ated. With the system maintained continuously under vacuum (approximately 1 mm.), the temperature was increased slowly in relatively small increments to 396° over a period of 585 hours during which 40 diffraction patterns were obtained. No change in the diffraction pattern was observed until after 25 hours of operation at 215°. The change, however, did not represent decomposition of CrO_3 to Cr_2O_3; instead, a number of reflections distinct from those attributable to chromium in both of these structures was noted. Moreover, these unidentified lines persisted over a period of about 375 hours while the temperature was being increased from 215 to 396°. Operations at the latter temperature for 19 hours finally yielded a diffraction pattern showing only the presence of Cr_2O_3. That the unknown material observed in the temperature range of 215 to 396° bears a close resemblance to the phase I (Cr_3O_8) reported by Fankuchen, *et al.*,[1] is apparent from the diffraction patterns shown in Table I.

TABLE I

X-RAY POWDER PATTERNS

This work		Cr_3O_8[1,a]	
d, Å.	Intensity	*d*, Å.	Intensity
11.6	M	11.8	M
6.01	VW	6.19	W
		5.84	W
4.91	VW	4.95	VVW
4.49	VW	4.49	VW
3.78	S	3.88	S
		3.72	M
3.30	MS	3.34	MS
3.05	MS	3.08	MS
2.61	W	2.60	VVW

[a] Only comparable lines listed.

Although there is no apparent explanation for the failure to observe the other oxidation states, Cr_2O_5 and CrO_2, reported by Fankuchen, *et al.*,[1] as intermediates between CrO_3 and Cr_2O_3, it is possible that the heat treatments may not have been sufficiently severe.

Once formed, the Cr_2O_3 proved refractory to further change. No change in its diffraction pattern was noted throughout the following consecutive treatments: (1) continued heating *in vacuo* for 240 hours over the temperature range of 396 to 593°; (2) heating in flowing air at 1.2 atmospheres for 612 hours over the temperature range of room temperature to 671° and (3) heating in flowing H_2 at 1.7 atmospheres for 745 hours over the temperature range of 130 to 660°. The results of the latter two treatments are in accord with those reported by Lazier and Vaughen[3] which indicated that only amorphous Cr_2O_3 underwent reduction and oxidation.

In view of the results obtained on bulk Cr_2O_3 by treatment with both air and H_2 at elevated temperatures, it was considered unlikely that the Cr_2O_3 catalyst composed of alumina-supported Cr_2O_3 would prove less stable. Such proved to be the case for a catalyst containing 22% Cr_2O_3 and small quantities of potassium and cerium as promoters. This catalyst, after prior use in a large scale pilot unit, was observed to undergo no change in chromium oxidation state when contacted initially with air over a period of 271 hours in which the temperature was increased from 263 to 660°, and subsequently with H_2 during a period of 249 hours in which the temperature was increased from 263 to 583°. Based on these observations it appears that the rapid and severe deactivation generally experienced with Cr_2O_3–Al_2O_3 catalysts in aromatization processes does not stem primarily from a change in oxidation state of the chromium.

RESEARCH & DEVELOPMENT DIVISION
HUMBLE OIL & REFINING COMPANY
BAYTOWN, TEXAS

---

[3] W. A. Lazier and J. V. Vaughen, THIS JOURNAL, **54**, 3080 (1932).

The Reactivity of the Methyl Group in 2-Methyl-3-nitronaphthalene[1]

BY LEONARD E. MILLER, W. W. HANNEMAN, W. L. ST. JOHN AND R. R. SMEBY

RECEIVED SEPTEMBER 14, 1953

The preparation of 2-methyl-3-nitronaphthalene described in the literature,[2] for which tetralin is the starting material, is tedious and the yields in some of the steps are low or unstated. As a consequence a new synthetic route has been devised.

Commercially available 3-hydroxy-2-naphthoic acid was first converted to its methyl ester I[3] which was then reduced with lithium aluminum hydride according to the method of Nystrom and Brown[4] to give 3-hydroxymethyl-2-naphthol (II) in a yield of 87% of the theoretical amount.[5]

The 3-hydroxymethyl-2-naphthol underwent hydrogenolysis at 142° in the presence of copper–chromium oxide to give 3-methyl-2-naphthol (IIIa) in 87% yield. This procedure is analogous to that used by Cason[6] to convert 4-hydroxy-2-naphthaldehyde to 4-hydroxy-2-methylnaphthalene. When 3-methyl-2-naphthol was mixed with a solid calcium chloride–ammonia complex and heated at 270°, 3-methyl-2-naphthylamine (IIIb) was formed in yields up to 88%. Fries and Hübner[7] have used this technique to prepare 1-methyl-2-naphthylamine from 1-methyl-2-naphthol, another compound which does not undergo the Bucherer reaction satisfactorily.

