will react with *metallic tin* to form dimethyltin dibromide, but methyl iodide undergoes pyrolysis at the temperatures used with methyl chloride (300–400°) to form free iodine and no detectable amount of dimethyltin diiodide. Instead, some tin diiodide is formed which reacts with methyl iodide to give trimethyltin iodide.[3]

Similar reactions were carried out using ethyl chloride as a reactant, both with and without copper as catalyst.[1] Under conditions similar to those used for the preparation of dimethyltin dichloride, diethyltin dichloride was formed in very small quantities. Lower operating temperatures gave better results, and it was found advantageous to remove the product from the hot reaction zone as rapidly as possible, as by passing a stream of dry nitrogen over the surface of the molten tin and into the condenser. A spray-type reaction vessel was devised in order to obtain the largest possible surface of molten tin for reaction and to remove the product rapidly from the reaction zone. In this apparatus a fine stream of molten tin was sprayed into an atmosphere of ethyl chloride at 350°, and diethyltin dichloride was condensed from the excess gas. The conversion of ethyl chloride was low, due in part to the necessity for blowing two to four liters of ethyl chloride per minute past the atomizing jet of molten tin in order to maintain an adequate spray of metal; only a small part of this ethyl chloride could react in the 2.8 by 60 cm. chamber following the jet.

In the preparation of phenylchlorosilanes[6] it has been found advantageous to add dry hydrogen chloride to the chlorobenzene used. This modification was tested with ethyl chloride and molten tin, but no improvement in the reaction was noted.

The greater difficulty experienced in preparing diethyltin dichloride over that found in preparing dimethyltin dichloride indicated that higher members of the series might be even less readily obtained. Several attempts to prepare *n*-butyltin chlorides and bromides or phenyltin bromides by reactions in sealed tubes or in vessels of the type described in reference 1 were unsuccessful.

Experimental

Trimethyltin Chloride.—A stream of CH_3Cl at 15 cc./min. was passed through a mixture of 20 g. of SnO and 2 g. of Cu at 300°. $(CH_3)_3SnCl$ was formed, which upon recrystallization from benzene gave a melting point of 37.5–39.5° (37° in ref. 2).

Anal. Calcd. for C_3H_9SnCl: C, 18.08; H, 4.55; Cl, 17.80. Found: C, 17.78; H, 4.63; Cl, 18.07.

Trimethyltin Bromide.—A stream of CH_3Br at 15 cc./min. was passed through a mixture of SnO and 10% by weight of Cu. The initial reaction temperature rose to 500°, but was dropped rapidly to 300°. About 20 cc. of liquid was collected in 7 hr. The product was fractionally distilled, and $(CH_3)_3SnBr$ was obtained at 163–166° (165° in ref. 2) m.p. 26–27° (27° in ref. 2).

Anal. Calcd. for C_3H_9SnBr: C, 14.81; H, 3.70. Found: C, 15.19; H, 3.79.

Trimethyltin Iodide.—Two hundred grams of CH_3I was passed through a tube containing a mixture of SnO and 10% by weight of Cu heated to 350°, at a rate corresponding to 29 cc. of liquid per hour. About 20 cc. of liquid was collected in the receiving flask. The liquid was fractionally distilled giving mostly methyl iodide, but a small amount of liquid boiling at 160–170° (b.p. $(CH_3)_3SnI$ 170° in ref. 2). The freezing range of this fraction was −3 to −5°.

Methyltin Trichloride.—A stream of CH_3Cl at 30 cc./min. was bubbled through molten anhyd. $SnCl_2$ at 365°. About 70 g. of crystalline product was obtained in four days. The product was easily recrystallized from benzene and sublimed readily. An analytical sample was prepared by sublimation into an evacuated vial which was then sealed.

Anal. Calcd. for CH_3SnCl_3: C, 5.00; H, 1.25. Found: C, 5.37; H, 1.47.

Dimethyltin Dichloride.—A stream of CH_3Cl at 10 cc./min. was passed through a mixture of 50 g. of SnO_2 and 4 g. CuO at 300°. A condensate appeared in less than 18 hr., and at 48 hr. a considerable quantity of $(CH_3)_2SnCl_2$ containing some $SnCl_2$ was obtained.

Dimethyltin Dibromide.—A reaction vessel of the type described in ref. 1 was charged with 200 g. of tin at 395° under an atmosphere of CH_3Br. More CH_3Br was bubbled through the molten metal at a rate of 15 cc./min. until a total of 400 g. had been introduced. About 30 cc. of $(CH_3)_2SnBr_2$ was obtained, which was recrystallized from benzene and was found to melt at 75–77° (74–76° in ref. 2). The crystals sublimed at room temperature.

Anal. Calcd. for $C_2H_6SnBr_2$: C, 7.78; H, 1.94. Found: C, 7.79; H, 2.06.

