TABLE II

QUATERNARY SALTS

Salt from	Empirical formula	M.p., °C.	Analyses, % Ionic halogen Calcd.	Analyses, % Ionic halogen Found
1-Methyl-1,2,3,4-tetrahydroquinoline and:				
p-*t*-Butylphenacyl bromide	$C_{22}H_{28}BrNO$	175	19.86	20.01, 19.72
p-Iodophenacyl bromide	$C_{18}H_{19}BrINO$	176	16.92	16.96, 17.01
2-Methyl-1,2,3,4-tetrahydroisoquinoline and:				
Phenacyl bromide	$C_{18}H_{20}BrNO$	102	23.12	22.98
p-Fluorophenacyl bromide	$C_{18}H_{19}BrFNO$	116	21.13	21.22, 21.21
2,3-Dimethyl-1,2,3,4-tetrahydroisoquinoline and:				
m-Nitrophenacyl iodide	$C_{19}H_{21}IN_2O_3$	173	28.06	27.78, 28.32

quaternary iodide salts in 95% ethanol at room temperature and 40 pounds per square inch gage pressure in the presence of platinum oxide catalyst until the theoretical amount of hydrogen had been absorbed (about 12 hours), distilling off excess solvent, liberating the tertiary amine from the salt by treatment with alkali and purifying in the usual way. (Crude 2,3-dimethyl-1,2,3,4-tetrahydroisoquinoline hydriodide was obtained as a dark brown, hygroscopic solid. After repeated recrystallization by dissolving in hot absolute ethanol, cooling in an ice-bath and adding isopropyl ether, followed by careful drying in a vacuum desiccator over fresh calcium hydride, the white crystals melted at 108–109°. *Anal.* Calcd. for $C_{11}H_{16}IN$: C, 45.68; H, 5.58. Found: C, 45.54; H, 5.56.)

Samples of the compounds listed have been sent to the National Cancer Institute or the Midwest Research Institute for screening against sarcomas in mice, and the results obtained are to be published elsewhere. Preliminary data do not indicate that as a group they possess a high level of biological activity.

We wish to express our appreciation to Dr. M. J. Shear and Dr. J. L. Hartwell of the National Cancer Institute for their interest in this project and for obtaining carbon and hydrogen analyses on several of the compounds, to Dr. L. H. Goodson and Dr. W. M. Hoehn of the Midwest Research Institute for their encouragement and coöperation, to Miss Betty Gay Walden and Miss Marguerite Close for carrying out Volhard halogen determinations on the quaternary salts, to Miss Mary Ellen Tubb for carrying out the hydrogenations and to Dr. George P. Mueller of the University of Tennessee Chemistry Department for making available the hydrogenation apparatus used.

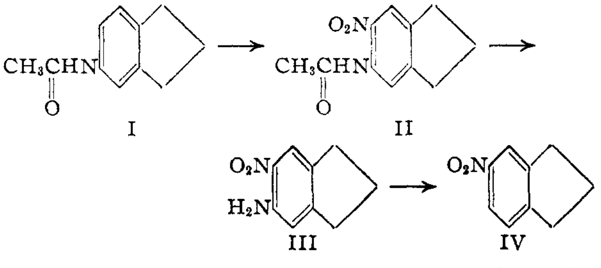
CARSON–NEWMAN COLLEGE
JEFFERSON CITY, TENNESSEE

5,6-Disubstituted Hydrindenes

BY RODERICK A. BARNES AND GEOFFREY R. BUCKWALTER

RECEIVED APRIL 3, 1952

We have found that when 5-acetylaminohydrindene (I) was nitrated at 0° a single mononitration product (II) was isolated in 93% yield.



The position of the nitro group was established by diazotizing III and treating the diazonium salt with ethanol; hypophosphorous acid was not effective for replacing the diazonium group by a hydrogen atom. The 5-nitrohydrindene (IV) obtained by this procedure melted at 39.5–40° alone or when mixed with an authentic sample.[1]

Our 5-amino-6-nitrohydrindene III is the same substance which has been described by Borsche and Bodenstein as 5-amino-4-nitrohydrindene.[2] This mistake has been previously noted by McLeish and Campbell[3] who indirectly related the aminonitrohydrindene of Borsche and Bodenstein to 5-bromo-6-aminohydrindene.[4] Previously the only real evidence that any of these substances actually had the two substituents in the 5,6-position was the work on the electron diffraction[5] and dipole moment[6] of 5,6-dibromohydrindene.

Three new 5,6-disubstituted hydrindenes have been prepared from III by conventional procedures.

Experimental[7]

5-Acetylamino-6-nitrohydrindene (II).—5-Nitrohydrindene was prepared according to a modification[8] of the procedure of Lindner and Bruhin[1] and reduced with hydrogen in the presence of Raney nickel. The 5-aminohydrindene (m.p. 37–38°) obtained by this method was then acetylated with acetic anhydride.

