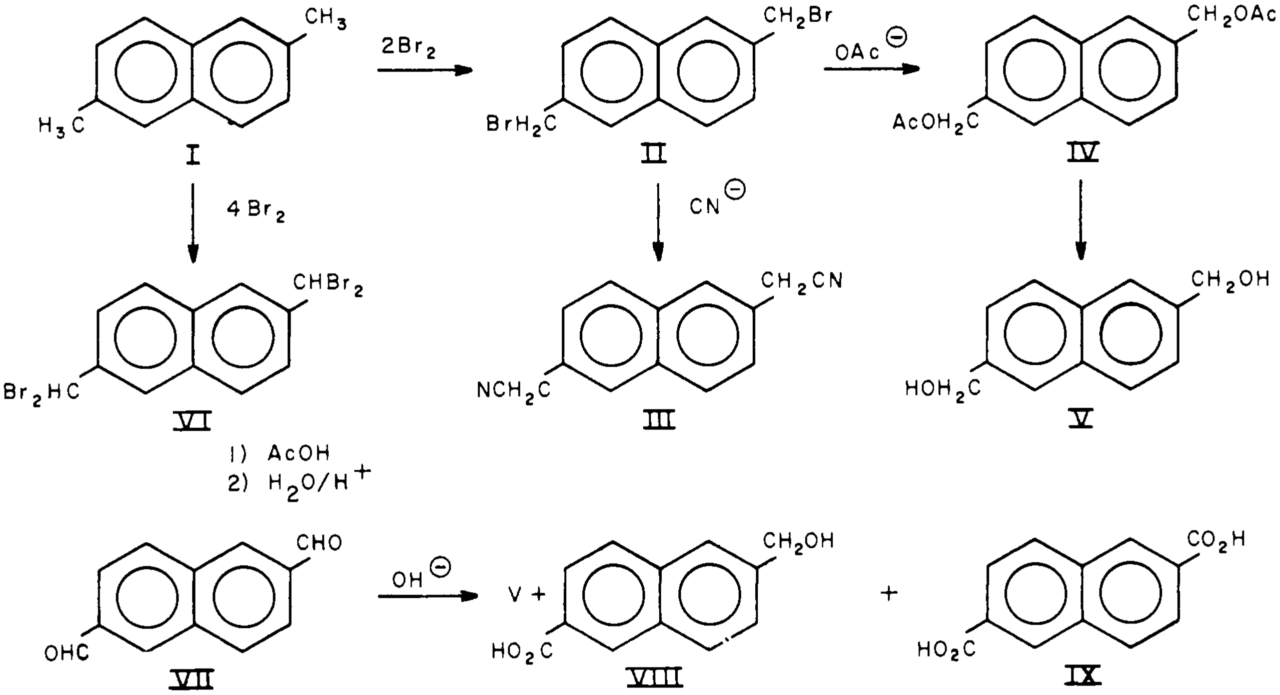
Bifunctional Derivatives of 2,6-Dimethylnaphthalene

P. W. STORMS and P. R. TAUSSIG[1]
Marathon Oil Company, Denver Research Center, Littleton, Colo.

The photobromination of 2,6-dimethylnaphthalene gave good yields of 2,6-bis(bromomethyl)naphthalene or 2,6-bis(dibromomethyl)naphthalene. Several new derivatives were prepared from these halogenated compounds via displacement reactions.

THE PHOTOBROMINATION of methyl naphthalenes to give exclusively side-chain substituted products has recently been reported (*2*). The synthesis of some new difunctional naphthalene compounds from these halogenated compounds is reported here.

The following sequence of reactions was employed:



Reaction of 2,6-dimethylnaphthalene with two moles of bromine gives a high selectivity to 2,6-bis(bromomethyl)-naphthalene (II). Displacement reactions carried out on II with cyanide and acetate ion produce the dinitrile (III) and the diacetate (IV), respectively. Saponification of the diacetate gives 2,6-bis(hydroxymethyl)naphthalene (V).

Photobromination of I with four moles of bromine gives as the major product 2,6-bis(dibromomethyl)naphthalene (VI). Acetolysis of VI, followed by treatment with dilute mineral acid yields the dialdehyde (VII). Ordinary Cannizzaro reactions of this dialdehyde give equal quantities of V, 6-hydroxymethyl-2-naphthoic acid (VIII), and 2,6-naphthalenedicarboxylic acid (IX). Crossed Cannizzaro reactions with VII and formaldehyde produce a high yield of V, some hydroxyacid (VIII), but no diacid (IX). Table I summarizes the results obtained.

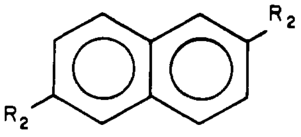
EXPERIMENTAL

2,6-Bis(bromomethyl)naphthalene (II). To a 2-liter reaction flask equipped with stirrer, dropping funnel reflux condenser, and nitrogen inlet tube, was added 50 grams (0.32 moles) of 2,6-dimethylnaphthalene in 1000 ml. of carbon tetrachloride. While stirring, sweeping with nitrogen, refluxing, and illuminating with a 200-watt incandescent bulb, bromine (103 grams, 0.64 mole) in 100 ml. of carbon tetrachloride was added dropwise to the reaction solution. The

---

[1] Present address: Mobil Chemical Company, Edison Township Laboratories, Metuchen, N. J.

