After hydrolysis of the resulting white solid, and measurement of the hydrogen evolved, gallium was precipitated from the solution as the 8-hydroxyquinolate. The 0.2250 g. of product yielded 233.4 cc. (10.42 mmoles.) of hydrogen and contained 0.178 g. (2.56 mmoles.) of gallium. These data correspond to an atomic ratio of 4.07:1.00, a purity of 93% and a yield of 76%. The low yield was probably due in large part to incomplete washing of the lithium chloride, and the low purity to inadequate removal of ether from the product. The fact that the compound turns gray; *i. e.*, begins to decompose in a comparatively short time even at room temperature, necessitated the defects in procedure. Complete pyrolysis of the compound leads to the formation of metallic gallium and, presumably, lithium hydride and hydrogen.

Acknowledgment.—It gives us pleasure to acknowledge the coöperation of Dr. Kenneth Wilzbach, who carried out many of the reactions of lithium aluminum hydride. We desire also to acknowledge the financial support and continued interest of the Naval Research Laboratory in this investigation.

Summary

1. The preparation and some of the properties of the new compounds, lithium aluminum hydride, $LiAlH_4$, and of lithium gallium hydride, $LiGaH_4$, have been described. Included is a new, simple procedure for preparing an ether solution of aluminum hydride, $(AlH_3)_x$, as well as an insoluble, probably polymerized, ether-containing solid form of the latter.

2. The interaction of lithium aluminum hydride with halides or alkyls of elements of the second, third, fourth and fifth groups of the periodic system constitutes a convenient procedure for preparing hydrogen compounds of these elements in pure form and in good yield. As a specific example, a new method for preparing diborane has been described in detail.

3. Aluminum hydride behaves in many respects like lithium aluminum hydride, except for the greater solubility of the latter in ether and the consequent greater convenience of its reactions. As an example of the usefulness of aluminum hydride, the development of a new method for preparing aluminum borohydride is described.

4. Attention is called to the usefulness of lithium aluminum hydride in the reduction of organic compounds. The smoothness of such reactions, as well as their specificity in certain cases, has been emphasized.

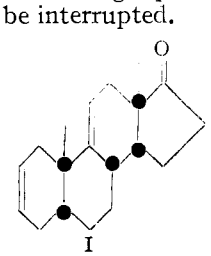
CHICAGO, ILLINOIS RECEIVED DECEMBER 19, 1946

[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

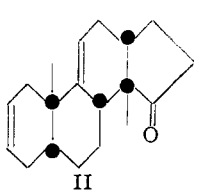
The Synthesis of Condensed Ring Compounds. XVIII.[1] Dimethylsteradienones

BY ADAM M. GADDIS AND LEWIS W. BUTZ

The mixture of hydrocarbons containing 10-methyl-1-vinyl-1,7?-naphthitadiene which was described in the preceding paper[1] and an excess of 1-methylcyclopenten-5-one were allowed to react at 200°. The preparation and analysis of a semicarbazone showed that the products contained a ketone, $C_{19}H_{26}O$. Since the same mixture of hydrocarbons with *p*-benzoquinone at 50° gave a D-homosteroid,[1] it is probable that the new compound is a dimethylsteradienone, I, II, or an isomer with other positions of the C=C bonds. The configurations shown are the most likely for the reasons discussed before.[1] Not enough material has been prepared for a proof of structure. The work is being reported at this stage because it has to be interrupted.



I



II

(1) For preceding paper see THIS JOURNAL, **69**, 1165 (1947). This work was supported by an allotment from the Special Research Fund (Bankhead–Jones Act of June 29, 1935). Not subject to copyright.