The methods which have been reported[8] for the conversion of aromatic amines to nitro compounds were not adaptable in our hands for the preparation of 2-methyl-3-nitronaphthalene (IIIc). A

---

(1) Presented before the Organic Division at the 118th meeting of the American Chemical Society, Chicago, September 3 to 9, 1950.

(2) V. Veselý and F. Štursa, *Collection Czechoslov. Chem. Commun.*, **6**, 137 (1934); *Chem. Listy*, **29**, 361 (1935).

(3) Cohen and Dudley, *J. Chem. Soc.*, **97**, 1748 (1910).

(4) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

(5) After this work had been reported,[1] W. T. Smith, Jr., and L. Campanaro, *ibid.*, **74**, 1107 (1952), described the preparation of this compound in 23% yield, by the direct reduction of 3-hydroxy-2-naphthoic acid. Our over-all yield from the same acid was 77% (88% for the esterification; 88% for the reduction).

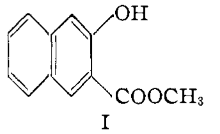
(6) J. Cason, THIS JOURNAL, **63**, 831 (1941).

(7) K. Fries and E. Hübner, *Ber.*, **39**, 444 (1906).

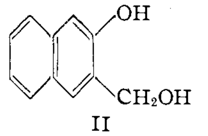
(8) (a) H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 127 (1947); (b) H. H. Hodgson, A. P. Mahadevan and E. R. Ward, *ibid.*, 1392 (1947); (c) M. F. W. Dunker, E. B. Starkey and G. L. Jenkins, THIS JOURNAL, **58**, 2308 (1936); (d) E. B. Starkey, *ibid.*, **59**, 1479 (1937).

small measure of success was achieved in the preparation of this desired material by the formation of the cobaltinitrite complex of the diazotized amine[8a] and the decomposition of this complex using Starkey's[8d] procedure to give a 10–15% yield of 2-methyl-3-nitronaphthalene.

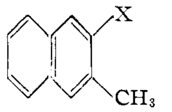
Many efforts were made to condense 2-methyl-3-nitronaphthalene with ethyl oxalate under various conditions.[9,10] When ether was used as the solvent no reaction occurred. When benzene was employed it appeared that traces of the condensation product had formed, but it could not be obtained in sufficient quantity to permit isolation in pure form and characterization. This result is in contrast to that obtained with 1-nitro-2-methylnaphthalene which did condense with ethyl oxalate in diethyl ether to give ethyl 1-nitro-2-naphthylpyruvate in 86.5% yield.



I



II



III

a, X = OH
b, X = NH_2
c, X = NO_2

Experimental[11]

3-Hydroxymethyl-2-naphthol (II).—A solution of 375 g. (1.99 moles) of 3-hydroxy-2-naphthoic acid in 1500 ml. of methanol and 75 ml. of concd. sulfuric acid was heated under reflux for 18 hours. Upon cooling, the ester, which separated as needles, was collected on a filter. The filtrate was concentrated to obtain a second crop of crystals. The two crops were combined, dissolved in ether, washed with 5% aq. sodium bicarbonate and finally water. The ether solution was evaporated to dryness and the residual methyl 3-hydroxy-2-naphthoate(I)[3] was recrystallized from methanol; m.p. 73–74°. The yield was 357 g. or 88.6% of the theoretical amount.

A 3-l. three-necked flask was fitted with an efficient reflux condenser protected with a calcium chloride drying tube, a dropping funnel similarly protected and a Hershberg stirrer fitted with a ground glass sleeve. This apparatus had been dried overnight in an oven at 110°; the ester prepared above was dried in an oven at 60°. A solution of 37 g. (0.98 mole) of lithium aluminum hydride in 1-l. of dry diethyl ether was prepared in the flask. To this solution was added dropwise 121 g. (0.60 mole) of the above ester dissolved in 600 ml. of dry diethyl ether. When this addition was completed, the reaction mixture was stirred for two additional hours. About 200 ml. of water was added slowly followed by approximately 1600 ml. of 10% aq. sulfuric acid to make the mixture acid to congo red paper. The solid product was extracted with 10 l. of diethyl ether. This solution was washed with 5% aq. sodium bicarbonate, then water and was finally evaporated to dryness. The resulting residue was recrystallized three times from methanol to give colorless flakes, m.p. 189.5–190.5° (reported[5] 190–191°). The yield was 91.6 g. or 87.9% of the theoretical amount.

