Anal. Calcd. for $C_{22}H_{26}N_4O_4$: C, 64.37; H, 6.39; N, 13.65. Found: C, 64.43; H, 6.49; N, 13.64.

Method B.—To a solution of 20 ml. of concentrated nitric acid and 20 ml. of concentrated sulfuric acid kept at 0 to −5° was added, with stirring, 10 g. (0.03 mole) of 3-methyl-3-phenyl-2-butanone azine in 10 minutes. The mixture was stirred at 0 to −5° for 1.25 hours, then added to crushed ice and the oil was washed by decanting with water. The product crystallized upon the addition of 50 ml. of methanol. Successive recrystallizations from glacial acetic acid, xylene, and isopropyl alcohol raised the melting point to 157–158°, 1.66 g. (13%). A mixed melting point with material, m.p. 159–160°, prepared from method A melted at 158–160°.

3-(*p*-Acetamidophenyl)-3-methyl-2-butanone Azine.—A solution of 14.16 g. (0.035 mole) of 3-methyl-3-(*p*-nitrophenyl)-2-butanone azine in 150 ml. of dry tetrahydrofuran was reduced under 3.5 atmospheres of hydrogen with 1.2 g. of 10% palladium-on-charcoal. The reduction was highly exothermic and was controlled with cooling and intermittent shaking of the autoclave. The theoretical amount of hydrogen was absorbed and the reaction ceased in about 30 minutes of total shaking time. The catalyst was removed by filtration and the solution was concentrated to about 35 ml. by warming under vacuum. Upon the addition of 50 ml. of acetic anhydride crystallization occurred and the mixture was cooled, treated with an equal volume of Skellysolve A (b.p. 30–40°) and the product was removed by filtration. Recrystallization from 430 ml. of *n*-butyl alcohol gave 10 g., m.p. 276–276.5° (67%). The infrared absorption spectrum showed a medium band at 6.12 μ (azomethine), a strong band at 6.0 μ (amide carbonyl) and a medium band at 3.04 μ (imide).

Anal. Calcd. for $C_{26}H_{34}N_4O_2$: C, 71.86; H, 7.89; N, 12.89. Found: C, 72.01; H, 7.92; N, 12.74.

2-Azo-bis-3-(*p*-acetamidophenyl)-3-methylbutane.—Four hundred and thirty milligrams (1.0 mmole) of 3-methyl-3-(*p*-acetamidophenyl)-2-butanone azine was reduced over 75 mg. of prereduced Adams catalyst and 10 ml. of glacial acetic acid with hydrogen at atmospheric pressure. The reaction ceased in an hour when the theoretical amount of hydrogen was absorbed. The catalyst then was removed by filtration and the solvent removed by warming under vacuum. The remaining acetic acid was neutralized with a saturated sodium bicarbonate solution and the mixture extracted with 25 ml. of chloroform. The organic layer was then separated, dried over anhydrous magnesium sulfate, and after removal of the drying agent by filtration was stirred overnight with 1 g. of yellow mercuric oxide. After filtration and evaporation of the solvent the resultant residue was recrystallized rapidly from 1.5 ml. of *n*-butyl alcohol. The solid was dissolved in a minimum of chloroform, any insoluble material was removed by filtration and finally precipitated with Skellysolve A (b.p. 30–40°), m.p. 214.5–216.5°, 46 mg. (10.5%), ϵ_{max} 43.2, λ_{max} 365 mμ in chloroform.

Anal. Calcd. for $C_{26}H_{36}N_4O_2$: C, 71.52; H, 8.31; N, 12.83. Found: C, 71.67; H, 8.43; N, 13.16.

Acknowledgment—The authors gratefully acknowledge numerous helpful discussions with Dr. Richard G. Hiskey during the investigation.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Neophyl-type Azo Compounds[1]; Their Decomposition and Rearrangement of the Neophyl-type Free Radical

BY C. G. OVERBERGER AND HAROLD GAINER[2]

RECEIVED FEBRUARY 5, 1958

Neophyl radicals were generated by thermal decomposition in solution of azo compounds of the type $[p\text{-}RC_6H_4C(CH_3)_2\text{-}CH(CH_3)\text{-}N{=}]_2$ where R = H, CH_3O or CH_3CONH. The rates of decomposition of the three compounds did not differ from each other by more than 31%, from which it was concluded that the phenyl group did not participate appreciably in the dissociation of the carbon–nitrogen bond (the rate-determining step). The products isolated from the decomposition of the azo compound R = H indicated that at least 23% rearrangement of the neophyl radical had occurred.