Experimental

1-Methylcyclopenten-5-one.—1-Methylcyclopentene, b. p. 75–79°, was prepared from cyclopentanone. To a mixture of 8.2 g. of 1-methylcyclopentene, 10.2 g. of ethyl nitrite, and 8 ml. of acetic acid, cooled in an ice–salt-bath, 9.8 ml. of concentrated hydrochloric acid was added slowly with shaking. Filtration through a cooled apparatus and washing the crystals three times with cold methanol gave 7.5 g. of nearly white 1-methylcyclopentene nitrosochloride, m. p. 82–85°. A mixture of 9.5 g. of nitrosochloride, 22 ml. of dry acetone, and 5.5 ml. of pyridine dried over barium hydroxide was warmed to about 30° to completely dissolve the nitrosochloride. The solution was heated cautiously on a steam-bath, as the beginning of reaction may be violent. Separation of the solid pyridine oxime hydrochloride,[2] $C_5H_5N \cdot C_6H_9NO \cdot HCl$, occurred in a few minutes. Cooling, filtration, and washing with small volumes of acetone gave 8.5 g., pure enough for conversion to 1-methylcyclopenten-5-one. For analysis, some of the salt was washed with ether, dissolved in methanol, and reprecipitated with ether; m. p. 156–159° cor. (dec.).

Anal.[3] Calcd. for $C_{11}H_{15}N_2OCl$: C, 58.3; H, 6.7; N, 12.4; Cl, 15.6. Found: C, 58.5; H, 6.7; N, 12.3; Cl, 15.4. Careful concentration of the mother liquor from the salt gave 1.76 g. of 1-methylcyclopenten-5-one oxime, m. p. 125–127°. About 1 g. more of the oxime was obtained by removing all of the solvent and subliming the residue. Yield of oxime and salt (calcd. as oxime) was 88.2%. This is essentially the procedure used by Wallach[4] for the decomposition of limonene nitrosochloride. We

(2) By Dr. Eleanore W. J. Butz.

(3) By Arlington Laboratories, Fairfax, Virginia.

(4) Wallach, *Ann.*, **414**, 257 (1918).

usually hydrolyzed the oxime and the salt separately. Thus steam distillation of 29.2 g. of the salt in 370 ml. of 10% sulfuric acid gave by collection of about a liter and half of distillate, salting out with sodium sulfate, extracting four times with ether, treating with solid sodium bicarbonate, washing three times with saturated sodium chloride solution, drying and removing the ether, 6.68 g. (54%) of 1-methylcyclopenten-5-one, b. p. 158–161° (760 mm.), $n^{20}D$ 1.4771.

Ketones, $C_{19}H_{26}O$ (Dimethylsteradienones?).—Hydrocarbon, containing 10% of 10-methyl-1-vinyl-1,7?-naphthitadiene, b. p. 61–63° (0.1 mm.), $n^{20}D$ 1.5270, 6.24 g., 3.61 g. (10 moles) of 1-methylcyclopenten-5-one and a few crystals of hydroquinone were sealed in a Pyrex tube in an atmosphere of nitrogen and held at 200° for forty-eight hours. The viscous product was transferred with ether and distilled. Fifty per cent. of the methylcyclopentenone, 70% of the hydrocarbon, and 3 g. of nonvolatile product were recovered. This last was dissolved in 40 ml. of ethanol and refluxed for six hours with 3 g. of semicarbazide hydrochloride and 4.5 g. of sodium acetate in 15 ml. of water and 50 ml. of ethanol. Removal of solvents and keeping in vacuum overnight with calcium chloride and soda-lime gave a residue which was thoroughly extracted with ether. Concentration of the solution gave 121 mg. of semicarbazone, m. p. 230–254° (dec.). The ether was removed from the mother liquor and the residue was taken up in ethanol. Concentration of this solution gave 72 mg., m. p. 242–251°. The semicarbazone appears to form very slowly from some products of the triene-methylcyclopentenone reaction for removal of the ethanol, which gave 1.7 g. of material which did not crystallize, and refluxing the residue for six hours with 1.7 g. of semicarbazide hydrochloride, 6 ml. of dry pyridine and 54 ml. of methanol gave 181 mg. more of semicarbazone, m. p. 254–257° (dec.). Filtration, continued refluxing of the filtrate for eleven hours more, and concentration gave still more semicarbazone (80 mg.); total 454 mg.; 39%, calculated on reactive triene (according to reaction with *p*-benzoquinone); 13%, calculated on the hydrocarbon consumed. A portion of the semicarbazone was recrystallized from ethanol for analysis, m. p. 254.6–256.6°, cor.

Anal.[5] Calcd. for $C_{20}H_{29}N_3O$: C, 73.35; H, 8.9; N, 12.80. Found: C, 73.7; H, 8.55; N, 12.7.