A mixture of concentrated nitric acid (16 ml.) was cooled to 0° and added dropwise during 30 minutes to a well-stirred cold (0°) solution of 5-acetylaminohydrindene (17.5 g.) in glacial acetic acid (50 ml.) and acetic anhydride (50 ml.). The temperature of the reaction mixture rose rapidly 23° shortly after the addition was complete. The solution was cooled and stirred until the temperature fell to 0° and then for an additional hour at this temperature. When the reaction mixture was poured into ice and water (400 ml.) a yellow solid separated. After recrystallization from eth-

---

[1] J. Lindner and J. Bruhin, *Ber.*, **60**, 435 (1927), first prepared pure samples of 4- and 5-nitrohydrindene and definitely established their structures.

[2] W. Borsche and A. Bodenstein, *Ber.*, **59**, 1909 (1926), nitrated 5-acetylhydrindene and separated one compound in pure form from the mixture of nitration products. The oxime of this isomer was subjected to the Beckmann rearrangement to yield the supposed 5-acetylamino-4-nitrohydrindene.

[3] N. McLeish and N. Campbell, *J. Chem. Soc.*, 1103 (1937).

[4] Borsche and Bodenstein, ref. 2, first prepared this substance by brominating 5-acetylaminohydrindene. An attempt was made to prove the position of the bromine by deamination to yield a liquid bromohydrindene. This was stated to be 5-bromohydrindene but no comparisons of solid derivatives or physical constants other than boiling point were made.

[5] A. Kossiakoff and H. D. Springall, THIS JOURNAL, **63**, 2223 (1941).

[6] N. V. Sidgewick and H. D. Springall, *J. Chem. Soc.*, 1532 (1936).

[7] Melting points were determined using the Kofler hot-stage melting point apparatus. Analyses were by W. Manser, Zurich, Switzerland.

[8] Private communication from Dr. V. J. Webers.

anol there was obtained 20.5 g. (93%) of II which melted at 108°.[9]

Anal. Calcd. for $C_{11}H_{12}O_3N_2$: C, 60.0; H, 5.50. Found: C, 59.97; H, 5.42.

5-Amino-6-nitrohydrindene (III).—A mixture of 5-acetylamino-6-nitrohydrindene (11 g.) and 20% hydrochloric acid was refluxed for two hours. The cooled solution was stirred with activated charcoal (5 g.), filtered and made alkaline with sodium carbonate solution. The orange precipitate was filtered, dried and recrystallized from ligroin. There was obtained 7.8 g. (87%) of III which melted at 129–130°.[9]

Anal. Calcd. for $C_9H_{10}O_2N_2$: C, 60.6; H, 5.6; N, 15.7. Found: C, 60.5; H, 5.6; N, 15.8.

Deamination of III.—A solution of 5-amino-6-nitrohydrindene (1.0 g.) in ethanol (5 ml.) and concentrated sulfuric acid (0.7 ml.) was cooled to 10° and sodium nitrite (0.5 g.) dissolved in a minimum of water was added slowly with stirring. The mixture was then warmed on the steam-bath until the evolution of nitrogen was complete. The reaction mixture was diluted with water and the product extracted with ether. The residue remaining after evaporation of the ether was sublimed twice. The light yellow crystals which were obtained melted at 39.5–40°. A mixture of this substance and authentic 5-nitrohydrindene also melted at 39.5–40°. A mixture with authentic 4-nitrohydrindene liquefied at room temperature.

5-Chloro-6-nitrohydrindene.—5-Amino-6-nitrohydrindene (17.8 g.) was dissolved in concentrated hydrochloric acid (100 ml.) by heating to 90°. The solution was rapidly cooled to 0° by addition of chopped ice and then a cold solution of sodium nitrite (7.0 g.) was added during 15 minutes to the well-stirred suspension. A cold solution of cuprous chloride (prepared from 31.2 g. of copper sulfate) in concentrated hydrochloric acid (34 ml.) was added keeping the temperature at 0–5°. The reaction mixture was allowed to warm to room temperature and finally was heated at 60° for one hour. The product was separated by ether extraction. There was obtained 17 g. of crude product. A by-product (2 g., m.p. 193–194°) remained undissolved when this substance was treated with warm methanol. Recrystallization from methanol yielded 13 g. (66%) pure 5-chloro-6-nitrohydrindene which melted at 40.5–41.0°.

Anal. Calcd. for $C_9H_8O_2NCl$: C, 54.69; H, 4.08. Found: C, 54.30; H, 3.81.

5-Acetylamino-6-chlorohydrindene.—A mixture of iron powder (17 g.), acetic acid (10 ml.) and water (36 ml.) was stirred and heated on a water-bath until there was no further evolution of hydrogen. Ethanol (20 ml.) was added, followed by 5-nitro-6-chlorohydrindene (15.9 g.) in portions during 10 minutes. The mixture was heated and stirred at reflux temperature for four hours, then filtered and the filtrate diluted with water. The crude amine was extracted with ether and separated from any starting material by extracting with dilute hydrochloric acid. The amine (12.2 g., 90%) obtained by addition of 20% sodium hydroxide solution solidified in an ice-bath but melted again at room temperature. It reacted with acetic anhydride to yield an acetyl derivative which melted at 138–139° after recrystallization from ligroin.