Of the several known methods for the generation of neophyl free radicals in solution, none involves the formation of the radical in a primary step.[3-6] This lack of a primary process thus complicates any study of the kinetics of the reaction. When aliphatic azo compounds are thermally decomposed in solution, free radicals usually are formed by an essentially unequivocally first-order unimolecular decomposition.[7] With a free radical of the type derived from VIII there is a great likelihood of rearrangement of the phenyl group.[3-6] A question arises as to whether there is phenyl participation in the rate-determining step, the dissociation of the carbon–nitrogen bond. Substituents in the *p*-position of the phenyl ring might be expected to have some effect, small though measurable, due to resonance interaction of intermediate of type VIa and b on the rate of dissociation of the carbon–nitrogen bond if the phenyl group is participating.

The thermal decomposition in solution of four neophyl-type azo compounds were studied; two diastereoisomers of 2-azo-bis-3-methyl-3-phenylbutane, VIIIa and b, and the *p*-substituted analogs, VIIIc and d. Further, it was of interest to isolate the products of the decomposition of 2-azo-bis-3-methyl-3-phenylbutane to test whether rearrangement of the neophyl radical occurred. An unsuccessful attempt also was made to trap the unrearranged neophyl radical by decomposition of the neophyl azo compound (VIIIa in 1-dodecanethiol).

Decomposition Products. A. Results.—The products which were identified in the decomposition of 2-azo-bis-3-methyl-3-phenylbutane in diphenyl ether as solvent at 255° are indicated

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[1] This is the 23rd in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and H. Gainer, THIS JOURNAL, **80**, 4556 (1958).

[2] This paper comprises a portion of a Dissertation presented by Harold Gainer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

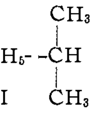
[3] W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944).

[4] S. Winstein and F. H. Seubold, Jr., *ibid.*, **69**, 2916 (1947).

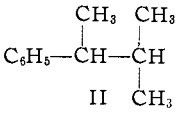
[5] W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

[6] D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

[7] J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, p. 422.


I

$\mathrm{C_6H_5{-}\underset{CH_3}{\overset{CH_3}{CH}}}$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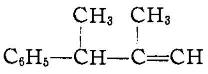
$\mathrm{C_6H_5{-}\overset{CH_3}{CH}{-}\underset{CH_3}{\overset{CH_3}{CH}}}$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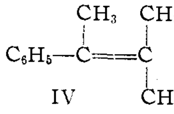
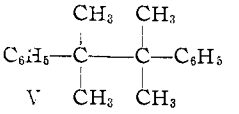
$\mathrm{C_6H_5{-}\overset{CH_3}{CH}{-}\overset{CH_3}{C}{=}CH}$


IV

$\mathrm{C_6H_5{-}\overset{CH_3}{C}{=}\underset{CH_3}{\overset{CH_3}{C}}}$


V

$\mathrm{C_6H_5{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}C_6H_5}$

These compounds were obtained by the following procedure. Solutions (0.2 *M*) of 10 to 20 g. of 2-azo-bis-3-methyl-3-phenylbutane in diphenyl ether were refluxed at 255° till the evolution of nitrogen ceased. The solution was then fractionally distilled. The first fraction, cumene (I, 6%), was identified by the boiling point, index of refraction and its diacetamido derivative.

The second fraction analyzed well for a mixture of $C_{11}H_{14}$ and $C_{11}H_{16}$ hydrocarbons (II, III, and IV) and was obtained in 23% yield. Catalytic reduction indicated that the mixture consisted of about 17% of the unsaturated $C_{11}H_{14}$ material. The reduced hydrocarbon was treated with chlorosulfonic acid and ammonia—the yield of 2-methyl-3-(*p*-sulfonamidophenyl)-butane indicated that the C_{11} mixture contained at least 69% of the rearranged product, both saturated and unsaturated. The yield of rearranged material from the decomposition of the azo compound calculated on this basis was a minimum of 16%. The ultraviolet absorption spectrum of the reduced hydrocarbon was very similar to that of an authentic sample of 2-methyl-3-phenylbutane.

