in 2780 ml. of methanol–acetone (1:99). After filtration, the filtrate was cooled to about −60° in order to precipitate the amine nitrite. Further crystallizations from methanol–acetone (1:9; 2300 ml.) were carried out until a constant melting point was reached. Each time the product was washed with cold acetone, and dried in a vacuum desiccator. The final product (19.3 g., 68% yield) melted[8] with decomposition at 125.4–127.2°. Didodecylammonium nitrite is a white solid with a very slight odor, insoluble in water, soluble in methanol, chloroform and slightly soluble in acetone. It was stored in an amber-colored bottle, since discoloration developed on exposure to ordinary light.

Anal.[9] Calcd. for $C_{24}H_{52}N_2O_2$: C, 71.9; H, 13.1; N, 7.0. Found: C, 72.4; H, 12.9; N, 6.8.

Dioctadecylammonium Nitrite.—Prepared in a similar manner and crystallized as white, glistening leaflets from chloroform, yield 83%, m.p.[8] 114.5–114.7°, discoloring at 100°. It is soluble in chloroform and methanol but insoluble in water.

Anal.[9] Calcd. for $C_{36}H_{76}N_2O_2$: C, 76.0; H, 13.5; N, 4.9. Found: C, 76.9; H, 13.6; N, 5.6.

Attempted Synthesis of Di-*n*-hexylammonium Nitrite.—Di-*n*-hexylamine[10] (50 g.), purified by vacuum fractional distillation, was added to 100 ml. of methanol. Finely divided sodium nitrite (28 g.), dissolved in 900 ml. of methanol containing 10 ml. of water, was added. After cooling to about −10°, while stirring, concentrated sulfuric acid (7.46 ml.) was added dropwise. At the end of the reaction, acetone was added and the mixture filtered. The filtrate was evaporated under reduced pressure to a volume of about 300 ml., acetone (100 ml.) added, and the mixture filtered. A saturated aqueous solution of sodium nitrite was added slowly to the filtrate until the top layer separated out as a wax-like solid. The latter was filtered off and the residue pressed between filter papers. Crystallizations were made from pentane–acetone (23:2). The purified substance (30.6 g., 49%) was white and wax-like, soluble in methanol and acetone, insoluble in petroleum ether (b. range 30–60°), and in pentane.

Technical difficulties were encountered in analyzing this substance. It melted[8] with decomposition at 134.8–135.8°.

Didodecylamine Hydrochloride.—Didodecylamine (5 g.) was dissolved in 100 ml. of isopropyl alcohol, and then 1.22 ml. of concentrated hydrochloric acid added slowly, while stirring. The solution was evaporated almost to dryness under reduced pressure, and the residue recrystallized from isopropyl alcohol. The product (82%) showed shiny, white plates, and melted[8] with decomposition at 207.8–210.8° (literature value[11] m. 203–204°).

Anal.[9] Calcd. for $C_{24}H_{52}NCl$: C, 73.9; H, 12.9; N, 3.6. Found: C, 73.7; H, 13.5; N, 3.6.

Didodecylamine Hydroiodide.—To a solution of didodecylamine (5 g.) dissolved in 100 ml. of isopropyl alcohol, 2.68 ml. of hydriodic acid (45%) was added while cooling. The reaction mixture was filtered, and the residue washed with cold methanol until it became white. The hydroiodide (84%), a shiny, white, crystalline powder, melted[8] with decomposition at 232.8–234.0°.

Anal.[9] Calcd. for $C_{24}H_{52}NI$: C, 59.9; H, 10.9; N, 2.9. Found: C, 60.3; H, 11.2; N, 3.0.

Acknowledgment.—The author wishes to express his grateful appreciation for the coöperation of Dr. G. K. Holmes, Messrs. P. A. Gelber and J. H. Bowen, Jr., of the Aeronautical Materials Laboratory, and to the Department of the Navy for permission to publish this material.

AERONAUTICAL MATERIALS LABORATORY
NAVAL AIR MATERIAL CENTER
PHILADELPHIA 12, PENNA.
RECEIVED JANUARY 23, 1951

---

[8] Bath was heated at a rate of about 10° per minute, and sealed melting point tube introduced into the bath when the temperature reached about 10° below that of the expected melting point. Final melting point was corrected.

[9] The author acknowledges the help of Dr. N. L. Drake, Chemistry Department, University of Maryland, for arranging for the analyses on the compounds reported herein.

[10] Obtained from Sharples Chemicals, Incorporated.

[11] Wibaut, Heiermann and Wegtendonk, *Rec. trav. chim.*, **57**, 456 (1938).

