

added 0.023 mole of phenylmagnesium bromide in 25 ml. of anhydrous ether. The addition was complete in 1.5 hours and the mixture was then refluxed for an additional hour. The mixture was decomposed with 25 ml. of 6 *N* hydrochloric acid and crushed ice. The ethereal layer was separated and the aqueous layer washed with ether. The organic layers were then combined, washed with water and finally dried over anhydrous sodium sulfate. Evaporation of the ether gave 3.1 g. of crude yellow solid. By mixing the solid with small amounts of ether 2.5 g. (60%) of 1,1,4,4-tetraphenylbutadiene was separated. Recrystallization of the diene from chloroform-methanol gave long fine white needles melting at 196–196.6° (cor.). On standing in concentrated sulfuric overnight the compound did not dissolve, and it did not react with bromine or permanganate. A characteristic bluish fluorescence was shown by the compound.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.86; H, 6.20.

The reaction of diethyl succinate with phenylmagnesium bromide, according to the method of Valeur,¹⁰ and dehydration of the resulting alcohol, by the method of Wittig and Lupin,¹¹ gave authentic 1,1,4,4-tetraphenylbutadiene-1,3, m.p. 200–201° (uncor.). This compound and the product of the Grignard reaction gave no depression of melting point on mixing, and the chemical properties and crystalline forms of the two materials were identical.

2,2-Diphenylcyclopropyldiphenylcarbinol (II).—A solution of 3.80 g. (0.0151 mole) of methyl 2,2-diphenylcyclopropanecarboxylate in 25 ml. of anhydrous ether was added slowly to a solution of 0.0453 mole of phenylmagnesium bromide in 30 ml. of anhydrous ether. The reaction was stirred for two days and heated under reflux for 30 minutes. The cautious addition of a solution of 2.50 g. of ammonium chloride in 25 ml. of water caused the formation of a pasty layer which was separated from the ethereal solution and washed with ether. The solvent was evaporated from the combined ethereal extracts giving 5.20 g. of crude II, m.p. 125–129°. Recrystallization from ether or methanol-benzene gave 3.50 g. (62%) of product, m.p. 131–132.2°.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.58; H, 6.70.

Dehydration of II with Various Reagents.—The product of all the following reactions was 1,1,4,4-tetraphenylbutadiene-1,3. This identity was confirmed by mixed melting point, comparison of crystalline form, fluorescence, and behavior in sulfuric acid with an authentic sample.

(a) **Phosphorus Tribromide.**—After shaking a mixture of 0.20 g. of II with 1 ml. of phosphorus tribromide for 30 min., water was added slowly with cooling. The resulting precipitate after washing and drying weighed 0.19 g., and melted at 195–198°. Recrystallization from methanol-chloroform gave 0.13 g. (68%) of I, m.p. 200–200.6°.

(b) **Acetyl Chloride.**—A solution of 0.20 g. of II in 1 ml. of acetyl chloride was shaken for 5 min. The mixture was added to ice and water, and the resulting precipitate was removed by filtration, washed and dried giving 0.16 g. of crude I, m.p. 197.2–198.5°. Recrystallization as in (a) gave 0.12 g. (63%) of pure I, m.p. 201.0–201.5°.

(c) **Acetyl Chloride-Pyridine.**—To a cooled solution of 2 ml. of acetyl chloride and 0.5 ml. of dry pyridine was added 0.20 g. of II and the solution allowed to stand for 15 min. The reaction mixture was worked up as in (b) to yield 0.11 g. of I, m.p. 200–201°.

(d) **Thionyl Chloride.**—A solution of 1 ml. of thionyl chloride and 0.20 g. of II was allowed to stand at room temperature for 10 min. and then worked up as in (a) to yield 0.10 g. (53%) of I, m.p. 198–201°.

(e) **Boric Anhydride.**—A mixture of 0.40 g. of boric anhydride and 0.20 g. of II was heated to 190° in a sublimation apparatus. The sublimed material was collected and returned to residue. This procedure was repeated twice and then the residue was extracted with chloroform and recrystallized to yield 0.11 g. (58%) of I, m.p. 199–200.5°.