The components of the C_{11}-mixture were determined in the following manner: the mixture was subjected to ozonolysis and then after decomposition of the ozonides with zinc dust and water was separated into ethyl acetate- and water-soluble fractions. From the water-soluble portion was precipitated the 2,4-dinitrophenylhydrazone of formaldehyde in 0.8% yield (based on the azo compound) which indicated the presence of the terminal methylene group in the C_{11}-mixture. The ethyl acetate layer was treated with hydrogen peroxide in order to oxidize any organic-soluble aldehydes, but no acidic product could be detected. Thus there was no evidence for the presence of any 3-methyl-3-phenyl-1-butene, representing unrearranged products in the C_{11}-mixture. From the ethyl acetate layer was then precipitated all ketonic material with 2,4-dinitrophenylhydrazine. This product consisted of the hydrazones of 3-phenyl-2-butanone, 3.6% (based on azo compound), and acetophenone, 0.1% (based on azo compound). In a separate ozonolysis experiment the semicarbazide of 3-phenyl-2-butanone also was obtained. These products were indicative of the presence of 2-methyl-3-phenyl-1-butene (III) and α,β,β-trimethylstyrene (IV) in the C_{11}-fraction. Distillation of the mother liquor from the 2,4-dinitrophenylhydrazones gave a hydrocarbon, 2-methyl-3-phenylbutane (II) (19%), which was identified by the boiling point, index of refraction and its mono- and diacetamido derivatives.

The third fraction from the distillation of the decomposition mixture, 24% of the yield by weight, had no well-defined boiling point, 110–200° (4 mm.). A small amount (0.15%) of 2,3-dimethyl-2-3-diphenylbutane (V) was obtained by crystallization from this fraction and was identified by a mixed melting point with an authentic sample. Treatment of this third fraction and the residue from the distillations with hydrochloric acid did not yield any 3-methyl-3-phenyl-2-butanone. Thus, the hydrazone derived from the original azo compound either was not present in this fraction or did not hydrolyze.

When a 0.22 *M* solution of 2-azo-bis-3-methyl-3-phenylbutane in 1-dodecanethiol was refluxed until the evolution of nitrogen ceased, distillation of the reaction mixture gave three products: cumene (I) in 24% yield, identified by elementary analysis, boiling point, index of refraction and its mono- and diacetamido derivatives; 3-methyl-3-phenyl-2-butanone azine in 5% yield, identified by mixed melting point with an authentic sample; and 0.59 g. of 1-dodecyl sulfide, identified by analysis and as the sulfone. No fraction could be found which corresponded to a $C_{11}H_{14}/C_{11}H_{16}$ mixture of hydrocarbons. When a solution of *t*-amylbenzene in 1-dodecanethiol was similarly refluxed and distilled, 66% of the starting material was recovered unchanged and no cumene was detected. This was an indication that the cumene did not arise from the decomposition of *t*-amylbenzene, the product which would result from the unrearranged radical.

B. Experimental.[8] **The Decomposition of 2-Azo-bis-3-methyl-3-phenylbutane (VIIIa) in Phenyl Ether and Isolation of Products.**—A stream of nitrogen was passed through 225 ml. of gently refluxing twice distilled diphenyl ether. The nitrogen was discontinued and 15 g. (0.047 mole) of 2-azo-bis-3-methyl-3-phenylbutane was added all at once. There was an instantaneous pale yellow coloration which faded in a few moments. The dissolution was endothermic and it therefore took several minutes before refluxing recommenced. Refluxing was continued for two and a quarter hours when about 500 ml. of nitrogen (44%) had been collected. The solution was then fractionally distilled.

The fraction boiling at 150–165° (760 mm.), was identified as cumene, 0.66 g. (6%), $n^{22}\mathrm{D}$ 1.4973 (b.p. 152–153° (760 mm.), $n^{20}\mathrm{D}$ 1.4932[9]). The second fraction, b.p. 175–185° (760 mm.), 3.1 g. (23%), was shown to be a mixture of C_{11}-hydrocarbons. The fraction obtained, b.p. 165–175° (760 mm.), 0.47 g. (4%), was probably a mixture of the two former fractions. The next major fraction was principally phenyl ether, and some higher boiling material, b.p. 110–200° (4 mm.), 3.4 g. (24%), was obtained. Except for the isolation by crystallization from this fraction of a product identified as 2,3-dimethyl-2,3-diphenylbutane, 16.4 mg. (0.2%), this fraction could not be further identified. The high boiling fractions and residue were dissolved in 10 ml. of absolute ethyl alcohol and one ml. of concentrated hydrochloric acid. After standing at room temperature for two weeks no 3-methyl-3-phenyl-2-butanone could be recovered. The total material accounted for was 56%.

***p*-Acetamido- and 2,4-Diacetamidocumene.**—These crystalline derivatives were prepared according to Ipatieff and Schmerling[10]; *p*-acetamidocumene, m.p. 104–105°, 3% (m.p. 106°)[10] and diacetamidocumene, m.p. 216–217.5°, 24% (m.p. 216°).[10]

The cumene fraction from the decomposition of 2-azo-bis-3-methyl-3-phenylbutane, b.p. 150–165° (760 mm.), $n^{22}\mathrm{D}$ 1.4973 (b.p. 152–153° (760 mm.), $n^{20}\mathrm{D}$ 1.4932[9]), was treated similarly. The diacetamido derivative was obtained, m.p. 214–216° (3.5%). A mixed melting point with an authentic sample, m.p. 216–217°, melted at 215–217°.

