added and the irradiation continued for 20 hr. The vpc trace (using an internal standard) showed a 3% yield of ethers which were composed of CBME and CPCME in a ratio of 47:53 and a trace of homoallyl methyl ether. These yields represent minimum values due to the loss of butadiene during the irradiation under the conditions employed.

The crude irradiation mixture was distilled through a 24-in. spinning-band column and the first 100 ml of distillate collected. The distillate was diluted with an equal volume of water and extracted with two 15-ml portions of pure pentane. The pentane solution was dried and the pentane distilled through a 24-in spinning-band column. The residue was purified by preparative vpc and the CBME and CPCME possessed nmr and mass spectra identical with those of authentic samples.

When the reaction was run in methanol-O-*d*, the ethers obtained possessed mass spectra identical with those reported above for the deuterated species derived from BCB.

Irradiation of 1,3-Butadiene in Methanol in the Absence of Acid.—A 0.10 *M* solution of butadiene in methanol which had been freshly distilled from magnesium was prepared in base-washed glassware. The sample also contained 1,2-*trans*-dimethylcyclohexane (3.4×10^{-4} *M*), which is used as an internal standard. Aliquots (3 ml) of this solution were placed in rigorously base washed quartz tubes,[22] degassed, and sealed. The irradiation was performed in the merry-go-round apparatus using no filter. After 4.5 hr a sample was withdrawn. The concentration of butadiene, measured by uv spectroscopy, was 0.084 *M*. The vpc trace showed a new peak corresponding in retention time to bicyclobutane; no ethers were observed. A 3-μl sample of 70% aqueous perchloric acid was added to the solution, which was allowed to stand a few minutes and analyzed again. There was no peak corresponding to BCB and two new peaks, shown by coinjection with authentic materials to be CBME and CPCME, were found.

Registry No.—**1**, 18593-33-4; **1** (1-d_1), 18593-34-5; **2**, 1003-13-0; **2** (1-d_2), 18593-36-7; **3**, 157-33-5.

Acknowledgment.—We wish to thank Professor A. L. Burlingame, Dr. C. Fenselau, and Miss Sherri Firth for their interest and cooperation in the investigation of the mass spectra of the materials reported.

[22] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

Free-Radical Reactions of 3,3-Dimethylbutene, 3-Methyl-3-phenylbutene, and *t*-Pentylbenzene Induced by Di-*t*-butyl Peroxide[1]

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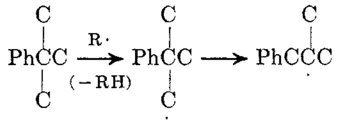
The effect of di-*t*-butyl peroxide (DTBP) at 150° upon skeletal isomerization of some model hydrocarbons was investigated. The hydrocarbons used for this study were 3,3-dimethylbutene, 3-methyl-3-phenylbutene, and *t*-pentylbenzene. The 1,2-vinyl migration in the olefins was not observed. The methyl radical, produced from the decomposition of the DTBP, added to the olefinic double bonds. 3,3-Dimethylbutene formed 2,2-dimethylpentane and the corresponding olefins, and 2,2,3-trimethylpentane. The addition of the methyl radical to 3-methyl-3-phenylbutene was accompanied by phenyl migration leading to the ultimate formation of 2-methyl-3-phenylpentane and of the corresponding olefins. *t*-Pentylbenzene underwent skeletal isomerization in the presence of DTBP at 150° with the production of 2-methyl-3-phenylbutane, 2-benzylbutane, and 2-methyl-2-phenylpentane. The methyl radical was also noted to add to the aromatic ring to form *p*-*t*-pentyltoluene.

