tion processes has revealed another way to prepare this compound and has given some additional information about the behavior of carbon disulfide and carbonyl sulfide.

Electrolytic Preparation of Trifluoromethylsulfur Pentafluoride.—An electrolytic cell of 2.5 liters volume similar to those of Simons and his co-workers[2] was constructed from a piece of four-inch iron pipe. The electrodes were of nickel and it was possible to collect gas separately from the anode and from the cathode. The cell was filled with liquid hydrogen fluoride to a level about 6 cm. below the top; then 150 ml. of carbon disulfide and 1 ml. of water were added, the latter to increase the electrical conductivity. A bath of ice and water surrounded the cell. As electrolysis took place the potential difference between electrodes was kept between six and seven volts and the current was held close to five amperes. At times it was necessary to add more water to maintain the electrical conductivity. A total of 5.6 faradays of electricity was passed.

No gaseous product was set free at the anode. Hydrogen was produced at the cathode at a rate of 0.41 mole per faraday. The gas stream from the cathode passed through a trap cooled by liquid oxygen. At the end of the run the condensed material was filtered at about −123° to obtain sulfur hexafluoride as a solid phase, and the other components as a liquid mixture which was later fractionally distilled. The volume of trifluoromethylsulfur pentafluoride obtained was 1.75 liters, at 0° (760 mm.). Approximately 4.5 liters of sulfur hexafluoride and 1 liter of carbon tetrafluoride were found. One or more other products boiling below −40° were also present. These substances were not identified but they were found to hydrolyze rapidly in 6 N NaOH.

At the end of the run carbon disulfide no longer remained as a separate liquid phase in the cell. It must have reacted to give a soluble product, for it is not very soluble in liquid hydrogen fluoride. When the liquid from the cell was allowed to evaporate in a vessel standing in the room, all but about 1 g. of the material boiled away. The interior walls of the cell were thinly coated with an unidentified dark colored material.

Reaction of Carbon Disulfide with Fluorine Highly Diluted by Nitrogen.—When a stream of carbon disulfide vapor diluted with some nitrogen is passed into an atmosphere of fluorine it burns with a blue flame. As the degree of dilution becomes larger the flame becomes larger but less easily visible. The purpose of the experiment now to be described was to carry out the reaction with the gases so highly diluted that only a small temperature rise would occur and no flame would be visible. Under these conditions it was hoped that the carbon–sulfur bonds would not break and that compounds of carbon, sulfur and fluorine would be produced. No evidence was found for the presence of such compounds among the products.

A one-liter glass flask was used as the reaction vessel. Fluorine diluted with 30 times its volume of nitrogen entered at the center of the flask, and carbon disulfide vapor diluted with 12 times its volume of nitrogen entered at the top. The products left the flask through a tube at the bottom and were passed through a trap cooled by liquid oxygen. As the reaction occurred no flame could be seen, even in a dark room. Heat was liberated but the warmest spot on the flask was not over 40°. A total of two grams of carbon disulfide was caused to react in a six-hour run with a sufficient excess of fluorine to permit one easily to detect the unreacted halogen in the effluent gases.

At the end of the run the product in the cold trap was distilled, from bulb to bulb, and gas densities along the way were found to be 99, 104, 106 g. per g.m.v (sulfur tetrafluoride has a molecular weight of 108). The vapor pressure of the last of the liquid to distil was about the same as that of sulfur tetrafluoride. Like sulfur tetrafluoride the product had a bad odor and it fumed in moist air. No attempt was made to purify this material, because a previous trial with sulfur tetrafluoride had resulted in severe corrosion of the metal packing in the fractionating column. No trifluoromethylsulfur pentafluoride was found in the product. If SF_6 and CF_4 were present, the amounts were small. The latter substance was probably one of the principal products, but nitrogen must have carried it through the cold trap without condensation.

Under the above conditions the action of fluorine upon carbon disulfide broke carbon–sulfur bonds and gave rise to products which appeared to be sulfur tetrafluoride and, probably, carbon tetrafluoride.

Fluorination of Carbonyl Sulfide by Cobalt Trifluoride.—A 7.5-g. sample of carbonyl sulfide was fluorinated by a large excess of cobalt trifluoride at about 200° using apparatus described in other publications.[1,3] Nitrogen was used as a diluent and carrier, and the product was condensed in a trap cooled by liquid oxygen. The product was warmed without appreciable loss to −110° and it was filtered at this temperature. The solid collected on the filter was found to be nearly pure sulfur hexafluoride and the liquid to be a mixture of sulfur hexafluoride and carbonyl fluoride. Since these two substances made up all or nearly all of the product, the reaction may be represented by the equation

$$8CoF_3 + COS = 8CoF_2 + COF_2 + SF_6$$

Acknowledgment.—This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

---

[2] J. H. Simons and co-workers, *Trans. Electrochem. Soc.*, **95**, 47 (1949).

[3] E. J. Barber, L. L. Burger and G. H. Cady, This Journal, **73**, 4241 (1951).

