gas formed on the surface of the aluminum chloride immediately. The flask was warmed to 50° at which temperature the aluminum chloride dissolved or dispersed in the liquid and a very vigorous evolution of gas took place. After a few hours at 50° no more gas was produced and suddenly the liquid crystallized to a solid mass. This was broken up in water to remove the aluminum chloride, filtered and dried. The dried product was essentially pure tetraphenylsilane (20.6 g., 0.061 mole, 97.6% yield based on equation I), m.p. 234–235°. It showed no depression of m.p. mixed with authentic tetraphenylsilane.[3] The explosion and spontaneous flammability of the gas agrees well with the properties of silane.[4]

In the presence of ether even on prolonged refluxing no such reaction occurs. This is probably due to the formation of the etherate of aluminum chloride which is ineffective as a catalyst for disproportionation making possible the successful synthesis of silanes by reduction of chlorosilanes with lithium aluminum hydride.[5]

Phenylmethylsilane and Aluminum Chloride.—Phenylmethylsilane (64 g., 0.524 mole) under the same conditions also yielded tetraphenylsilane m.p. 210–233°. Recrystallized once from alcohol the m.p. became 233–234°, yield 96% based on equation II.

In this case the gaseous products were swept on the stream of nitrogen through a small tower packed with glass helices and filled with absolute ethanol made alkaline with sodium ethoxide to convert the silanes to ethoxysilanes. Distillation of the solution from this tower yielded first a mixture of alcohol and a silicon compound boiling constantly at 77°. This was presumed to be alcohol and the alcohol–dimethyldiethoxysilane azeotrope reported to boil at 77°[6] containing 17% dimethyldiethoxysilane. This was followed by methyltriethoxysilane (48 g., 0.26 mole, 99% yield based on equation II), b.p. 143° at 743 mm.[7]

Phenylchlorosilane and Aluminum Chloride.—Phenylchlorosilane (71 g., 0.5 mole) was used under the same conditions and also gave evidence of disproportionation. Unfortunately the products caught fire while being made ready for distillation. Enough silane or chlorosilane may have remained in the liquid to cause its ignition. The fire was extinguished and the material remaining was distilled. Diphenyldichlorosilane (14 g., 0.051 mole, 51% yield) was obtained, b.p. 183–184° at 25 mm.[8]; neut. equiv. 125; calcd. neut. equiv. 126.5. An impure black crystalline residue of triphenylchlorosilane remained, m.p. 80–90°, 0.054 mole, 54% yield based on equation III; neut. equiv. 254, calcd. neut. equiv. 294, 16 g. The melting point became 90–92° after the product was recrystallized once from hexane,[9] neut. equiv. 285.

No other silicon compound was detected in the liquid products.

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[3] F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, **132**, 360 (1929), give the m.p. as 235–236°; J. S. Peake, W. H. Nebergall and Yun Ti Chen, This Journal, **74**, 1526 (1952), reported m.p. 234–235°.

[4] A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916).

[5] W. H. Nebergall, This Journal, **72**, 4702 (1950).

[6] L. H. Horsley, "Azeotropic Data," American Chemical Society, 1155 16th St., N.W., Washington, D.C., 1952, p. 63.

[7] H. J. Fletcher and M. J. Hunter, This Journal, **71**, 2922 (1949), reported b.p. 143° at 760 mm.

[8] A. C. Jenkins and G. A. Chambers, *Ind. Eng. Chem.*, **46**, 2367 (1954), give the Antoine equation constants for diphenyldichlorosilane: from this is calculated a b.p. of 181° at 25 mm.

[9] C. Curran, R. Witucki and P. A. McCusker, This Journal, **72**, 4471 (1950), give m.p. 94–95°.