Recent studies in this laboratory have demonstrated that free-radical intermediates are involved in the aromatization of alkanes[2] and cyclanes[3] and in the dehydrogenation of alkylbenzenes[4] over "nonacidic" chromia–alumina catalyst. These free radicals were responsible for the skeletal isomerization accompanying the dehydrogenation reaction either through a phenyl and/or vinyl migration. This was demonstrated in the case of 2-phenylbutane-2-^{14}C, which rearranged to a mixture of 1-phenylbutenes-1-^{14}C and 1-phenylbutenes-2-^{14}C.[4c]

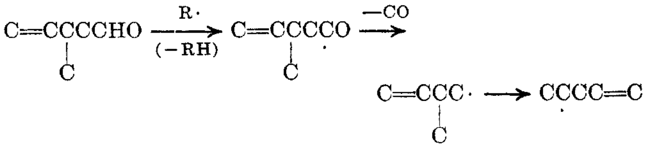
In order to obtain a better understanding of free-radical participation in the catalytic dehydrogenation reactions, it was decided to investigate the behavior of free-radical-induced reactions of hydrocarbons formed under mild conditions by the decomposition of di-*t*-butyl peroxide (DTBP).

It has been shown previously by one of us that *t*-butylbenzene refluxed in the presence of DTBP undergoes isomerization to isobutylbenzene.[5]



$$\mathrm{Ph}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{C} \xrightarrow[(-\mathrm{RH})]{\mathrm{R}\cdot} \mathrm{Ph}\overset{\mathrm{C}}{\underset{\underset{\cdot}{\mathrm{C}}}{\mathrm{C}}}\mathrm{C} \longrightarrow \mathrm{PhC}\overset{\mathrm{C}}{\underset{\cdot}{\mathrm{C}}}\mathrm{C}$$

More recently, 1,2-vinyl migration had been observed to occur during the decarbonylation of 3-methyl-4-pentenal and *trans*-3-methyl-4-hexenal.[6]



$$\mathrm{C{=}}\underset{\mathrm{C}}{\mathrm{C}}\mathrm{CCHO} \xrightarrow[(-\mathrm{RH})]{\mathrm{R}\cdot} \mathrm{C{=}}\underset{\mathrm{C}}{\mathrm{C}}\mathrm{C}\underset{\cdot}{\mathrm{C}}\mathrm{O} \xrightarrow{-\mathrm{CO}} \mathrm{C{=}}\underset{\mathrm{C}}{\mathrm{C}}\mathrm{C}\cdot \longrightarrow \mathrm{C}\underset{\cdot}{\mathrm{C}}\mathrm{CC{=}C}$$

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[1] This research was supported by the Atomic Energy Commission Contract AT-(11-1)-1096, COO-1096-19.

[2] H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965).

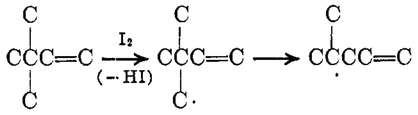
[3] (a) H. Pines, W. R. Fry, N. C. Sih, and C. T. Goetschel, *ibid.*, **31**, 4094 (1966); (b) W. F. Fry and H. Pines, *ibid.*, **33**, 602 (1968).

[4] (a) H. Pines and C. T. Goetschel, *J. Amer. Chem. Soc.*, **87**, 4207 (1965); (b) H. Pines and C. T. Goetschel, *J. Catal.*, **6**, 371 (1966); (c) H. Pines and C. T. Goetschel, *ibid.*, **6**, 380 (1966); (d) H. Pines and M. Abramovici, *J. Org. Chem.*, **34**, 70 (1969).

[5] H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.*, **82**, 2921 (1960).

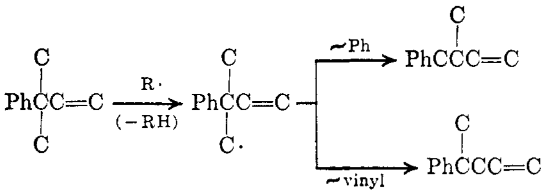
[6] L. K. Montgomery, J. Matt, and J. R. Webster, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 29N.

The present paper deals with the effect of free radicals, generated by the decomposition of DTBP, upon 3,3-dimethylbutene, 3-methyl-3-phenylbutene, and *t*-pentylbenzene. Since vinyl migration was noted in the case of iodine-initiated free-radical reactions at 500°,[7] it was of interest to determine if an analogous reaction would occur in 3,3-dimethylbutene under present conditions.