Department of Chemistry
University of Washington
Seattle 5, Washington

Decyanoation by Grignard Reagent

By Everett M. Schultz

Received June 11, 1952

In view of the smooth reaction of 4-dimethylamino-2,2-diphenylpentanenitrile with ethylmagnesium bromide to form the expected compound, 6-dimethylamino-4,4-diphenyl-2-heptanone (Methadon),[1] an observation made in this Laboratory is of interest. When ethylmagnesium bromide reacted with 4,5-bis-(dimethylamino)-2,2-diphenyl pentanenitrile (I) in xylene solution the product was not the expected aminoketone but the oxygen-free base, 3,4-bis-(dimethylamino)-1,1-diphenylbutane (II), formed from (I) by the replacement of the cyano group by hydrogen. The decyanoation of amines in which a cyano group is linked to a quaternary carbon has been reported previously[2,3] but heretofore very strong bases such as sodamide[2] or potassium hydroxide[3] have been employed to accomplish the degradation. Cleavage by the Grignard reagent in preference to addition to the cyano group was, therefore, unexpected. That the structure of the oxygen-free base corresponds to II was demonstrated by the decyanoation of I by the action of potassium hydroxide in boiling "polyethylene glycol 200"[3] to obtain a base identical with II.

The 4,5-bis-(dimethylamino)-2,2-diphenylpentanenitrile (I) used in this work was prepared from 2,2-diphenyl-4-pentenenitrile[4] which was brominated to give 4,5-dibromo-2,2-diphenylpentanenitrile (III).[5] This upon heating with ethanolic dimethylamine gave a small yield of I. The

[1] Office of the Production Board, Department of Commerce, Report No. PB-981, p. 96-A, October 1, 1945.

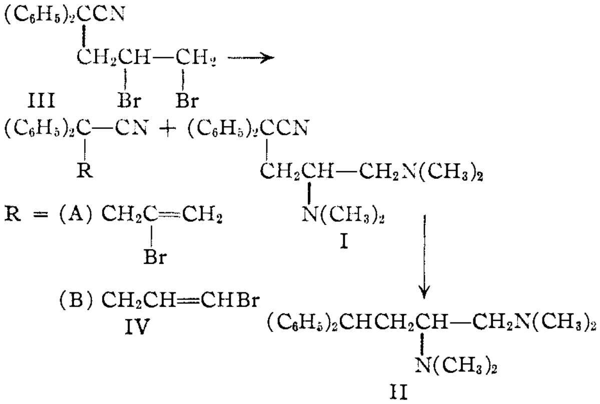
[2] M. Bockmuhl and G. Ehrhardt, *Ann.*, **561**, 71 (1949).

[3] E. L. May and E. Mosettig, *J. Org. Chem.*, **13**, 459 (1948).

[4] E. M. Schultz, C. M. Robb and J. M. Sprague, This Journal, **69**, 2454 (1947).

[5] J. Attenburrow, J. Elks, B. A. Hems and K. N. Speyer, *J. Chem. Soc.*, 512 (1949).

major portion of the dibromide suffered partial dehydrobromination to yield a liquid unsaturated monobromonitrile, IVA or IVB, but probably B since Attenburrow, *et al.*,[5] have reported that the compound to which they assign the structure A is a solid, m.p. 54–55°. No water-insoluble base and no bromide ion was formed when an alcoholic solution of the monobromide and piperidine was boiled for over two days. Upon catalytic hydrogenation, two moles of hydrogen was absorbed and one mole of hydrogen bromide was formed. This behavior indicates the saturation of a double bond by hydrogen and the hydrogenolysis of a carbon–bromine linkage. The hydrogenation product exhibited no basic properties, hence no hydrogen was absorbed by the cyano group to convert it to an amino group. Observation of a similar behavior by III and IVa was reported by Attenburrow, *et al.*,[5] after the work described here had been completed.



Experimental

3,4-Dibromo-2,2-diphenylpentanenitrile.—This compound was prepared by the method of Attenburrow, *et al.*[5] The compound exists in two forms, one melting at 63–64° and the other at 71–72°, as reported by Attenburrow, *et al.*[5]

4,5-Bis-(dimethylamino)-2,2-diphenylpentanenitrile (I).—A mixture of III (39.3 g., 0.1 mole), 33% alcoholic dimethylamine (60 g., 0.44 mole) and absolute alcohol (100 ml.) was heated in an autoclave at 70–80° for 20 hours. After evaporation of the alcohol, the semi-solid residue was stirred with 150 ml. of benzene and the dimethylamine hydrobromide (12.65 g., 0.087 mole) was removed by filtration. After evaporation of the benzene, the residue was shaken in a mixture of dilute hydrochloric acid and ether. The ether layer was removed, dried over anhydrous sodium sulfate and evaporated leaving 18.4 g. of neutral oil, IV.

The acidic water layer was made basic by the addition of 20% sodium hydroxide. The oil that separated soon solidified and was dried in a vacuum desiccator over phosphorus pentoxide. Upon crystallization from low-boiling petroleum ether, there was obtained 8 g. (25%) of white fluffy needles, m.p. 73–74°. For analysis, 0.5 g. was crystallized again from benzene to obtain a sample whose m.p. of 74.5–75.5° was unchanged by further crystallization.