Anal. Calcd. for $C_{11}H_{12}ONCl$: C, 62.99; H, 5.77. Found: C, 62.85; H, 5.85.

5-Iodo-6-chlorohydrindene.—The liquid 5-amino-6-chlorohydrindene (11.4 g.) obtained in the previous experiment was diazotized using concentrated sulfuric acid (20 ml.), water (61 ml.) and sodium nitrite (4.8 g.). Potassium iodide (11.3 g.) was added to the cold diazonium salt and the solution slowly warmed to 45–50°. The product was removed by ether extraction and obtained as a brown oil (11 g., 58%) which crystallized on cooling in ice. This product could be purified by recrystallization from aqueous methanol, m.p. 46–47°.

Anal. Calcd. for C_9H_8ClI: C, 38.82; H, 2.90. Found: C, 38.57; H, 3.01.

(9) W. Borsche and A. Bodenstein, ref. 2, report the melting point of their "5-acetylamino-4-nitrohydrindene" to be 107° and that of its hydrolysis product, "5-amino-4-nitrohydrindene" to be 128–129°.

SCHOOL OF CHEMISTRY
RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY

The Reaction of Organosilanes with Sodium–Potassium Alloy

BY ROBERT A. BENKESER AND DONALD J. FOSTER

RECEIVED FEBRUARY 25, 1952

In a previous publication[1] from this Laboratory it was suggested that the formation of tetraphenylsilane from the reactions of diphenylsilane and phenylsilane with sodium–potassium alloy proceeded by a different mechanism than that of triphenylsilane with alloy. This is now confirmed since it has been shown that both diphenylsilane and phenylsilane when treated with sodium–potassium alloy form tetraphenylsilane *without* the subsequent addition of bromobenzene. On the other hand tetraphenylsilane is formed in only negligible yields from triphenylsilane and alloy, *unless* bromobenzene is added to the reaction mixture. In the latter case, triphenylsilylpotassium is the reactive intermediate which couples with bromobenzene to form tetraphenylsilane.[1]

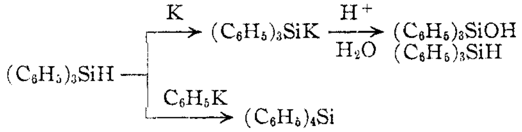
$$(C_6H_5)_3SiH \xrightarrow[\text{ether}]{Na/K} (C_6H_5)_3SiK + KH \xrightarrow{C_6H_5Br} (C_6H_5)_4Si + KBr$$

The formation of triphenylsilylpotassium can be further confirmed by coupling it with trimethylchlorosilane to form 1,1,1-trimethyl-2,2,2-triphenyldisilane.[2]

One can account for the formation of tetraphenylsilane in the case of diphenylsilane and phenylsilane by assuming the intermediate formation of phenylsodium or phenylpotassium. These compounds probably arise from a cleavage of the phenyl groups by the alkali metal. On this basis diphenylsilane reacts as

$$(1)\quad (C_6H_5)_2SiH_2 + 2K \longrightarrow C_6H_5K + C_6H_5SiKH_2$$

$$(2)\quad (C_6H_5)_2SiH_2 + C_6H_5K \longrightarrow$$



$$\begin{tikzcd} & (C_6H_5)_3SiK \arrow[r, "H^+", "H_2O"'] & (C_6H_5)_3SiOH \quad (C_6H_5)_3SiH \\ (C_6H_5)_3SiH \arrow[ur, "K"] \arrow[dr, "C_6H_5K"'] & & \\ & (C_6H_5)_4Si & \end{tikzcd}$$

The presence of triphenylsilane and triphenylsilanol in these reaction products is interesting since it clearly supports the previous observation that when three phenyl groups are attached to the silane molecule, triphenylsilylpotassium forms, and relatively few phenyl groups are lost by cleavage. When only one or two phenyl groups are attached, however, they are readily cleaved by the alkali metal. The low yields of triphenylsilane and triphenylsilanol can be attributed to the greater speed of the reaction of phenylpotassium with triphenylsilane as compared to the reaction of triphenylsilane with potassium.

The infusible products obtained in these reactions appear to be largely SiO_2, silicic acid or partially dehydrated silicic acid, with or without some Si–C and Si–H compound copolymerized with it. Such materials could arise easily if the $C_6H_5SiKH_2$ postulated in Equation 1 above were stripped of another phenyl group by alkali metal and the product then hydrolyzed.

---

[1] R. A. Benkeser, H. Landesman and D. J. Foster, THIS JOURNAL, **74**, 648 (1952).

[2] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).