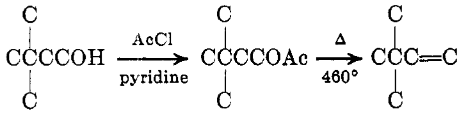
$$\mathrm{C\overset{C}{\underset{C}{C}}C{=}C \xrightarrow[(-HI)]{I_2} C\overset{C}{\underset{C\cdot}{C}}C{=}C \longrightarrow C\overset{C}{\underset{\cdot}{C}}CC{=}C}$$

3-Methyl-3-phenylbutene was elected for this study in order to determine whether DTBP would cause it to undergo a phenyl and/or a vinyl migration; and, if this occurred, to assess the relative ease of their migrations.



$$\mathrm{Ph\overset{C}{\underset{C}{C}}C{=}C \xrightarrow[(-RH)]{R\cdot} Ph\overset{C}{\underset{C\cdot}{C}}C{=}C \xrightarrow{\sim Ph} PhC\overset{C}{C}C{=}C;\quad \xrightarrow[\sim vinyl]{} PhC\overset{C}{C}C{=}C}$$

3,3-Dimethylbutene.—The title hydrocarbon was synthesized in purity greater than 99% by the sequence of reactions shown.



$$\mathrm{C\overset{C}{\underset{C}{C}}COH \xrightarrow[pyridine]{AcCl} C\overset{C}{\underset{C}{C}}COAc \xrightarrow[460^\circ]{\Delta} C\overset{C}{\underset{C}{C}}C{=}C}$$

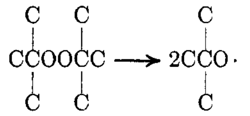
The reaction of 3,3-dimethylbutene with DTBP was carried out in a 125-cc-capacity stainless steel rotating autoclave, heated at 140–150° for 3.5 hr. The autoclave was then cooled, and both liquid and gaseous reaction products were collected and analyzed using a F & M Model 720 programmed temperature gas chromatograph. The results are given in Table I. From the data obtained it was calculated that the molar ratio of olefin reacted to free radicals ($C_3CO\cdot$) produced was 1.35.

The composition of the "monomeric" product showed that the expected 4-methyl-1-pentene which would be formed through a 1,2-vinyl migration was absent. The reaction products result from the double bond reacting with the methyl radical formed from the decomposition of the peroxides, and can be explained by eq 1–9.

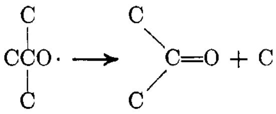
3-Methyl-3-phenylbutene was synthesized in over 99% purity according to Scheme I.

The free-radical reaction was made in a round-bottomed flask provided with a 6-in. distilling column. The flask was heated at 135–140° for 24 hr, and the products boiling below that temperature were removed. Table II summarizes the experimental results.

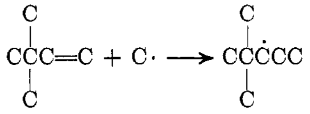
The expected products, to be formed through a 1,2-phenyl migration and/or 1,2-vinyl migration, were absent. Instead, the reaction products, as shown in



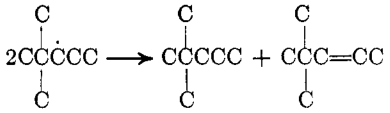
$$\mathrm{C\overset{C}{\underset{C}{C}}OO\overset{C}{\underset{C}{C}}C \longrightarrow 2C\overset{C}{\underset{C}{C}}O\cdot} \qquad (1)$$



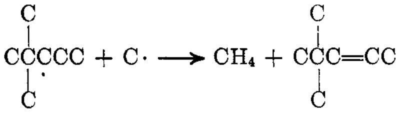
$$\mathrm{C\overset{C}{\underset{C}{C}}O\cdot \longrightarrow \substack{C\\C}{>}C{=}O + C\cdot} \qquad (2)$$



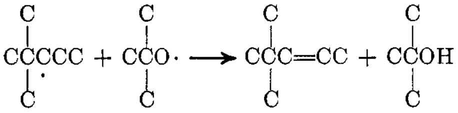
$$\mathrm{C\overset{C}{\underset{C}{C}}C{=}C + C\cdot \longrightarrow C\overset{C}{\underset{C}{C}}\dot{C}CC} \qquad (3)$$