Methyltin Triiodide.—Two hundred grams of CH_3I was bubbled through 200 g. of tin at 385° at a rate of 15 cc. of liquid per hour. Bright orange-red crystals of SnI_2 formed on top of the molten tin, and a suspension of yellow crystals of SnI_4 in a yellow liquid collected in the condenser. The mixture was filtered to remove the solid, and the filtrate was reduced in volume by evaporation. A crop of yellow crystals of CH_3SnI_3 was obtained. The product was recrystallized from benzene and melted at 84–85.5° (86.5° in ref. 2).

Anal. Calcd. for CH_3SnI_3: C, 2.34; H, 0.59. Found: C, 2.86; H, 0.75.

Diethyltin Dichloride.—Molten tin was sprayed in a fine stream into a reaction chamber 60 cm. × 28 mm. heated to 350°, through which preheated C_2H_5Cl was passed. After 5 hr. a yield of 2 g. of $(C_2H_5)_2SnCl_2$ was obtained. The product was recrystallized from benzene and melted at 83–84° (84° in ref. 2).

Anal. Calcd. for $C_4H_{10}SnCl_2$: C, 19.41; H, 4.07. Found: C, 19.25; H, 4.19.

MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY
CAMBRIDGE, MASS.

---

(6) E. G. Rochow and W. F. Gilliam, THIS JOURNAL, **67**, 1772 (1945).

N-Substituted 2-Nitrocarbazoles[1]

BY EUGENE SAWICKI

RECEIVED APRIL 25, 1953

In the investigation of chemical and physical properties of aromatic carcinogens and allied compounds, a series of N-substituted 2-nitrocarbazoles have been prepared. The analogous 2-nitrofluorene has been shown to be carcinogenic to rats.[2]

The physical properties and yields of the compounds are given in Table I. The chemical, physical and biological properties of these compounds are being further studied.

General Procedure.—Two ml. of 66% aqueous potassium hydroxide was added to a solution of 2.12 g. (0.01 mole) of 2-nitrocarbazole[3] in 30 ml. of acetone. To this red-brown solution was added 0.015 mole of RX. The mixture was allowed to stand for 4 hours with occasional shaking. The change in color of the mixture from red-brown to yellow

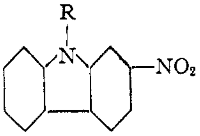
---

(1) This investigation was supported by research grant C-1308 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) H. P. Morris, C. S. Dubnik, T. B. Dunn and J. M. Johnson, *Cancer Research*, **7**, 730 (1947).

(3) P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

TABLE I



R	M.p.,[a] °C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl	166–166.5	98	12.4[b]	12.4
Ethyl	148.5–149	85	11.7[c]	11.6
Acetyl	229–230	85	11.0	10.8
Methanesulfonyl	202–204	80	9.66	9.97
C_2H_5OCO[d]	153–154.5	90	9.86	9.73
FC_2H_4OCO[e]	167–168	90	9.27	9.10
p-Methylbenzenesulfonyl	272	70	7.65	7.65
Propargyl[f]	188–189	95	11.2	10.9

[a] All melting points are uncorrected. [b] Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.03; H, 4.42. Found: C, 68.90; H, 4.65. [c] Calcd. for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00. Found: C, 70.01; H, 4.81. [d] Prepared using ethyl chlorocarbonate. [e] Prepared using β-fluoroethyl chlorocarbonate. [f] Propargyl bromide was generously supplied by General Aniline & Film Corporation.

denoted completion of the reaction. In some cases it was necessary to charge the mixture with a fresh batch of RX and alkali to complete the reaction. On completion of the reaction the yellow alkaline mixture was poured into excess water. Crystallization from heptane gave yellow needles and plates for the methyl and ethyl compounds, respectively. The remainder of the compounds were crystallized from heptane or benzene–heptane to give light yellow needles. Alcohol can also be used as a crystallizing solvent.

Acknowledgment.—The author is indebted to Dr. Francis E. Ray for his encouragement and interest in this work.

CANCER RESEARCH LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

On the Formic Acid Rearrangement of 2-Phenyl-3-butyn-2-ol

BY TATSUO TAKESHIMA

RECEIVED MARCH 14, 1953

Introduction and Discussion

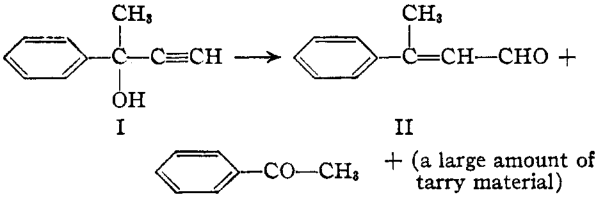
It was reported by Rupe and Giesler[1] that 2-phenyl-3-butyn-2-ol (I) rearranged to β-methylcinnamaldehyde (II) in small yields. The semicarbazone obtained by them is described to give a melting point of 201° after the several crystallizations. However, the melting point of authentic semicarbazone of II has been reported as 205.5–206.5°,[2] 206°.[3]

Hurd and Christ[4] later tried the same reaction, but found no evidence to support Rupe and Giesler's statement. They obtained simply acetophenone (semicarbazone, m.p. 201°) in addition to tarry material.