Heating 0.30 g. of II for 4 hours at 200° yielded 50 mg. of I, m.p. 195–198°, and 0.15 g. of starting material, m.p. 132–133°.

(10) M. Valeur, *Bull. Soc. Chim.*, **29**, 683 (1903).

(11) C. Wittig and F. von Lupin, *Ber.*, **61**, 1630 (1928).

(f) **Sulfuric Acid.**—A mixture of 1 ml. of concentrated sulfuric acid and 0.10 g. of II was stirred for 15 min. The reaction mixture was worked up as in (b) to yield 0.08 g. (81%) of I, m.p. 198–199°.

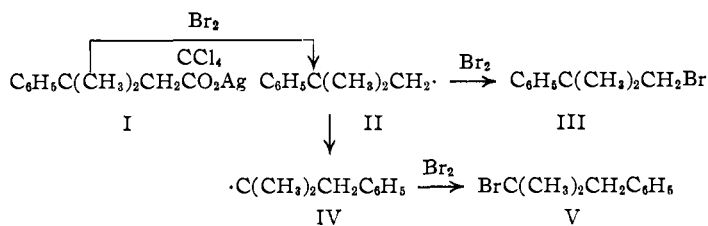
DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

The Reaction of Silver β -Phenylisovalerate with Bromine

By JAMES W. WILT¹

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As part of an investigation of the possible free radical nature of the silver salt-bromine reaction,² the reaction of silver β -phenylisovalerate (I) with bromine was studied. If this reaction were free radical in type, the β -phenylisobutyl ("neophyl") free radical (II) would be an intermediate. It has been shown previously in other types of reactions³ that the β -phenylisobutyl free radical rearranges appreciably to the β -phenyl-*t*-butyl free radical (IV). It was thought of interest to see if the reaction at hand involved this rearrangement. Such a result would imply a free radical mechanism for the silver salt-bromine reaction in this instance.⁴ No evidence, however, was found for rearrangement in this reaction since the unrearranged (bromo-*t*-butyl)-benzene (III) was the only halide isolated. To eliminate the possibility that a free radical rearrangement did occur, but that the (bromoisobutyl)-benzene (V) thereby resulting was isomerized by silver bromide⁵ to the isolated bromide III, both bromides III and V were examined and found to be stable to silver bromide under reaction conditions. While rearrangement would be indicative of a free radical process here, non-rearrangement does not necessarily rule out such a mechanism,⁶ and this work therefore precludes a decision concerning the nature of this silver salt-bromine reaction.



Experimental

Silver β -Phenylisovalerate (I).— β -Phenylisovaleric acid

- (1) Department of Chemistry, Loyola University, Chicago, Ill.
- (2) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942); J. Kleinberg, *Chem. Revs.*, **40**, 381 (1947).
- (3) W. H. Urry and M. S. Kharasch, *THIS JOURNAL*, **66**, 1438 (1944); S. Winstein and F. Seubold, *ibid.*, **69**, 2916 (1947).
- (4) Carbonium ion intermediates would be improbable here because only neopentyl bromide was obtained from the reaction of silver *t*-butylacetate and bromine; cf. W. T. Smith and R. L. Hull, *ibid.*, **72**, 3309 (1950). As these authors point out, if the neopentyl carbonium ion were a reaction intermediate, a rearranged bromide should have resulted.
- (5) W. von E. Doering and M. Farber, *ibid.*, **71**, 1514 (1949), reported an instance of rearrangement in a silver salt-bromine reaction involving the bicyclo[2.2.2]octane ring. Mechanistic hypotheses were ruled out, however, when the same rearrangement was effected by silver bromide.
- (6) For instance, the radical II may, in this case, form the halide III significantly faster than II rearranges to IV.

(b.p. 127° (3 mm.), m.p. 53–55°, 58.5 g., 0.33 mole), prepared from 4-methyl-4-phenyl-2-pentanone by hypohalite oxidation,⁷ was converted to the silver salt by standard procedures. The resulting off-white solid weighed 72.5 g. (77%).