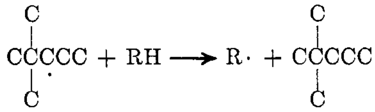
$$\mathrm{2C\overset{C}{\underset{C}{C}}\dot{C}CC \longrightarrow C\overset{C}{\underset{C}{C}}CCC + C\overset{C}{\underset{C}{C}}C{=}CC} \qquad (4)$$



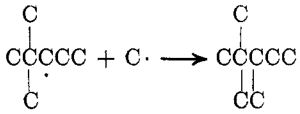
$$\mathrm{C\overset{C}{\underset{C}{C}}\underset{\cdot}{C}CC + C\cdot \longrightarrow CH_4 + C\overset{C}{\underset{C}{C}}C{=}CC} \qquad (5)$$



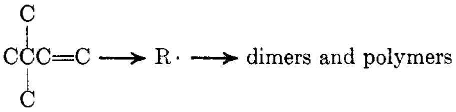
$$\mathrm{C\overset{C}{\underset{C}{C}}\underset{\cdot}{C}CC + C\overset{C}{\underset{C}{C}}O\cdot \longrightarrow C\overset{C}{\underset{C}{C}}C{=}CC + C\overset{C}{\underset{C}{C}}OH} \qquad (6)$$



$$\mathrm{C\overset{C}{\underset{C}{C}}\underset{\cdot}{C}CC + RH \longrightarrow R\cdot + C\overset{C}{\underset{C}{C}}CCC} \qquad (7)$$

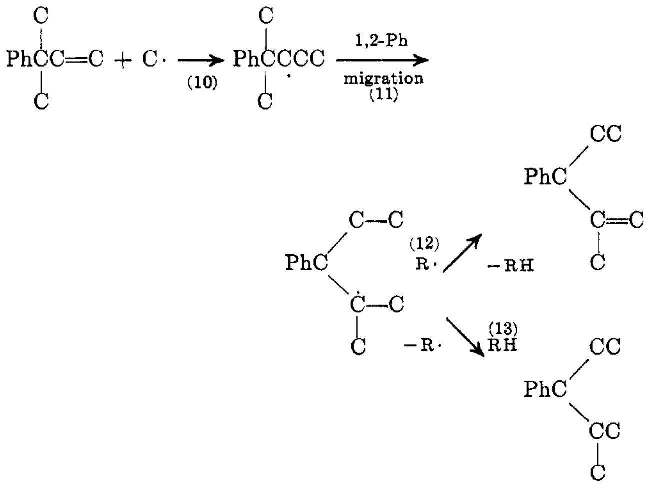


$$\mathrm{C\overset{C}{\underset{C}{C}}\underset{\cdot}{C}CC + C\cdot \longrightarrow C\overset{C}{\underset{C}{C}}\underset{C}{C}CC} \qquad (8)$$



$$\mathrm{C\overset{C}{\underset{C}{C}}C{=}C \longrightarrow R\cdot \longrightarrow dimers\ and\ polymers} \qquad (9)$$

Table II, resulted from a novel type of reaction resulting from a methyl radical addition to the olefinic double bond, followed by a 1,2-phenyl migration to form a new free radical. This free radical may then lose a hydrogen atom to form an alkenylbenzene, or it may abstract a hydrogen to produce an alkylbenzene (steps 10–13).



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[7] J. H. Raley, R. D. Mullineaux, and C. W. Bittner, *J. Amer. Chem. Soc.*, **85**, 3180 (1963).

Table I

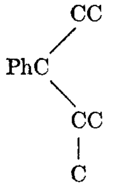
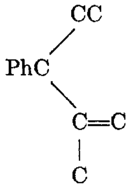
Reaction of 3,3-Dimethylhexene with Di-*t*-butyl Peroxide (DTBP)[a]

			Monomeric Product[e]			
Material	Amt charged, g (mol)	Amt reacted, mol (mol %)	Kind[e]	Mol %[b]	Mol %[c]	Yield,[d] %
3,3-Dimethylbutene	28.0 (0.33)	0.29 (88.0)	C | CCCCC | C I	58.0	11.6	16.4
DTBP	19.5 (0.133)	0.107 (80.5)				
			C | CCC=CC | C *cis* IIa	18.3	3.7	5.1
			C | CCC=CC | C *trans* IIb	8.9	1.8	2.3
			C | CCCCC | | CC III	14.4	2.9	4.2

[a] Conditions: autoclave, 125-cc capacity; temperature, 140–150°; duration, 3.5 hr. [b] Composition of "monomeric" product. [c] Based on reacted 3,3-dimethylbutene. [d] Based on reacted DTBP; assuming $2(CH_3)_3CO\cdot$ per mole of DTBP reacted. [e] Liquid product formed (based on converted olefin): monomeric 20%, di- and polymeric 80%; gas produced, 450 cc (99% methane).