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(8) All melting points are uncorrected. Analyses are by Dr. K. Ritter, Basel, Switzerland, and Dr. F. Schwarzkopf, New York, N. Y.

(9) A. Klages, *Ber.*, **35**, 3506 (1902).

(10) V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **59**, 1056 (1937).

Ozonolysis of the C_{11}-Fraction.—A solution of 1.24 g. (8.5 mmoles) of the C_{11}-fraction obtained from the diphenyl ether decomposition of 2-azo-3-methyl-3-phenylbutane in 35 ml. of ethyl acetate was cooled at Dry Ice temperatures and a stream of 3% ozone was passed through the solution for 20 minutes at the rate of 0.5 liter per minute. The solution was then shaken for two hours with 1 ml. of water and 5 g. of zinc dust. After filtration the water-soluble components were extracted three times with 1-ml. portions of water. The aqueous extract was treated with 4 ml. of ethyl alcohol and 2 ml. of 0.25 *M* 2,4-dinitrophenylhydrazine reagent[11] which yielded 59 mg. (3%) of the corresponding hydrazone of formaldehyde, m.p. 160–162°; a mixed melting point with an authentic sample, m.p. 165–166°, melted at 161–165°.

The ethyl acetate layer was further shaken for two hours with 0.5 ml. of 30% hydrogen peroxide and then extracted with 1 ml. of 1 *N* sodium bicarbonate. Acidification of the bicarbonate extract yielded no acidic material. After washing the ethyl acetate layer with water the solvent was evaporated to about 6 ml. under reduced pressure and treated with 20 ml. of 0.25 *M* 2,4-dinitrophenylhydrazine reagent.[11] The precipitate was filtered and washed successively with ethyl acetate and alcohol. The filtrate was set aside for the recovery of saturated hydrocarbons. The precipitated hydrazones (0.49 g.) were fractionally crystallized from absolute alcohol and recrystallized from ethyl acetate to yield 20 mg. (0.8%) of acetophenone 2,4-dinitrophenylhydrazone, m.p. 241–241.5°. A mixed melting point with an authentic sample, m.p. 242–243°, melted at 241–241.5°. The infrared spectrum was identical with that of an authentic sample. The second product was 3-phenyl-2-butanone 2,4-dinitrophenylhydrazone, m.p. 175–176°, 390 mg. (14%). A mixed melting point with an authentic sample, m.p. 173–175°, melted at 174–175°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.36; H, 4.95; N, 17.16.

The filtrate, which was set aside for the recovery of saturated hydrocarbons, was then extracted with small amounts of Skellysolve A (b.p. 30–40°) and fractionally distilled to yield 300 mg., b.p. 183–184° (24%); the product was identified as 2-methyl-3-phenylbutane by means of its acetamido derivatives.

In a similar ozonolysis procedure 2.04 g. of the C_{11}-fraction was ozonized and treated as above except that semicarbazide was added to the evaporated ethyl acetate fraction to yield the semicarbazone of 3-phenyl-2-butanone, m.p. 170–171°, 117 mg. (3%). A mixed melting point with an authentic sample, m.p. 170–171°, melted at 170–171°.

***p*-Acetamido and 2,4-Diacetamido Derivatives of 2-Methyl-3-phenylbutane.**—These two compounds were prepared according to Ipatieff and Schmerling[12]; 2-methyl-3-(*p*-acetamidophenyl)-butane, m.p. 148–148.5°, 9% (m.p. 147–148°),[12] and 2-methyl-3-(2,4-diacetamidophenyl)-butane, m.p. 190–191°, 11% (m.p. 193°).[12]

The fraction obtained in the previous ozonolysis experiment and believed to be 2-methyl-3-phenylbutane, b.p. 183–184°, $n^{24}D$ 1.4796 (b.p. 186°, $n^{20}D$ 1.4882[12]), was converted to its acetamido derivatives: 2-methyl-3-(*p*-acetamidophenyl)-butane, m.p. 145–145.5° (11%); a mixed melting point with an authentic sample, m.p. 147–148°, melted at 146–147°, and 2-methyl-3-(2,4-diacetamidophenyl)-butane, m.p. 193–193.5° (24%); a mixed melting point with an authentic sample, m.p. 190–191°, melted at 193–194°.