Reaction of I with Bromine at Room Temperature.—To a vigorously stirred suspension of dried silver β -phenylisovalerate (I, 51.3 g., 0.18 mole) in dry carbon tetrachloride (400 ml., stored over phosphorus pentoxide for one week and freshly distilled) cooled to 0° in an ice-salt-bath was added dropwise a solution of bromine (28.8 g., 0.18 mole, dried over phosphorus pentoxide for three days) in further carbon tetrachloride (30 ml.). After the addition of the bromine, the mixture was stirred at room temperature for 1.5 hours, and then warmed to 65° for 15 minutes. The silver bromide was removed by filtration and the red solution treated with dilute potassium hydroxide to remove the unreacted bromine and any acid produced. The organic phase was washed well with water, dried over sodium sulfate and distilled. Removal of the solvent under a slight vacuum left an orange residue (18.7 g.), which was fractionated through a tantalum wire spiral column to give (bromo-*t*-butyl)-benzene (III), 6.1 g. (16%), b.p. 68–70° (2 mm.), n_D^{20} 1.5442, d_4^{20} 1.260; M_R 53.2, calcd. 52.6.

The viscous dark material (10 g.) remaining as distillation residue was presumed to contain ester material in that it partially dissolved in concentrated alkali to form a clear solution from which β -phenylisovaleric acid (m.p. 53–55°) was precipitated upon acidification. This residue was not investigated further. The basic extract of the original reaction mixture yielded β -phenylisovaleric acid (13.5 g., m.p. 52–54°, 42% yield) upon acidification.

Reaction of I with Bromine at Reflux Temperature.—When the reaction of silver β -phenylisovalerate (I, 36.0 g., 0.127 mole) in dry carbon tetrachloride (300 ml.) with bromine (20.3 g., 0.127 mole) in carbon tetrachloride (3.5 ml.) was carried out under reflux, only 75% of the bromine was decolorized. No further bromine was introduced after this point and the customary work-up of the reaction mixture gave (bromo-*t*-butyl)-benzene (III), 6.6 g. (34% based on reacted silver salt), b.p. 73–75° (3 mm.), n_D^{20} 1.5440, d_4^{20} 1.258; M_R 53.5, calcd. 52.6.

The thick distillation residue (4.8 g.) was presumed to be crude ester material because of its similarity in reaction to the residue obtained in the previous experiment. The alkaline extract of the original reaction mixture gave β -phenylisovaleric acid (5.0 g., 30.5%, m.p. 53–55°) upon acidification.

Identification of (Bromo-*t*-butyl)-benzene (III).—Authentic (bromo-*t*-butyl)-benzene (*vide infra*) and the reaction product were found to be identical in physical and chemical properties. The infrared spectrum of each sample⁸ exhibited an absorption peak attributed to the methylene group at 1446 cm^{-1} , some 12 cm^{-1} below the normal frequency for this group. Such a shift is commonly observed for methylene groups bearing a bromine atom.⁹ Both samples gave an immediate precipitate with alcoholic silver nitrate, but only a slow formation of silver bromide with aqueous silver nitrate. Sodium iodide in acetone developed a yellow color upon mixing with either sample and formed a precipitate overnight.¹⁰ No visible reaction oc-

curred upon mixing either sample (5 drops) with pyridine (10 drops), although upon heating the solution at 95° for one hour crystals of pyridinium bromide (colorless crystals which were soluble in water and gave an immediate precipitate with aqueous silver nitrate) were formed. No reaction was found with either sample upon stirring one hour with an aqueous suspension of silver oxide at room temperature, while the action of water alone at reflux temperature produced demonstrable bromide ion only after four hours. Both samples dissolved in concentrated sulfuric acid with the formation of a yellow color which slowly deepened to a brownish-red as hydrogen bromide was evolved.