Table I. Synthesis Products



Compd.	R_1	R_2	M.P., ° C.[a]	Lit. M.P., ° C., (*1*)	Yield, %[b]	Recrystallization Solvent
II	—CH_2Br	—CH_2Br	182-4	182-2	50	Dioxane
III	—CH_2CN	—CH_2CN	165-6	...	43	EtOH
IV	—CH_2OAc	—CH_2OAc	135-6	...	84	EtOH
V	—CH_2OH	—CH_2OH	170-1	...	93	EtOH
VI	—$CHBr_2$	—$CHBr_2$	164-4	164	80	Dioxane
VII	—CHO	—CHO	173-4	176	86	Dioxane
VIII	—CO_2H	—CH_2OH	234-5	...	40[a]	Ethyl acetate

[a] All melting points were determined on a Thomas-Hoover capillary melting-point apparatus and are uncorrected. [b] This corresponds to 80% of a statistical yield.

addition rate was slow enough to avoid any significant buildup of molecular bromine. After the addition was complete, the mixture was refluxed for an additional 30 minutes and then cooled to room temperature. Filtration gave 57.2 grams of an insoluble product. One recrystallization from dioxane gave a 50% yield of 2,6-bis(bromomethyl)naphthalene, m.p. 182-4° C. Literature m.p., 182-2 (*1*).

2,6-Bis(cyanomethyl)naphthalene (III). 2,6-Bis(bromomethyl)naphthalene, 13.5 grams, and 10.3 grams of potassium cyanide were stirred with 200 ml. of refluxing methanol for 10 hours. Three volumes of water were added and the mixture filtered. Yield of crude dinitrile was 4.2 grams (43%). Recrystallization from ethanol gave pure III, m.p. 165-6° C. Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.53; H, 4.98; N, 13.58. Found: C, 81.48; H, 4.89; N, 13.39.

2,6-Bis(acetoxymethyl)naphthalene (IV). 2,6-Bis(bromomethyl)naphthalene (50 grams or 0.159 moles) and 130 grams of lead diacetate (0.397 mole) was stirred in 500 ml. of refluxing glacial acetic acid for 4 hours. The insoluble lead bromide was filtered and the filtrate diluted with three volumes of water. The resulting crude IV was filtered and washed with 5% sodium bicarbonate solution. One recrystallization from ethanol gave pure IV (m.p. 135-6° C.) in 84.5% yield. Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.99; H, 5.91.

2,6-Bis(hydroxymethyl)naphthalene (V). 2,6-Bis(acetoxymethyl)naphthalene, 50 grams, and 16 grams of KOH were refluxed with 500 ml. of ethanol for 6 hours. Three volumes of water were added and the crude alcohol (32.0 grams or 93%) was filtered. One recrystallization from ethanol gave pure V, m.p. 170-1° C. Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.80; H, 6.21.

2,6-Bis(dibromomethyl)naphthalene (VI). The procedure used was the same as that for the preparation of II except 4 moles of bromine was added. The isolated yield was 80%. Recrystallization from dioxane gave pure VI, m.p. 162-4° C. Literature m.p., 164° C. (*1*).

2,6-Naphthalenedicarboxaldehyde (VII). Seventy-five grams (0.159 mole) VI was refluxed 24 hours in 400 ml. of acetic acid. Three volumes of water were added to the solution along with a small quantity of dilute hydrochloric acid. This mixture was stirred 1 hour and filtered. Twenty-five grams of crude VII (86%) was recovered. Two recrystallizations from dioxane gave a pale yellow solid, m.p. 173-4° C. Anal. Calcd. for $C_{12}H_8O_2$: C, 78.3; H, 4.4. Found: C, 77.5; H, 4.3.

Cannizzaro Reaction of VII. The dialdehyde (10 grams, 54 moles), dioxane (20 ml.), potassium hydroxide (30 grams), and water were stirred and refluxed for 6 hours. The mixture was extracted several times with dioxane and the extracts evaporated to yield 3.4 grams of V. Acidification of the water layer gave a white solid which was repulped several times with hot dioxane. The insoluble acid (3.7 grams) was identified as crude 2,6-naphthalenedicarboxylic acid (IX), N.E. 104.6 (theory 108.0). Evaporation of the dioxane gave 4.4 grams of crude 6-hydroxymethyl-2-naphthoic acid (VIII), m.p. 230-5° C. N.E. 204.9 (theory 202). One recrystallization from ethyl acetate gave the pure compound, m.p. 234-5° C.

Crossed Cannizzaro Reaction of VII. The dialdehyde, 10 grams, was reacted with 45 grams of 45% formaldehyde, 150 ml. of dioxane, 200 ml. of water, and 50 grams of potassium hydroxide. Usual work-up gave 8.3 grams of V and 1.0 grams of VIII. No IX was obtained.

LITERATURE CITED

(1) Ried, W., Boden, H., *Chem. Ber.* **91**, 1981-2, 2479-84 (1958).
(2) Taussig, P.R., Miller, G.B., Storms, P.W., *J. Org. Chem.* **30**, 3122 (1965).

RECEIVED for review August 23, 1965. Accepted February 14, 1966.