α,β,β-Trimethylstyrene was prepared in 44% yield by the procedure of Broun and Voronkov[13] except that *p*-toluenesulfonic acid was used instead of oxalic acid as the dehydrating agent, b.p. 189–190.5° (760 mm.), $n^{24}D$ 1.5191 (b.p. 189.8–191.3° (760 mm.), $n^{20}D$ 1.5204[13]).

2-Methyl-3-phenylbutane was prepared in 50% yield according to the procedure of Ipatieff, Pines and Schmerling.[14] The crude reduction product was shaken with dilute potassium permanganate until no decolorization was observed in order to eliminate any unsaturated material, b.p. 187–188.5° (760 mm.), $n^{21}D$ 1.4910 (b.p. 184° (760 mm.), $n^{20}D$ 1.4882[14]). It was later found that α,β,β-trimethylstyrene would absorb the theoretical amount of hydrogen in methanol with 10% palladium-on-charcoal as catalyst. However no attempt was made to isolate the product.

Reduction of the C_{11}-Fraction.—A solution of 0.4 g. (2.7 mmoles) of the C_{11}-fraction in 2 ml. of methanol was added to 100 mg. of hydrogen treated 10% palladium-on-charcoal and 8 ml. of methanol, and this mixture was then hydrogenated at atmospheric pressure; 10.5 ml. of hydrogen was absorbed in eight minutes, or 17% of theory if the C_{11}-fraction is considered to be $C_{11}H_{14}$. In a similar experiment with 100 mg. of 10% palladium-on-charcoal, 8 ml. of cyclohexane and 1 g. of the C_{11}-fraction, 32 ml. of hydrogen was absorbed, corresponding to 19% unsaturation.

In the latter case, the catalyst was removed by filtration and the product, 2-methyl-3-phenylbutane, was distilled, b.p. 175–181° (760 mm.), 0.49 g. (49%), $n^{25}D$ 1.4908 (b.p. 184° (760 mm.), $n^{20}D$ 1.4882[14]).

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.36; H, 10.87.

2-Methyl-3-(*p*-sulfonamidophenyl)-butane.—This crystalline compound was made in 10% yield according to the method of Huntress and Autenrieth,[15] m.p. 87–88°.

Anal. Calcd. for $C_{11}H_{17}O_2NS$: C, 58.11; H, 7.54; N, 6.16. Found: C, 58.05; H, 7.43; N, 6.39.

The material believed to be 2-methyl-3-phenylbutane, obtained in the previous experiment, was similarly sulfonamidated, m.p. 86–87° (7%). A mixed melting point with an authentic sample, m.p. 87–88°, melted at 87–88°.

***p*-Sulfamylbenzoic Acid.**—A mixture of 0.12 g. (0.5 mmole) of 2-methyl-3-(*p*-sulfonamidophenyl)-butane, 1.5 ml. of concentrated sulfuric acid, 3 ml. of water and 2 g. of potassium dichromate was refluxed gently for five hours. After addition of some water and removal of the product by filtration, 7.8 mg. (8%) was obtained. The product was recrystallized from water, m.p. 283–284.5°. A mixed melting point with an authentic sample, m.p. 283–284°, prepared from a similar oxidation of the known *p*-toluenesulfonamide, melted at 283–284°.

3-Phenyl-2-butanone was made in 74% yield according to Crossley,[16] b.p. 215° (760 mm.), $n^{25}D$ 1.5082, (b.p. 105–110° (22 mm.), $n^{25}D$ 1.5117[16]).

The 2,4-dinitrophenylhydrazone of the ketone was prepared in the usual way,[11a] m.p. 173–175° (m.p. 125–126°).[17] Because of the discrepancy in the melting point, the 2,4-dinitrophenylhydrazone and the semicarbazone were analyzed.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.52; H, 4.91; N, 17.07. Found: C, 58.36; H, 4.95; N, 17.16.

The semicarbazone of the ketone was prepared in the usual way,[11] m.p. 170–171° (m.p. 171–172°).[18]

Anal. Calcd. for $C_{11}H_{15}N_3O$: C, 64.36; H, 7.37; N, 20.47. Found: C, 64.59; H, 7.42; N, 20.77.