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Cyclopropanes. II. A Cyclopropylcarbinyl Rearrangement

BY H. M. WALBORSKY AND F. M. HORNYAK[1]

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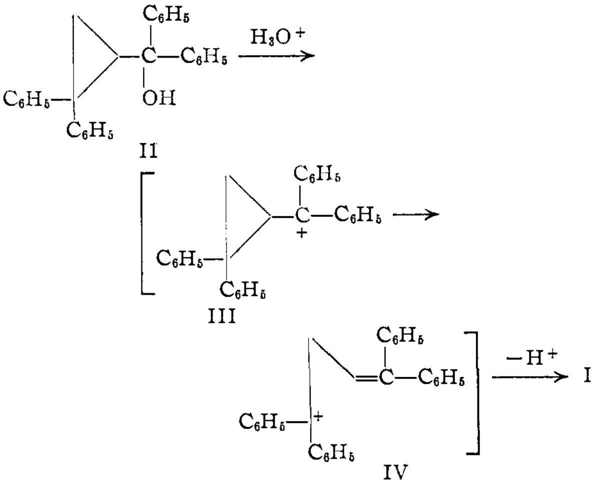
In connection with other investigations in this Laboratory concerning cyclopropane derivatives[2] an attempt was made to synthesize 1-benzoyl-2,2-diphenylcyclopropane by the reaction of 2,2-diphenylcyclopropane carbonyl chloride with phenylmagnesium bromide following the procedure described by Lyle.[3] Acid hydrolysis of the Grignard adduct did not yield the desired ketone but gave, as the principal product, 1,1,4,4-tetraphenylbutadiene-1,3 (I).

It was reasoned that 2,2-diphenylcyclopropyldiphenylcarbinol (II) was produced, which on acid hydrolysis underwent a facile rearrangement, (III–IV), which is characteristic of cyclopropylcarbinyl intermediates.[4–9]



It was of interest to confirm this transformation. The alcohol II was prepared in 62% yield by the reaction of phenylmagnesium bromide with methyl 2,2-diphenylcyclopropanecarboxylate and decomposition of the intermediate with a saturated solution of ammonium chloride. Treatment of the alcohol II with sulfuric acid, boric anhydride, thionyl chloride, acetyl chloride, acetyl chloride–pyridine and phosphorus tribromide produced, in all cases, 1,1,4,4-tetraphenylbutadiene-1,3. (The structure was proved by comparison with an authentic sample.)

The ready formation of I is explained by reference to the intermediate forms III and IV. The relief of ring strain and the formation of the resonance-stabilized diphenylmethyl-type carbonium ion are strong influences aiding ring opening. The stable nature of the extensively conjugated tetraphenylbutadiene favors its formation, by proton ejection, rather than the reaction of IV with a nucleophilic reagent.

Experimental

Attempted Preparation of 1-Benzoyl-2,2-diphenylcyclopropane.—To a boiling ethereal solution of 0.021 mole of 2,2-diphenylcyclopropanecarbonyl chloride[2] was slowly

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[1] This paper is based on a portion of the thesis submitted by F. M. Hornyak in 1955 to the Florida State University in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

[2] H. M. Walborsky and F. M. Hornyak, This Journal, **77**, 6026 (1955).

[3] R. E. Lyle and G. G. Lyle, *ibid.*, **74**, 4061 (1952).

[4] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2512 (1951).

[5] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[6] M. Doyarenka, *Ber.*, **60B**, 1536 (1927).

[7] T. A. Favorskaya and N. B. Shcherbinskaya, *Zhur. Obshchei Khim.*, **23**, 1667 (1953).

[8] P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

[9] P. Bruylants and A. Dewael, *Bull. soc. chim. Belg.*, **14**, 140 (1928).

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°.

(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°.

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

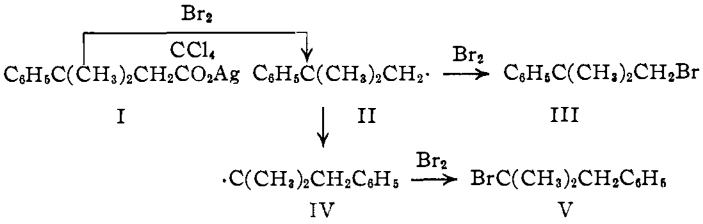
(11) G. Wittig and F. von Lupin, *Ber.*, **61**, 1630 (1928).

The Reaction of Silver β-Phenylisovalerate with Bromine

BY JAMES W. WILT[1]

RECEIVED JULY 7, 1955

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 reactions[3] 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 bromide[5] 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

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[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.