Table II

Reaction of 3-Methyl-3-phenylbutene with Di-*t*-butyl Peroxide (DTBP)[a]

			Monomeric Product[e]			
Material	Amt charged, g (mol × 10^{-2})	Amt reacted, mol × 10^{-2} (mol %)	Kind[e]	Mol %[b]	Mol %[c]	Yield,[d] %
3-Methyl-3-phenylbutene	11.0 (7.52)	4.27 (56.8)		56.9	6.8	5.7
DTBP	4.4 (3.01)	2.53 (84.1)				
				43.1	5.1	4.3
			C | PhCCCC | C	Traces		

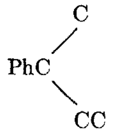
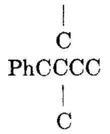
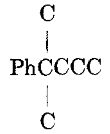
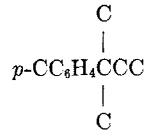
[a] Conditions: temperature, 135–140°; duration, 24 hr. [b] Composition of "monomeric" product. [c] Based on reacted 3-methyl-3-phenylbutene. [d] Based on converted DTBP, assuming $2(CH_3)_3CO\cdot$ per mole of DTBP reacted. [e] Composition of product (based on hydrocarbon reacted): monomeric 12%, di- and polymeric 88%. Gaseous hydrocarbons formed 275 cc; composition, methane 96.5%, ethane 3.3%, ethylene and propane 0.2%.

The possible driving force which causes phenyl migration, step 11, is the greater stability of the tertiary over the secondary free radical.

***t*-Pentylbenzene.**—Commercially available hydrocarbon was used and purified by means of preparative glpc to over 99% purity. The apparatus used was the same as described for 3-methyl-3-phenylbutene. The experimental conditions and results are shown in Table III. The reaction products are assumed to be formed through steps 14–22. The statistical probability of forming the primary free radical compared with the secondary free radical on the β carbon atom to the

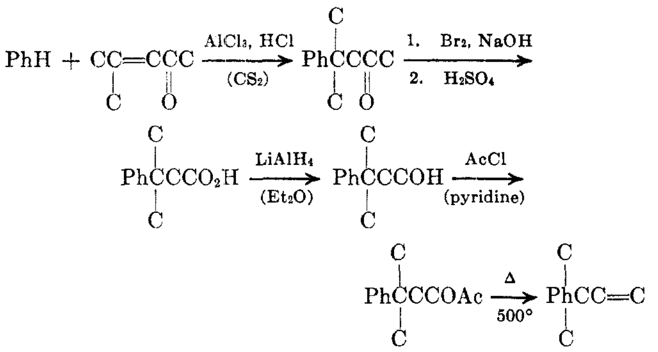
TABLE III

REACTION OF *t*-PENTYLBENZENE WITH DI-*t*-BUTYL PEROXIDE (DTBP)[a]

Material	Amt charged, g (mol × 10^{-2})	Amt reacted, mol × 10^{-2} (mol %)	Monomeric product[e] Kind[e]	 Mol %[b]	 Mol %[c]	 Yield,[d] %
t-Pentylbenzene	9.2 (6.20)	0.84 (13.5)		45.9	6.2	8.4
DTBP	3.6 (2.48)	2.26 (91.0)				
			 $\mathrm{PhC\overset{C}{\underset{C}{C}}CC}$	34.8	4.7	6.4
			 $\mathrm{Ph\overset{C}{\underset{C}{C}}CCC}$	8.9	1.2	1.8
			 $p\text{-}\mathrm{CC_6H_4\overset{C}{\underset{C}{C}}CC}$	10.4	1.4	2.0

[a] Conditions: temperature, 135–140°. [b] Composition of "monomeric" product. [c] Based on reacted *t*-pentylbenzene. [d] Based on converted DTBP, assuming $2(CH_3)_3CO\cdot$ per mole of DTBP reacted. [e] Only "monomeric" product was formed.