The Decomposition of 2-Azo-bis-3-methyl-3-phenylbutane in 1-Dodecanethiol and Isolation of the Products.—The solvent, commercial 1-dodecanethiol, was distilled twice over anhydrous potassium carbonate, b.p. 106° (3 mm.), $n^{25}D$ 1.4576 (b.p. 117–118° (7 mm.), $n^{20}D$ 1.4589[19]). A solution of 10 g. (0.03 mole) of 2-azo-bis-3-methyl-3-phenylbutane in 126 g. (0.63 mole) of 1-dodecanethiol was heated to reflux at 250° within 10 minutes. The solution was refluxed one hour longer while the temperature rose from 250–265°; the vapor gave a basic reaction with litmus. The solution was then fractionally distilled. The first fraction was cumene, b.p. 149–150° (760 mm.), 1.8 g. (24%), $n^{25}D$ 1.4889 (b.p. 152–153° (760 mm.), $n^{20}D$ 1.4932[9]); 2,4-diacetamido derivative, m.p. 216.5–217.5°. A mixed melting point with an authentic sample, m.p. 216–217.5°, melted at 216–218°.

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[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955; (a) p. 316; (b) p. 85.

[12] V. N. Ipatieff and L. Schmerling, This Journal, **60**, 1476 (1938).

[13] A. S. Broun and M. G. Voronkov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1162 (1947); *C. A.*, **42**, 1591 (1948).

[14] V. N. Ipatieff, H. Pines and L. Schmerling, This Journal, **60**, 53 (1938).

[15] E. H. Huntress and J. S. Autenrieth, *ibid.*, **63**, 3446 (1941).

[16] F. S. Crossley, U. S. Patent 2,644,843 (1953).

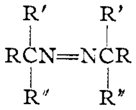
[17] E. M. Schultz, J. B. Bicking, S. Mickey and F. S. Crossley, This Journal, **75**, 1072 (1953).

[18] A. Favorskii and A. Chilingaren, *Compt. rend.*, **182**, 221 (1926).

[19] R. L. Frank, P. V. Smith, F. E. Woodward, W. B. Reynolds and P. J. Canterino, *J. Polymer Sci.*, **3**, 39 (1948).

TABLE I

THE DECOMPOSITION OF NEOPHYL AZO COMPOUNDS



$$R\overset{R'}{\underset{R''}{C}}N{=}N\overset{R'}{\underset{R''}{C}}R$$

Compd.	R	R′	R″	Concn., M	Solvent	Temp., °C.	N_2, %	k_1 × 10^3 sec.$^{-1}$	No. of expts.
VIIIa	$C_6H_5C(CH_3)_2$–	CH_3–	H–	0.1	Ph ether	254	94–101	1.33	2
b	$C_6H_5C(CH_3)_2$–	CH_3–	H–	.06	Ph ether	255	77	1.55 ± 0.05	1
c	p-$CH_3OC_6H_4C(CH_3)_2$–	CH_3–	H–	.017–0.05	Ph ether	256	70–86	1.35 ± .03	3
d	p-$CH_3CONHC_6H_4C(CH_3)_2$–	CH_3–	H–	.015	Ph ether	256	84	2.24 ± .05	1
IX	H–	H–	H–	Vapor	......	300	..	0.56[a]	..
X	CH_3–	CH_3–	H–	Vapor	......	250	..	0.48[a]	..

[a] Reference 23.

After removal of the solvent 1-dodecanethiol by distillation at 99–113° (3 mm.), a crystalline residue melting at room temperature remained. The residue was washed with methanol, in which it was mostly insoluble; the methanol washings were evaporated and the resultant residue recrystallized to give 0.47 g. (5%) of 3-methyl-3-phenyl-2-butanone azine, m.p. 79–80°. A mixed melting point with an authentic sample, m.p. 79–80°, melted at 79–80°.

The methanol-insoluble material was distilled, b.p. 200–240° (3 mm.), and the crystalline product was pressed on a porous plate. After recrystallization from acetone at Dry Ice temperatures, 0.59 g. of dodecyl sulfide was obtained, m.p. 39–40.5° (m.p. 41°).[20] It was identified by analysis and as the sulfone, m.p. 93–94° (m.p. 94.5–95.5°).[21]

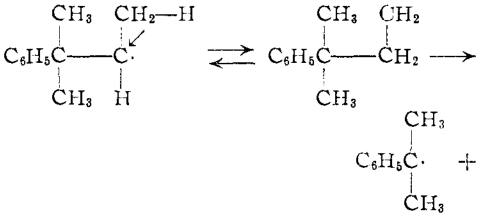
Kinetics. Procedure and Results.—The course of the decomposition of the azo compound was followed by determining the rate of evolution of nitrogen. An apparatus was fabricated to decompose 100- to 400-mg. quantities of azo compound at temperatures as high as 255°. A 25 × 70 mm. flat bottom tube with an added 19/38 joint was sealed at the top within a 45 × 110 mm. tube. The outer jacket was furnished with sealed on tubes at the bottom for the boiler flask and at the top for a condenser. A 10-mm. tube pierced the outer jacket and inner tube near the top. A small 100-mm. upright condenser was attached to this tube and in turn was led by the shortest possible length of Tygon tubing to a water-jacketed gas buret. Into the inner tube was placed a good quality unprotected magnet ground to dimensions such that the maximum horizontal area was created.