The Action of Sodium Hydride on Certain Aryl Bromides[1]

BY G. E. PHILBROOK, H. F. GOBER[2] AND C. L. HENRY[2]

The chemistry of sodium hydride has been reviewed by Hansley and Carlisle.[3] A re-examination of the literature to December, 1950, failed to disclose any report on the action of sodium hydride on aryl halides. Sodium hydride generally acts as a condensing agent on carbonyl compounds[3] and fails to show marked reducing properties. This paper reports the action of sodium hydride on bromobenzene, *o*-bromotoluene, *m*-bromotoluene, *p*-bromotoluene, 2-bromo-1,4-dimethylbenzene, 4-bromo-1,3-dimethylbenzene and 4-bromo-N,N-dimethylaniline.

The sodium hydride used was the 98% technical grade (Elchem. 704) from E. I. du Pont de Nemours and Co., Inc. The *m*-bromotoluene and 4-bromo-N,N-dimethylaniline were prepared by standard methods. The bromoxylenes were prepared by direct bromination of *p*-and *m*-xylene using iron as a carrier. The xylenes were purified by the method of Mair, *et al.*[4] The bromoxylenes were purified by repeated fractional crystallization from the melt. Physical constants: 2-bromo-1,4-dimethylbenzene, m.p. 9.0–10.0° (cor.), b.p. 205° (cor.) (760 mm.), $n^{20}D$ 1.5481, d^{20}_{20} 1.35026; 4-bromo-1,3-dimethylbenzene, m.p. −17.0 to −16.0° (cor.), b.p. 206° (cor.) (760 mm.), $n^{20}D$ 1.5481, d^{20}_{20} 1.34430.

The reactions were studied at the boiling points of the compounds employed except for bromobenzene which was studied at 180° and 1710 mm. pressure. The apparatus was constructed with ground joints sealed with sealing wax. Blank runs demonstrated the absence of moisture in the apparatus and reagents and the absence of leaks. The reactions were run in a 500-ml. three-necked flask equipped with a mercury-sealed mechanical stirrer and a short helix-packed column. The column prevented spray carry-over. The volatile products were led through a water condenser, a liquid receiver, an ice-cooled trap and a gasometer in that order. One gram mole of halide and hydride were used. The reaction period was 20 hours in all runs.

The hydrogen was collected over water and its volume measured directly. The residue in the flask was filtered with the exclusion of moisture and the solid residue was extracted with ether. The ether extract was combined with the liquid products and filtrate for analysis by fractional distillation in a low hold-up 20-plate column. The solid residue was analyzed for sodium hydride by titration with water and measurement of the volume of hydrogen evolved. The solution resulting from this determination was analyzed for bromide ion by the Volhard method.

These reactions give low conversion yields and low yields of hydrocarbons. For *m*-bromotoluene, *p*-bromotoluene, 2-bromo-1,4-dimethylbenzene and 4-bromo-N,N-dimethylaniline the conversions found were 19.5, 26.8, 6.5 and 32.2% respectively. The hydrocarbon produced in these cases accounts for approximately 50% of the reacting halide. In these cases the sodium bromide found accounts for 90% or more of the bromine in the reacting halide. The tars from these four compounds were found by sodium fusion to be practically free of bromine. *o*-Bromotoluene and 4-bromo-1,3-dimethylbenzene gave conversion yields of 5.8 and 5.9% and very low yields of

---

[1] This work was supported by a contract (N7-onr-351) with the Office of Naval Research.

[2] This paper is taken in part from theses submitted by H. F. Gober and C. L. Henry in partial fulfillment of the requirements for the degree of Master of Science.

[3] V. L. Hansley and P. J. Carlisle, *Chem. Eng. News*, Aug. 10, 1945, p. 1332.

[4] B. J. Mair, *et al.*, *J. Research Natl. Bur. Standards*, **37**, 229 (1946), RP1744.

hydrocarbon. A little less than 50% of the bromine in the reacting halide appears as sodium bromide. The tars were found by sodium fusion to contain large quantities of bromine. Bromobenzene falls between these two groups of compounds with respect to bromine distribution in the products. Conversion and hydrocarbon yields for bromobenzene were low.

Hydrogen was evolved slowly over periods of 10 to 15 hours in all the reactions studied. Blank runs made at room temperature with halide and sodium hydride gave no hydrogen evolution. Blank runs made with Nujol and sodium hydride at 180° evolved 10 to 15 ml. of hydrogen over a period of one hour after which hydrogen evolution ceased.

A careful examination failed to give any evidence for the formation of di- or polyphenyl derivatives in these reactions.

Attempts were made to force these reactions by grinding the sodium hydride during the course of the reactions. Seven 15-mm. glass balls and a Hershberg stirrer were employed for this purpose. The grinding action was sufficiently severe to score the reaction flask but the effects were uncertain since they were very close to the limits of experimental error in the analysis of the products.

Rates of stirring from 0 to 7000 r.p.m. in unbaffled flasks had no measurable effect on these reactions.

