzene. In fact, a material balance of acetyl peroxide residues is obtained only if it is assumed that the high boiling residue is composed mostly of compounds formed by the dimerization of the radicals resulting from hydrogen abstraction from the methylated *t*-butylbenzenes. Attempts to purify the high boiling residue by chromatography over silica gel were not successful. This fraction was unsaturated to the extent of 20%.

The isomeric methyl-*t*-butylbenzenes were not individually identified. However infrared spectra indicate that the *m*- and *p*-isomers are more predominant than the *o*-isomer.

Experimental

Experiment 1 was carried out by distilling the mixture from a small column until the temperature of the vapor started to rise above 90°. The gas formed during the reaction was collected and analyzed by mass spectroscopy[25] as well as by vapor phase chromatography using a dimethylsulfolane–propyl sulfone column.[26] The mixture of acetone, *t*-butyl alcohol and DTBP was analyzed by vapor phase chromatography using a tricresyl phosphate column at 80°. Mixtures of cumene, *n*-propylbenzene and α-methylstyrene were analyzed on the same column at 140°.

Experiment 2 was carried out by passing the reaction mixture down a heated glass-packed column at the rate of 25 cc./hour.

Experiment 3 was similarly carried out in a flow-type apparatus designed for work under pressure. Analyses for experiments 2 and 3 were carried out in the same way as for 1.

Experiments 4 and 5 were carried out by simply refluxing the reaction mixture for the required period.

Mixtures of *t*-butylbenzene and isobutylbenzene were analyzed by infrared spectroscopy making use of the strong absorption by isobutylbenzene at 13.5 μ. The mixture of *t*-amylbenzene, 2-methyl-3-phenylbutane, 1-phenyl-2-methylbutane and the corresponding olefins was first selectively hydrogenated over a palladium–charcoal catalyst and then distilled to separate into two mixtures, one containing 2-methyl-3-phenylbutane and *t*-amylbenzene and the other containing *t*-amylbenzene and 1-phenyl-2-methylbutane. The first mixture was analyzed by vapor phase chromatography using columns of tricresyl phosphate and silicone at 170°. The second mixture was analyzed by infrared spectroscopy using the absorption band at 13.6 μ due to 1-phenyl-2-methylbutane.

t-Amylbenzene was synthesized by the reaction of cumene with ethylene in the presence of sodium and anthracene under pressure at 200°[27]; b.p. 190° (760 mm.), n^{20}_{D} 1.4963.

2-Methyl-3-phenylbutane was synthesized by the reaction of isopropylmagnesium bromide with acetophenone followed by hydrogenolysis of the resulting carbinol; b.p. 186° (760 mm.), n^{20}_{D} 1.4910 (reported[28] b.p. 186°).

1-Phenyl-2-methylbutane was prepared in a similar manner from *sec*-butylmagnesium bromide and benzaldehyde; b.p. 193° (760 mm.), n^{20}_{D} 1.4896 (reported[28] b.p. 194–195°).

Experiments 6 and 7 were carried out by heating solutions of benzoyl peroxide in the alkylbenzene on a steam-bath until gas evolution ceased. Carbon dioxide was absorbed over soda-lime and weighed. After completion of the reaction the volatile components were removed under vacuum and analyzed by gas chromatography or infrared spectroscopy.

Acetyl peroxide was prepared by a modification of the method of Price and Morita.[29] *t*-Butylbenzene was used as solvent instead of ether. After the oxidation of the acetic anhydride by sodium peroxide, the solution was decanted off and washed repeatedly with sodium bicarbonate solution at 0° until all traces of acetic acid and acetic anhydride were removed. It was then washed with ice-cold water and dried over calcium chloride. Peroxide content was estimated by the method of Kokatnur and Jelling.[30] The yields of carbon dioxide and acetic acid in Table IV shows that this acetyl peroxide is better than 99% pure.

The solution was decomposed in a flask fitted with a reflux condenser and a side tube for introducing an inert gas. Gases evolved were passed through several weighed soda-lime tubes to remove carbon dioxide and collected over saturated sodium chloride solution. Before reaction, the system was flushed out with helium to avoid air during the gas chromatographic analysis of the gases. The decomposition was carried out at 90° and was complete in less than 5 hours. Estimation of the methylated butylbenzenes was made by gas chromatographic analysis over a silicon-on-fire brick column where the isomeric methylbutylbenzenes came out as a single peak.

EVANSTON, ILL.

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[25] Thanks are due to Dr. Dietrich Schultze for the mass spectral analyses.

[26] The authors are indebted to M. G. Bloch, Socony Mobil Oil Co., for supplying the information.

[27] H. Pines and V. Mark, THIS JOURNAL, **78**, 4316 (1956).

[28] V. N. Ipatieff and L. Schmerling, *ibid.*, **60**, 1476 (1938).

[29] C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[30] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).