For a typical run, about 15 ml. of solvent was placed in the stoppered inner tube. A suitable liquid, chosen according to the temperature desired, was refluxed in the "boiler" so that the vapors just enveloped the inner tube. When the solvent temperature had reached equilibrium the azo compound in a round flat-bottomed boat was quickly dropped in. Stirring was effected continuously with the magnetic bar. The apparatus was not flushed with nitrogen before its use. The variation in temperature of the solution during a run at 225° was not more than 0.5° and was probably due to momentary superheating of the refluxing liquid used as the heating medium. This represented the greatest source of error in obtaining the rate constants (2%). There was negligible error in the time factor. An error also was introduced due to the reading of the buret.[22] A good straight line was obtained when plotting time *vs.* 2.3 log $V_\infty/(V_\infty - V_t)$. Actual experimental values for V were used. For a discussion of errors see reference 22. The principal data are found in Table I. The data for the decomposition of two other azo compounds are included for comparison.[23] Plots of time *vs.* 2.3 log $V_\infty/(V_\infty - V_t)$ are represented in Fig. 1.

Discussion of the Results

The products or their derivatives which were isolated from the decomposition of 2-azo-bis-3-methyl-3-phenylbutane in diphenyl ether at 255° indicated that considerable rearrangement of the phenyl group had occurred (at least 23%). Cumene and 2,3-dimethyl-2,3-diphenylbutane may have been formed from fragmentation of dimerization products involving unrearranged radicals. Cumene and its "dimer" represented 6% of the total material obtained (56%). Loss of product occurred in distilling comparatively small amounts of C_{11}-hydrocarbons in the presence of large quantities of diphenyl ether. It is entirely possible that unrearranged products were present and could not be isolated.

When the same azo compound was decomposed in the presence of a large excess of 1-dodecanethiol, none of the C_{11}-hydrocarbons could be isolated and the yield of cumene was increased to 24%. It had been hoped to trap the unrearranged neophyl radical by the facile rapid reaction of aliphatic radicals with mercaptans. No *t*-amylbenzene could be found in the reaction mixture. The large yield of cumene was very unexpected. No good explanation is forthcoming at present. However, some of the cumene may arise from cleavage of unrearranged dimer at these temperatures or by the reactions



In the presence of 1-dodecanethiol the decomposition of the azo compound also led to 5% of 3-methyl-3-phenyl-2-butanone azine. This azine probably formed as a result of hydrogen abstraction from the azo compound by mercaptyl free radical and is an interesting case.[24] The 1-dodecyl sulfide which also was isolated probably arose from decomposition of the solvent, 1-dodecanethiol.

The results of the kinetic study of the effect of the *p*-substituents on the rate of decomposition of 2-azo-bis-3-methyl-3-phenylbutane were summarized in Table I, along with the data for related compounds. All four azo compounds, VIIIa, b, c and d, decomposed according to a first-order process. The differences in rates of decomposition of diastereoisomeric azonitriles have been shown to be very small.[25] If the unsubstituted phenyl compound

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[20] F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 970 (1951).

[21] B. A. Hunter, *Iowa State Coll. J. Sci.*, **15**, 215 (1941); *C. A.*, **36**, 4474 (1942).

[22] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949).

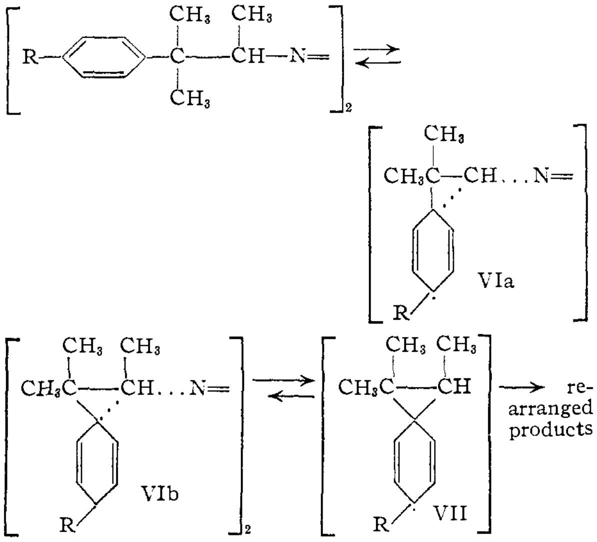
[23] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

[24] A. F. Bickel and E. C. Kooijman, *Nature*, **170**, 211 (1952).