SCHEME I



phenyl group, steps 14 and 17, is 3:1. The ratio of the products formed in steps 19 and 16 is 45.9/34.8 = 1.32. From this it can be concluded that the propensity of the formation of a secondary free radical relative to a primary free radical is equal to 1.32 × 3 ≅ 4, which corresponds to the values reported in the literature.[8] Both of these two free radicals are most likely stabilized by the proximity of a phenyl group through the formation of a phenonium-type radical intermediate.[4]

The presence of *t*-hexylbenzene can be explained by steps 20 and 21. It is less likely that this compound could have been produced by the addition of a methyl radical to 3-methyl-3-phenylbutene, which could have been generated by the loss of hydrogen from the radicals formed in steps 17 and 20. Such an addition is usually accompanied by a 1,2-phenyl migration as demonstrated by step 11.

The aromatic ring methylation, step 22, leading to the formation of *p*-*t*-pentyltoluene, is a scarcely known reaction under the present conditions.

Conclusions

The present study has shown that the expected 1,2-vinyl migration was not detected in the reactions of 3,3-dimethylbutene and of 3-methyl-3-phenylbutene with the free radicals generated from di-*t*-butyl peroxide. The reactivity of the above hydrocarbons toward the free-radical initiator was uniquely the reaction of their olefinic double bonds toward the attacking methyl radical. The addition of the methyl radical to the olefinic bond of 3-methyl-3-phenylbutene is followed by 1,2-phenyl migration. The free-radical-induced reaction of *t*-pentylbenzene is accompanied by 1,2-phenyl migration. Methylation of the aromatic ring leading to *p*-*t*-pentyltoluene was also observed.

Experimental Section

Synthesis of Hydrocarbons. 1. 3,3-Dimethylbutene. a. 3,3-Dimethylbutyl Acetate.—3,3-Dimethyl-1-butanol[9] (102 g, 1 mol) was allowed to react with 94 g (1.2 mol) of acetyl chloride in the presence of 158 g (2 mol) of pyrdine at 0°. The acetate thus obtained amounted to 128 g (89% yield).

b. 3,3-Dimethylbutene.—The olefin was obtained in over 99% purity by passing the acetate at 460° through a reaction tube filled with quartz chips.

2. 3-Methyl-3-phenylbutene. a. 4-Methyl-4-phenyl-2-pentanone was prepared by treating 468 g (6 mol) of benzene with 294 g (3 mol) of mesityl oxide in the presence of 600 g of carbon disulfide as solvent and 480 g (3.6 mol) of anhydrous aluminum chloride, according to the procedure described previously.[10] The yield of the ketone was 68%, based on mesityl oxide; it distilled at 130–133° (10 mm), $n^{20}\mathrm{D}$ 1.5110.

b. 3-Methyl-3-phenylbutyric Acid.—The ketone obtained above, 176 g (1 mol), was allowed to react with 479 g (3 mol) of bromine in the presence of a solution of 330 g (8.25 mol) of sodium hydroxide in 2.8 l. of water. The yield of the title acid thus obtained was 75%, bp 160–162° (10 mm).

c. 3-Methyl-3-phenylbutanol was prepared by the reduction of the 3-methyl-3-phenylbutyric acid, 133 g (0.75 mol), with 36