In another experiment, material which did not react with semicarbazide hydrochloride and sodium acetate under the conditions specified, gave some carbonyl derivative with Girard's T reagent. The yield of ketones $C_{19}H_{26}O$ is probably considerably higher than is indicated by the weight of semicarbazones. Distillation of the ketones in high vacuum gave no crystalline material of the composition $C_{19}H_{28}O$.

Hydrolysis of the Semicarbazones.—The semicarbazones employed melted from 239–254°. They had been precipitated from ether, recrystallized from ethanol, and then washed with ethanol and ether. In one experiment, 69.9 mg. was dissolved in 2.89 ml. of warm acetic acid, 0.3 g. of anhydrous oxalic acid was added, and the mixture was refluxed for four hours. Addition of 130 ml. of water, extraction with ether, washing, drying, evaporation of the ether, and purification of the residue gave 53.9 mg. which was sublimed in vacuum. A number of sublimed fractions were taken, two of which appeared crystalline, but these weighed only 2 mg. each. Three other fractions, 11.6 mg., collected at 1.5–3.0 × 10^{-5} mm. and bath temperature 44–55°, 11.8 mg., 1.5–5.0 × 10^{-5} mm. and 55–69°, and 8.7 mg., 0.2–25 × 10^{-5} mm. and 67–151° did not crystallize.

In another experiment, 200.8 mg. of semicarbazones by a similar procedure gave 149 mg. of sublimed ketones. Crystalline material was obtained from some of these sublimates by the use of ethanol, but the amounts separated were small.

It was not found possible to convert this quantity of material to a known steroid.

Summary

1. A mixture of semicarbazones, $C_{20}H_{29}N_3O$, has been obtained from the reaction products of *cis*?-10-methyl-1-vinyl-1,7?-naphthitadiene and 1-methylcyclopenten-5-one. This material is isomeric with and may contain the semicarbazone of 10,13-dimethyl-2,9(11)-steradien-17-one (2,4b-dimethyl-1,2,3,4b,5,8,8a,9,10,10a-decahydrocyclopenta[a]phenanthren-3'-one).

2. Hydrolysis of the semicarbazones and fractional distillation of the products did not give a crystalline compound.

3. A salt, $CH_3C_5H_5NOH \cdot C_5H_5N \cdot HCl$, has been prepared from pyridine and the nitrosochloride of 1-methylcyclopentene.

BELTSVILLE, MARYLAND RECEIVED SEPTEMBER 13, 1946

(5) By Dr. T. S. Ma, University of Chicago.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PYRIDIUM CORPORATION]

Tuberculostatic Compounds. I. Ethers of 2-Hydroxy-5-aminopyridine

BY HARRIS L. FRIEDMAN, LEO D. BRAITBERG, ALEXANDER V. TOLSTOOUHOV AND EDMOND T. TISZA

Ethers of 2-hydroxy-5-aminopyridine have been found in these laboratories to have an *in vitro* tuberculostatic activity.[1] In an effort to select the most active and the least toxic compound of this type a series of ethers was prepared.[2] This paper describes the preparation of these compounds.

The nitro ethers were prepared from 2-chloro-5-nitropyridine by interaction with the appropriate sodium alcoholate or phenolate. The nitro ethers were then reduced with iron and acetic acid in aqueous methanol and the corresponding amino ethers were isolated as the dihydrochlorides. Details of the procedures are included in the experimental part and the results are given in Table I. Most of the compounds are new. A few have been reported but the physical constants are not given in the literature. Our physical constants of known compounds are included for comparative purposes. It was not possible to prepare the ethers from *t*-butyl alcohol and dipropylcarbinol because the nitro compounds exploded during vacuum distillation. The products from *s*-butyl alcohol and diethylcarbinol were successfully isolated although mild explosions were often encountered during vacuum distillation of the nitro ethers.

(1) W. H. Feinstone, *Proc. Soc. Exp. Biol. Med.*, **63**, 153 (1946).

(2) W. H. Feinstone, H. L. Friedman, M. Rothlauf, A. Kelly, R. Williams, *J. Pharm. Exp. Therapy*, **89**, 153 (1947).