of this reaction, as it pertains to asymmetric synthesis, is currently being investigated.[10]

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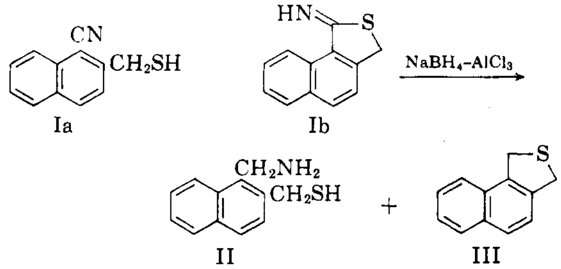
[10] We gratefully acknowledge the technical assistance of Mr. D. M. Borgnaes.

[11] Ethyl Fellow, 1960–1961.

A Tautomeric Nitrile–Thiol Iminothiolactone System

Sir:

In working with an intermediate, thought to be a 2-mercaptomethyl-1-naphthonitrile (Ia),[1] an interesting type of ring-chain tautomerism has been observed. When (Ia,b)[2] was reduced with sodium borohydride–aluminum chloride (3:1), its tautomeric character became apparent in that products corresponding to both chain (II, 17%) and ring (III, 48%) forms resulted. 2,5-Naphtho(1,2-*c*)-thiophene (III) was separated from the reaction mixture after it had been poured into ice water and recrystallized from ethanol, m.p. 111–112°. *Anal.* Calcd. for $C_{12}H_{10}S$: C, 77.38; H, 5.41; S, 17.21. Found: C, 77.50; H, 5.23; S, 17.12. After the separation of III, a tacky solid remained which was treated with concentrated hydrochloric acid; crystallization of the resulting material from methanol-ether gave 1-aminomethyl-2-mercaptomethylnaphthalene hydrochloride (II), m.p. 219–220.5° dec. *Anal.* Calcd. for $C_{12}H_{14}ClNS$: C, 60.11; H, 5.89; N, 5.84. Found: C, 59.91; H, 5.90; N, 5.87.



It was found that when the proportion of sodium borohydride to aluminum chloride was increased from 3:1 to 4:1, II was obtained as the sole product (90%). The formation of III under the alternate conditions constitutes a new sulfide synthesis. The structure of III was readily confirmed by desulfurization with Raney nickel to 1,2-dimethylnaphthalene.

In the solid state, the structure of Ia,b appears to be Ib as there is no band for the $C{\equiv}N$ at 2225 cm.$^{-1}$ or for SH at 2555 cm.$^{-1}$, as in the case for the corresponding 4-mercaptomethyl-1-naphthonitrile, m.p. 97–98°. *Anal.* Calcd. for $C_{12}H_9NS$: C, 72.31; H, 4.55; S, 16.09. Found: C, 72.19; H, 4.93; S, 15.91. Further, Ia,b forms a hydrochloride and acetyl derivative, and the latter derivative can be degraded with Raney nickel to yield the anticipated product.

Under basic conditions, it was possible to demonstrate the acyclic tautomeric structure by other reactions. With alkaline hydrogen peroxide, Ib oxidized smoothly to a disulfide (86%), m.p. 192.5–193°. *Anal.* Calcd. for $C_{24}H_{16}N_2S_2$: C, 72.70; H, 4.07; S, 16.17. Found: C, 72.62; H, 4.15; S, 16.35. Also Ib reacted with benzyl chloride in ethanolic sodium hydroxide to give the anticipated sulfide, 2-benzylmercaptomethyl-1-naphthonitrile, m.p. 53.5–54.5°. *Anal.* Calcd. for $C_{19}H_{15}NS$: C, 78.86; H, 5.23; S, 11.08. Found: C, 78.75; H, 5.32; S, 11.23.

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[1] Compound Ia,b was prepared from 2-(1-methylisothiuronium)-1-naphthonitrile bromide in 81% yield. The isothiouronium salt in turn was obtained from 2-bromomethyl-1-naphthonitrile (78%) while the latter substance was prepared by the action of *N*-bromosuccinimide on 2-methyl-1-naphthonitrile in a 71% yield.

[2] The form Ib may also be represented as an amino tautomer, *cf.*, A. J. Boulton and A. R. Katritzky, *Tetrahedron*, **12**, 51 (1961).

Titanium-Catalyzed Isomerization and Olefin-Exchange Reactions of Alkylmagnesium Halides: A Novel Method for Preparation of the Grignard Reagent

Sir:

George and Ladd[1] found that when isopropylmagnesium bromide reacts with chlorosilanes in the presence of titanium tetrachloride the coupled product contains both isopropyl and *n*-propyl groups.

$$(CH_3)_2CHMgBr + {\equiv}SiCl \xrightarrow{TiCl_4} (CH_3)_2CHSi{\equiv} + CH_3CH_2CH_2Si{\equiv} \quad (1)$$

This discovery prompted us to undertake a further investigation of the effect of small amounts of titanium tetrachloride on the reactions of Grignard reagents. It has been found that the formation of rearranged products from isopropylmagnesium bromide is not peculiar to reactions of chlorosilanes, but is a general reaction, presumably due to isom-

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[1] P. D. George and J. R. Ladd, Abstracts of Papers presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961.