Anal. Calcd. for $C_{21}H_{27}N_3$: C, 78.40; H, 8.46; N, 13.07. Found: C, 78.41; H, 8.22; N, 13.02.

Neutral Oil, IV.—The neutral oil obtained by the evaporation of the ether solution in an experiment as described above was distilled; b.p. 156–159° (1 mm.), $n^{20}D$ 1.5988.

Anal. Calcd. for $C_{17}H_{14}BrN$: C, 65.39; H, 4.52; N, 4.48. Found: C, 65.15; H, 4.31; N, 4.46.

Qualitative tests showed that halogen and nitrogen were present. The compound did not decolorize bromine in carbon tetrachloride but did slowly decolorize permanganate in acetone. Upon refluxing 15.8 g. of the monobromonitrile and 12 g. of piperidine in 100 ml. of alcohol for 64 hours, no water-insoluble amine nor bromide ion was formed and the starting material (12.5 g.) was recovered.

The analyses and chemical properties coupled with the fact that IVa is reported to be a solid[5] indicate that the neutral oil is IVb.

4,5-Bis-(dimethylamino)-2,2-diphenylpentane (II). A. **By Grignard Reaction.**—To a Grignard reagent prepared from magnesium (2.34 g., 0.096 atom) and ethyl bromide (10.46 g., 0.096 mole) in ether (50 ml.) was added a solution of I (12.8 g., 0.04 mole) in xylene (75 ml.); a gray precipitate formed at once. The water was removed from the reflux condenser and the ether was evaporated from the reaction mixture which then was heated for five hours on a steam-bath. The gray precipitate darkened and formed a thin brown insoluble sirup. After the mixture had stood overnight at 25–30°, it was poured slowly into 100 ml. of water containing 40 ml. of concentrated hydrochloric acid. The brown sirup reacted vigorously, its color was discharged and a colorless solid separated in the aqueous layer. The solid was collected by filtration and dissolved in water. The solution was extracted with ether and made basic with 20% sodium hydroxide. The oil that separated was extracted with ether and the ether solution was dried over sodium sulfate. Then 12 *N* alcoholic hydrogen chloride was added until no more precipitate formed. The white solid was collected by filtration and dried in air at 60°; m.p. 223–224° (dec.). The melting point was unchanged by crystallization from isopropyl alcohol and ethanol.

Base.—One gram of the hydrochloride was dissolved in 20 ml. of water and the solution was made basic by adding 20% sodium hydroxide. The solid base was collected by filtration and dried in vacuum over phosphorus pentoxide. After crystallization from low-boiling petroleum ether, from which it separated in large prisms, the compound melted at 59–60° and when mixed with I, the melting point was greatly depressed.

Anal. Calcd. for $C_{20}H_{28}N_2$: C, 81.04; H, 9.52; N, 9.45. Found: C, 80.58; H, 9.29; N, 9.41.

Picrate.—The picrate was prepared from an aqueous solution of the dihydrochloride by addition of aqueous picric acid solution. After drying and crystallizing from absolute alcohol (1 l./g.), it melted at 191–192°.

Anal. Calcd. for $C_{32}H_{35}N_8O_{14}$: N, 14.84. Found: N, 14.82.

B. **By Degradation of 4,5-Di-(dimethylamino)-2,2-diphenylpentanenitrile** (I).—The procedure of May and Mosettig,[3] as applied by them to the decyanoation of 4-dimethylamino-2,2-diphenylpentanenitrile, was followed.

Picrate.—From one-fourth of the crude product the picrate was prepared in alcohol and crystallized from absolute alcohol. The derivative melted at 191–192° alone or when mixed with the picrate of the Grignard product.

Base.—The remainder of the crude product was dissolved in low-boiling petroleum ether (25 ml.) and filtered, the filtrate was treated with Norite and the solvent was evaporated. The solid (3.05 g.) that formed on cooling the residue was dissolved in low-boiling petroleum ether (20 ml.) and the solution was cooled to −20° whereupon the product separated in heavy prisms, yield 2 g., m.p. 59–60°, mixed m.p. with free base from Grignard reaction 59–60°.

DEPARTMENT OF ORGANIC CHEMISTRY
MEDICAL RESEARCH DIVISION
SHARP AND DOHME
WEST POINT, PENNSYLVANIA

Exaltation of Refraction in Branched-Chain Organometallic Compounds. Tertiary Alkyl Tin Compounds[1]

BY ROBERT WEST, MARION H. WEBSTER AND GEOFFREY WILKINSON

RECEIVED JUNE 20, 1952

In the course of surveying the literature in order to establish a system of bond refractions for tin compounds, it was found that isoalkyl tin compounds had consistently higher molecular refraction than their straight-chain analogs.[2] This increase

---

[1] This work was partly supported by a grant from the Office of Naval Research.

[2] R. West and E. G. Rochow, THIS JOURNAL, **74**, 2490 (1952).