Attempts were made to employ Nujol, N,N-diethylaniline and eicosane as high boiling solvents for these reactions. These substances were found to be inert to sodium hydride at 200°. When employed as solvents, however, large quantities of tar resulted and the only identifiable products found in the reaction mixture were unreacted halide and residual solvent. No reaction occurred below 150°.

The results obtained in this study are apparently consistent with the general mechanism proposed by Morton for the action of sodium alkyls on chlorobenzene. Part of the hydrogen which should be produced if Morton's[5] mechanism applies is probably absorbed by the polymeric materials produced as tar.

Acknowledgments.—The authors wish to thank the E. I. du Pont de Nemours and Co., Inc., who furnished the sodium hydride used in this investigation, and the Office of Naval Research for the financial support which made the work possible.

[5] A. A. Morton, This Journal, **64**, 2242 (1942); *Chem. Revs.*, **35**, 1 (1944).

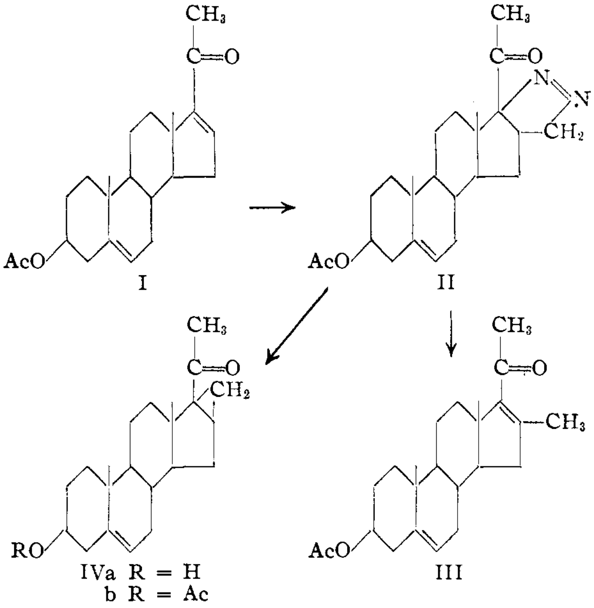
Chemistry Department
University of Georgia
Athens, Georgia

Received December 26, 1950

Steroids. XVII.[1] A Steroidal Cyclopropyl Ketone

By A. Sandoval, G. Rosenkranz and Carl Djerassi

During the thermal decomposition of the pyrazoline (II) arising from the action of diazomethane upon $\Delta^{5,16}$-pregnadien-3β-ol-20-one 3-acetate (I), Wettstein[2] observed the formation of two substances. The principal product was an α,β-unsaturated ketone, provisionally formulated as the 16-methyl-Δ^{16}-20-ketone III, but in addition there was isolated in poor, though unspecified yield an isomer which exhibited no absorption in the ultraviolet and by exclusion was tentatively assumed to be the cyclopropyl ketone IV. In connection with other experiments, we had occasion to carry out the large scale decomposition of this pyrazoline II and to accumulate enough of the by-product to establish its constitution.



The *a priori* assumption that the by-product of the pyrazoline decomposition is the cyclopropyl ketone IV is not unjustified, since *substituted* pyrazolines yield cyclopropanes in addition to the ethylene.[3] Wettstein[2] characterized the substance only by its m.p. (202.5–205°) and analysis which was consistent with the expression IVb. In our hands, the substance had m.p. 195–197°, $[\alpha]^{20}\text{D}$ +33[4] and could be saponified to the free alcohol IVa. The latter was stable to boiling methanolic potassium hydroxide or hydrochloric acid and could be reacetylated to the original product IVb, thus indicating the absence of a 20-ketopregnane structure with an enolizable hydrogen atom at C-17. In contrast to the 16-methyl-Δ^{16}-20-ketone III it was impossible to prepare a ketonic derivative and even forcing conditions[5] failed which had served successfully for the formation of the semicarbazone of the unsaturated ketone I. Similarly, the substance appeared in the non-ketonic fraction during a Girard separation. Nevertheless, the presence of a carbonyl group could be demonstrated in IV by both chemical and spectroscopic means. The infrared spectrum[6] (carbon disulfide) of the alcohol IVa exhibited a band at 1688 cm.^{-1} and

---

[1] Paper XVI, St. Kaufmann, This Journal, **73**, 1779 (1951).

[2] A. Wettstein, *Helv. Chim. Acta*, **27**, 1803 (1944).

[3] For a recent review, see L. I. Smith, *Record of Chem. Progress*, **11**, 65 (1950).

[4] The 16-methyl-Δ^{16}-20-ketone III has $[\alpha]^{20}\text{D}$ −105.7°.

[5] R. Fischer, G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **33**, 1335 (1950).

[6] We are grateful to Dr. K. Dobriner and Mrs. P. Humphries, Sloan-Kettering Institute for Cancer Research, New York, for these measurements.