[25] C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **73**, 2618 (1951).

VIIIb is taken as a reference, then the *p*-acetamido derivative increased the rate of decomposition by less than 31% and the methoxyl substituent decreased the rate by 13%. The latter difference is certainly close to experimental error.

In comparing the similarity of the first-order rate constants for the decomposition of the three azo compounds, it is concluded that phenyl substituents probably did not participate to any major extent in the dissociation of the carbon–nitrogen bond according to a process of the type



R = H, CH_3O or CH_3CONH

The very fact that these azo compounds require a temperature as high as 250° in solution for their decomposition indicates a mechanism of decomposition unassisted by any major aromatic participation. Gaseous azomethane and azoisopropane, as seen from Table I, require a decomposition temperature of the same order of magnitude and the first-order rate constant would be even higher (*i.e.*, in better agreement) if the decompositions were in solution (at the same temperature). Possible intermediates such as VI cannot be formed in the rate-determining step. This does not exclude the possibility of a transition state represented by VII in the rearrangement process.[5]

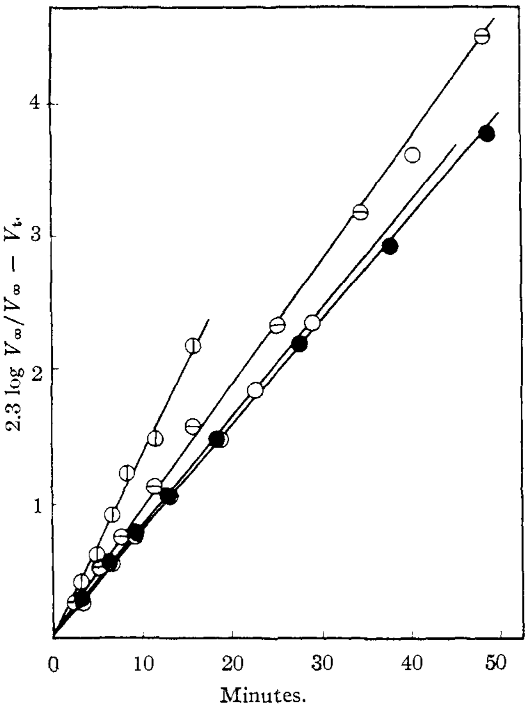
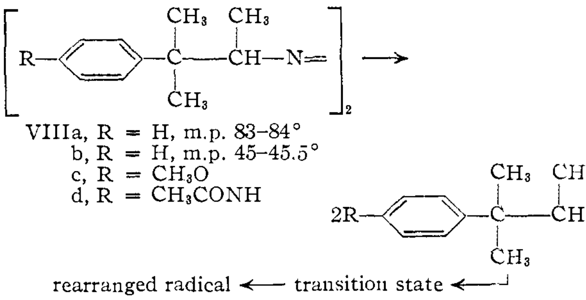


Fig. 1.—The decomposition of 2-azo-bis-3-methyl-3-phenylbutane: ●, high melting isomer at 254°; ⊖, low melting isomer at 255°; ○, 2-azo-bis-3-(*p*-methoxyphenyl)-3-methylbutane at 256°; ⦶, 2-azo-bis-3-(*p*-acetamidophenyl)-3-methylbutane at 256°.

It is tentatively concluded that in all probability distinct steps are involved in the decomposition.[26] First, the carbon–nitrogen bond is broken without participation of the phenyl or substituted phenyl group followed by rearrangement of the aryl group of the neophyl-type radical formed. The possibility that minor participation may be occurring



VIIIa, R = H, m.p. 83–84°
b, R = H, m.p. 45–45.5°
c, R = CH_3O
d, R = CH_3CONH

in the *p*-acetamide compound cannot be completely discarded; however, the evidence here favors little or no participation.

Acknowledgment.—We wish to acknowledge the many helpful discussions with Dr. Richard Hiskey and Mr. Adolph DiGiulio and the technical assistance of Mr. Stuart Ritter.

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[26] For a discussion related to this point, see F. H. Seubold, THIS JOURNAL, **75**, 2532 (1953), and J. Weinstock and S. N. Lewis, *ibid.*, **79**, 6243 (1957). These data support the idea that free radical rearrangements involving phenyl migration do not take place simultaneously with the formation of a radical capable of rearranging; see also S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).