Our work was undertaken to determine the exact nature of this reaction.

The reaction product obtained by treatment of I with formic acid was fractionated to yield principally two small fractions (b.p. 80–85° (12 mm.), *ca.* 109° (4 mm.)), the residue being a relatively large amount of tarry material. The lower-boiling fraction proved to be acetophenone. The higher-boiling fraction was reactive toward aldehyde reagents and was unsaturated. It gave a semicarbazone, the melting point of which was in good agreement with that of the semicarbazone of II, a 2,4-dinitrophenylhydrazone different from that of acetophenone, and on standing in air gave β-methylcinnamic acid. In addition a small amount of another semicarbazone corresponding to a $C_{10}H_{10}O$ carbonyl compound was obtained from the same fraction and converted to the corresponding 2,4-dinitrophenylhydrazone which was different from that of II. These compounds were not investigated further owing to lack of material.

Thus, II and not the isomeric 3-phenyl-3-buten-2-one was isolated as the rearrangement product. Acetophenone formation may result from cleavage of II[5] or I; its formation is consistent with the observation made by Hurd and Christ.[4]



Acknowledgment.—I wish to express my heartfelt thanks to Messrs. K. Furuhashi and K. Muto for the elementary analyses.

Experimental

2-Phenyl-3-butyn-2-ol (I).—The carbinol was prepared essentially according to the directions of Rupe and Giesler,[1] b.p. 101–104° (12 mm.).

Formic Acid Rearrangement of I.—13.5 g. of I was refluxed with 140 g. of *ca.* 80% formic acid for *ca.* 1.5 hr. and left overnight. The reaction product was then poured onto ice and potassium carbonate, extracted with ether, the ether extracts dried with calcium chloride, concentrated, and the residue was distilled under diminished pressure to yield the following fractions: (1) b.p. 80–85° (12 mm.), *ca.* 2 g., yield *ca.* 18%; (2) b.p. *ca.* 120° (12 mm.) or *ca.* 109° (4 mm.), 1.1 g., yield *ca.* 8%. In addition, a small amount of intermediate fraction boiling at 85–*ca.* 120° (12 mm.), and, as the residue, *ca.* 8 g. of brown-red tarry material were obtained.

Fraction (1) was only weakly reactive toward Schiff reagent.

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.71; H, 6.58.

Its semicarbazone was prepared in aqueous methanol and recrystallized from methanol to yield colorless needles, m.p. 198–200° (reported 201°,[6] 198–200°,[7] 207°,[8] 206°[8] for acetophenone semicarbazone[8]). (*Anal.* C, 61.29; H, 6.45; N, 23.26.) Its 2,4-dinitrophenylhydrazone was prepared from this semicarbazone in alcoholic sulfuric acid, and washed with ethanol to give orange crystals, m.p. 238–239.5°, which did not depress the melting point (240°) of authentic acetophenone 2,4-dinitrophenylhydrazone (reported 238–240°[9]).

Fraction (2) was a yellowish oil having a greater density than water. It was reactive toward Schiff reagent (light

---

(1) H. Rupe and L. Giesler, *Helv. Chim. Acta*, **11**, 656 (1928).

(2) J. F. Arens, D. A. van Dorp, G. van Dijk, B. J. Brandt, P. J. Hubers and H. Pieters, *Rec. trav. chim.*, **67**, 973 (1948).

(3) D. A. van Dorp and J. F. Arens, *ibid.*, **67**, 459 (1948).

(4) C. D. Hurd and R. E. Christ, THIS JOURNAL, **59**, 118 (1937).

(5) *Cf.* O. Wallach, *Ann.*, **289**, 338, 340 (1896); *Ber.*, **32**, 3338 (1899); L. Claisen, *Ann.*, **180**, 19 (1876).

(6) A. Klages, *Ber.*, **37**, 2306 (1904); F. Schlotterbeck, *ibid.*, **40**, 482 (1907).

(7) W. Borsche, *ibid.*, **34**, 4301 (1901).

(8) Beilstein, "Organische Chemie," Zweites Ergänzungs-Werk, Band 7, p. 217. The melting is described to range from 199° to 210° according to the rate of heating.

(9) W. Dirscherl and H. Nahm, *Ber.*, **73B**, 448 (1940).