3-Methyl-2-naphthol (IIIa).—A solution of 53.9 g. (0.31 mole) of 3-hydroxymethyl-2-naphthol (II) in 150 ml. of absolute ethanol was treated with hydrogen at 204 atmospheres and 142° in the presence of 6 g. of copper–chromium oxide catalyst.[12] The hydrogen uptake was completed after 45 minutes at which time the autoclave was cooled and the catalyst was separated on a filter. The ethanol solution was boiled with charcoal, filtered and evaporated to dryness. The residue was sublimed at 150° (0.01 mm.) and recrystallized from cyclohexane, from which it gave colorless plates; m.p. 156–157° (reported 155–156°[2]). The yield was 42.5 g. or 87% of the theoretical amount.

3-Methyl-2-naphthylamine (IIIb).—Anhydrous, powdered calcium chloride was placed in a 2-l., three-necked flask, fitted with a mechanical Hershberg stirrer and gas inlet and outlet tubes, and stirred vigorously while a constant stream of anhydrous ammonia gas was introduced until heat was no longer evolved. Since this complex is unstable in air it was used immediately.

A pulverized mixture of 15 g. of 3-methyl-2-naphthol (IIIa) and 75 g. of calcium chloride–ammonia complex was placed in a stationary autoclave and heated at 270° for eight hours. After removal from the cooled autoclave, the product was extracted with diethyl ether and the residual calcium chloride was dissolved in water. The water solution was extracted with diethyl ether and the combined ether extracts were washed with 2% aq. sodium hydroxide. Acidification of the alkaline solution afforded the recovery of unchanged starting material. After evaporation of the ether solution to dryness, the residue was sublimed at 110° (0.05 mm.) and recrystallized from cyclohexane. The yield, based upon starting material initially used, was 16.4 g. (82.5%) of pale yellow plates; m.p. 135–136° (reported[2] 135–135.5°).

2-Methyl-3-nitronaphthalene (IIIc).—A mixture of 13 ml. of hydrochloric acid (sp. gr. 1.18), 46 ml. of water and 5 g. (0.032 mole) of 3-methyl-2-naphthylamine (IIIb) was heated to give a clear solution. The solution was then cooled rapidly to obtain a finely divided precipitate of the amine hydrochloride. When the temperature of the mixture was below 0°, a solution of 2.6 g. of sodium nitrite in 13 ml. of water was added rapidly with vigorous stirring. The resulting diazonium salt solution was filtered and poured into a mixture of powdered calcium carbonate, ice and diethyl ether (to abate frothing). This mixture was filtered into a solution of 5.28 g. of sodium cobaltinitrite in 26 ml. of water contained in the filter flask. The diazonium–cobaltinitrite complex separated as a bright orange precipitate which was collected on a filter, washed with water and then with diethyl ether. This moist complex was stirred into a slurry with 20 ml. of water and was added to a solution of 80 g. of sodium nitrite in 160 ml. of water in which 10 g. of powdered copper was suspended by means of a mechanical stirrer. After stirring for three hours at room temperature, the solid material was collected on a filter and was extracted with diethyl ether. The residue, which remained after the evaporation of the ether, was sublimed at 120° (0.6 mm.) and recrystallized from cyclohexane to give 0.9 g. (15%) of pale yellow prisms; m.p. 120–120.5° (reported[2] 117–118.1°).

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois

---

(9) K. G. Blaikie and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 296 (1924).

(10) W. Wislicenus and E. Mundiger, *Ann.*, **436**, 62 (1924).

(11) All melting points are uncorrected.

(12) T. W. Riener, This Journal, **71**, 1130 (1949).

A New Form of Uranium Hydride[1]

By R. N. R. Mulford, F. H. Ellinger and W. H. Zachariasen

Received August 6, 1953

We have discovered the presence of a new crystal form of uranium hydride which appears under certain conditions of preparation. For reasons given below, we believe this new form to be an alternate structure of the compound UH_3, and thus we propose to name this new crystal form α-UH_3, and to call the common form of uranium hydride β-UH_3. This nomenclature will be followed in the subsequent report.

During the course of some work involving uranium hydride, extra lines were noticed in X-ray diffraction patterns of uranium hydride preparations. These lines could not be satisfactorily explained on the basis of extraneous compounds pres-

---

[1] Work done under the auspices of the A.E.C.