(Bromo-*t*-butyl)-benzene (III).¹¹—Into a vigorously stirred mixture of benzene (39 g., 0.50 mole) and concentrated sulfuric acid (d. 1.84, 1.5 ml.) held at 15–20° throughout was slowly added dropwise 1-bromo-2-methylpropene (17 g., 0.148 mole, b.p. 56° (232 mm.), n_D^{20} 1.4611, d_4^{20} 1.300) prepared¹² in 79% yield by the action of alcoholic potassium hydroxide upon 1,2-dibromo-2-methylpropane.¹³ After three hours the mixture was washed well with water and the organic layer separated and combined with ethereal extracts of the aqueous phase. The material was dried over sodium sulfate and the ether and excess benzene distilled off to leave a residue which was fractionated. (Bromo-*t*-butyl)-benzene distilled as a colorless oil of pleasant odor (an irritant at length), 6.62 g. (21%), b.p. 69–70° (2 mm.); literature b.p. 103° (12 mm.),¹⁴ n_D^{20} 1.5444, d_4^{20} 1.269; M_R 53.1, calcd. 52.6. The infrared spectrum was very similar to that of the reaction material (*vide supra*).

(Bromoisobutyl)-benzene (V).—Benzylidimethylcarbinol (13.1 g., 0.087 mole, b.p. 61.5–62° (2 mm.), n_D^{20} 1.5158, d_4^{20} 0.966; M_R 46.3, calcd. 47.0), prepared from ethyl phenylacetate by the action of methylmagnesium iodide,¹⁵ was stirred at room temperature with hydrobromic acid (48%, 100 ml.) until the refractive index no longer changed. The mixture was separated and the organic phase neutralized with dilute potassium carbonate. After a wash with water, the material was dried over sodium sulfate and distilled to give (bromoisobutyl)-benzene (V) as a colorless oil of pleasant odor¹⁶ (irritant at length), 13.2 g. (71%), b.p. 57° (2 mm.), n_D^{20} 1.5389, d_4^{20} 1.261; M_R 53.0, calcd. 52.6. The infrared spectrum⁸ showed a methylene absorption peak at 1458 cm^{-1} .

(Bromoisobutyl)-benzene (V) gave a precipitate immediately with either alcoholic or aqueous silver nitrate. Formation of a precipitate with liberation of iodine occurred after 30 minutes upon treatment of the bromide with sodium iodide in acetone. The bromide dissolved in concentrated sulfuric acid to give a colorless solution which slowly became yellow with evolution of hydrogen bromide.

Attempted Isomerization of III and V.—(Bromoisobutyl)-benzene (V, 10 drops, n_D^{20} 1.5389) was stirred at 60° for 40 minutes with a suspension of silver bromide (0.2 g.) in dry carbon tetrachloride (4 ml.). The oil remaining after filtration and evaporation of the solvent had n_D^{20} 1.5381.

(Bromo-*t*-butyl)-benzene (III, 20 drops, n_D^{20} 1.5444) was similarly treated. The residual oil had n_D^{20} 1.5420. The reactions of this oil were the same as those of III.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT

(7) C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).

(8) The author is indebted to Professor W. H. Urry and Mr. R. J. Gritter of the Department of Chemistry, University of Chicago, for their aid in obtaining these spectra.

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 21.

(10) This reactivity in $\text{S}_\text{N}1$ type reactions and relative inertness in $\text{S}_\text{N}2$ type reactions, as demonstrated here for (bromo-*t*-butyl)-benzene, is also found in the structurally similar neopentyl halides. Cf. *inter alia*, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 491–492.

(11) This procedure was patterned after that given by W. T. Smith, Jr., and J. T. Sellas, *Org. Syntheses*, **32**, 90 (1952), for the preparation of neophyl chloride (chloro-*t*-butyl)-benzene).

(12) A. Butlerow, *Z. Chem.*, 524 (1870).

(13) V. Meyer, *J. prakt. Chem.*, [2] **46**, 184 (1892).

(14) G. Darzens and A. Levy, *Compt. rend.*, **189**, 1289 (1924).

(15) A. Klages, *Ber.*, **37**, 1723 (1904).

(16) E. R. Trotman, *J. Chem. Soc.*, **127**, 94 (1925), prepared this bromide but gave no constants, describing the compound as a colorless oil with a pleasant odor