Martin and Crouthamel[19] give $\Delta F^0 = 39,870$ cal./ mole for cerium oxalate and $\Delta F^0 = 42,430$ cal./ mole for neodymium oxalate. The combination of data gives $\Delta H^0 = 15,770$ cal./mole and $\Delta S^0 = -80.84$ e.u. for the solubility reaction of cerium oxalate, for neodymium oxalate $\Delta H^0 = 16,460$ cal./mole and $\Delta S^0 = -87.09$ e.u.

By the utilization of data presented by Latimer,[16,20] the entropies and entropies of formation of the solid compounds of cerium and neodymium have been calculated; these values permitted the evaluation of the entropies of the two ions. The results are given in Table V. From that information it is possible to calculate for

$$Ce(s) = Ce^{+++} + 3e^-, \quad E^0 = 2.335 \quad (11)$$

and for

$$Nd(s) = Nd^{+++} + 3e^-, \quad E^0 = 2.246 \quad (12)$$
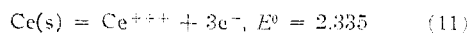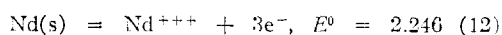
Yost, Russell and Garner[21] estimate the E^0 values for cerium and neodymium to be 2.3 and 2.2 volts, respectively. The calculated standard electrode potentials are based on an empirical calculation of the entropies of the oxalates, these values would be subject to revision when more accurate determinations of the entropies are made. However, the $T\Delta S^0$ contribution to the standard free energy of the two rare earths ions is only about 4% of the value of the free energy so that it is possible that any revision would not change the values of E^0 appreciably.

It might be added that the precipitation reactions

(20) W. M. Latimer, ibid., 73, 1480 (1951).

(21) D. M. Yost, H. Russell, and C. S. Garner, "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, 1947.

TABLE V

The values of ΔF^0 and ΔH^0 are in kcal./mole; ΔS^0 and S^0 are in e.u.

Substance	ΔF^0	ΔH^0	ΔS^0	S^0
Ce	....	....	.....	13.8
Ne	....	....	.....	13.9
CeCl₃	−235.16	−252.84	−59.3	34.5
NdCl₃	−227.93	−245.61	−59.3	34.6
CeCl₃·7H₂O	−644.26	−758.46	−383.0	101
NdCl₃·6H₂O	−583.31	−683.58	−336.3	92
Ce₂(C₂O₄)₃·9H₂O	−1349.08	−1550.93	−677	155
Nd₂(C₂O₄)₃·10H₂O	−1396.05	−1661.62	−723	165
Ce⁺⁺⁺	−161.54	−167.43	−19.8	−52.8
Nd⁺⁺⁺	−155.40	−163.27	−26.4	−59.3

in the calorimeter were very fast, clear-cut calorimetric processes. Shortly after the maximum temperature was reached, the temperature decreased for a few minutes before it settled to an equilibrium rating as determined previously from many calibrating runs. Hence, whether complete equilibrium had set in or not, the process was thermally complete as far as detection by the calorimetric apparatus was concerned. The slight cooling effect was attributed to the decrease of supersaturation and to orientation of the molecules in the crystals to an equilibrium state.

NOTES

Derivatives of Tetrahydroquinoline and Tetrahydroisoquinoline[1]

BY CARL TABB BAHNER, WILLIAM KENNETH EASLEY AND EMOGENE STEPHEN

A previous paper[2] from this Laboratory has described the preparation of salts of substituted piperidines and pyrrolidines for use in the study of cancer chemotherapy. Derivatives of tetrahydroquinoline and tetrahydroisoquinoline have been prepared for comparison with the quaternary salts of quinoline and isoquinoline. 1,2,3,4-Tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline, purchased from commercial sources, were used to prepare the tertiary amines listed in Table I by the method of Goode.[3] These pale yellow compounds

were insoluble in water, but soluble in alcohol and ether.

The quaternary salts listed in Table II were prepared by reaction of the corresponding N-methyl tertiary amines with the appropriate phenacyl halides. They were crystalline solids, only slightly soluble in water.

TABLE I

1-(SUBSTITUTED PHENACYL)-1,2,3,4-TETRAHYDROQUINOLINES

			Analyses, %			
	Empirical	M.p.,	Calcd.		Found	
Substituent	formula	°C.	C	H	C	H
p-Methyl-	C₁₈H₁₉NO	90	81.52	7.16	81.20	7.12
p-Methoxy-	C₁₈H₁₉NO₂	114	76.84	6.81	76.80	6.98
p-Fluoro-	C₁₇H₁₆FNO	94	75.74	5.94	75.77	6.17
p-Chloro-	C₁₇H₁₆ClNO	103	71.45	5.64	71.15	6.02
p-Bromo-	C₁₇H₁₆BrNO	124	61.83	4.83	61.69	4.95
p-Iodo-	C₁₇H₁₆INO	160	53.92	4.23	54.06	4.26
m-Nitro-	C₁₇H₁₆N₂O₄	136ᵃ	68.90	5.44	68.78	5.51

ᵃ Cf. Kunckell, Ber., 30, 576 (1897).

2-Methyl-1,2,3,4-tetrahydroisoquinoline was obtained from a commercial source. 1-Methyl-1,2,3,4-tetrahydroquinoline and 2,3-dimethyl-1,2,3,4-tetrahydroisoquinoline were both prepared by hydrogenation of the corresponding

TABLE II

QUATERNARY SALTS

Salt from	Empirical formula	M.p., °C.	Analyses, % Ionic halogen	
			Calcd.	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.
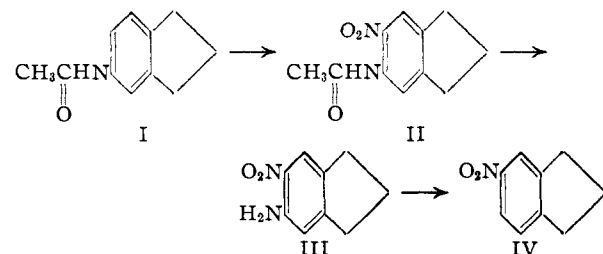
CARSON–NEWMAN COLLEGE
JEFFERSON CITY, TENNESSEE

5,6-Disubstituted Hydrindenes

BY RODERICK A. BARNES AND GEOFFREY R. BUCKWALTER

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. Weber.