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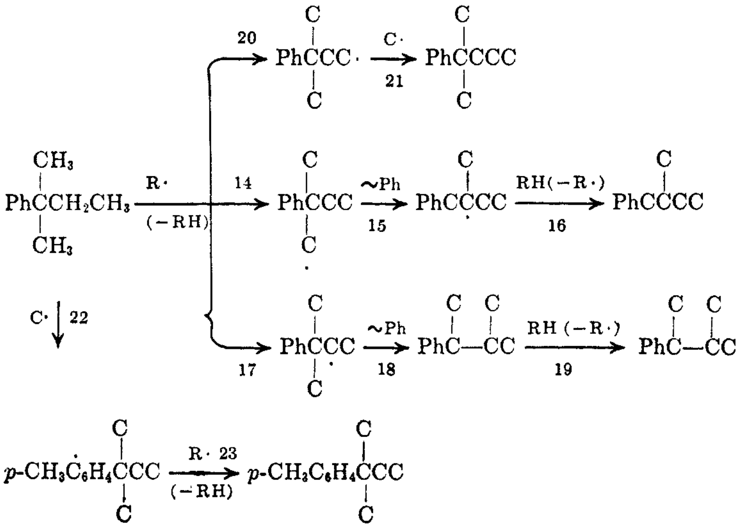
[8] H. B. Hass, E. T. McBee, and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935).

[9] V. N. Ipatieff, W. W. Thompson, and H. Pines, *J. Amer. Chem. Soc.*, **73**, 553 (1951).

[10] V. N. Ipatieff, H. Pines, and R. C. Olberg, *ibid.*, **70**, 2123 (1948).



g (0.94 mol) of lithium aluminum hydride in 800 cc of anhydrous ether, according to the described procedure.[11] The alcohol which was obtained in 90% yield distilled at 137–142° (16 mm), $n^{25}\text{D}$ 1.5207.

d. **3-Methyl-3-phenylbutyl Acetate.**—The acetylation was made at 0° by the usual procedure employing 110 g (0.67 mol) of the alcohol, 63 g (0.8 mol) of acetyl chloride, and 140 g (1.8 mol) of pyridine. The yield of the acetate was 92%, bp 131–133° (10 mm).

e. **3-Methyl-3-phenylbutene.**—The acetate was pyrolyzed at 462° over quartz chips, the conversion per pass being 25–30%. The recovered acetate was repassed through the pyrolytic tube. The title hydrocarbon thus produced was over 99% pure.

Apparatus and Procedure.—The experiments were carried out by the methods already described in the former sections.

The starting materials and the reaction products were analyzed by vapor phase chromatography using a F & M Model 720 dual column programmed temperature gas chromatograph.

A "polar" 0.25 in. × 10 m column, filled half of its length with 10% GEXF 1100 on Gas Pack W 80/100 and the other half with 10% Carbowax 20M on the same support, was used alternately with a "nonpolar" 0.25 in. × 5 m column filled with 15% silicone gum SE-30 on 60/80 WAB (White Celite).

The same silicone gum column was used for the analysis, at room temperature, of the gases evolved during the reactions.

For the separation of reaction products, a $^3/_8$ in. × 5 m preparative gas chromatography column filled with 12% silicone 550 on Chromosorb P 30/60 was used.

A 0.25 in. × 2.5 m column filled with 18% Carbowax 20M on Chromosorb P 60/80 was used to determine the amount of DTBP which was consumed during the reactions. The column was kept at 40°, the injection port at 90°, and the detector at 300°, in order to avoid the decomposition of the DTBP during the run, inside the instrument.

As a general procedure, the reaction products were tentatively identified by comparison of their retention times with known samples, using the above-mentioned analytical gas chromatographic columns.

The initial identification trial was followed by separation of the products with the use of preparative gas chromatography, and then the indices of refraction, ir spectra, and occasionally the nmr and uv spectra were taken, analyzed and compared with those of known samples.

The position of the double bond, which led to the characterization of 2-methyl-3-phenyl-1-pentene, was determined with the help of uv spectroscopy. The spectrum obtained, using a Cary 14 instrument, showed lack of conjugation between the aromatic ring and the side-chain olefinic double bond.

Selective hydrogenations using 10% Pd-C as catalyst, in a Paar microhydrogenator, were carried out to prove the olefinic character of some reaction products, and also to identify their structure by comparison of their hydrogenation products with known, readily available samples.

Registry No.—3,3-Dimethylbutene, 558-37-2; 3-methyl-3-phenylbutene, 18321-36-3; *t*-pentylbenzene, 2049-95-8; di-*t*-butyl peroxide, 110-05-4.

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[11] H. Pines and L. Schaap, *J. Amer. Chem. Soc.*, **80**, 4378 (1958).