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

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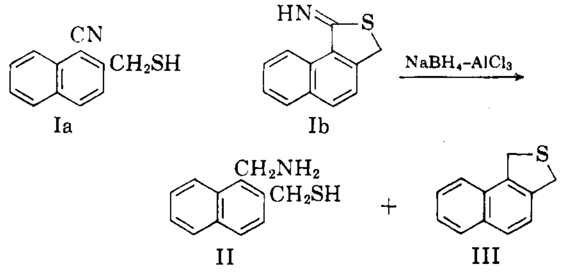
[10] We gratefully acknowledge the technical assistance of Mr. D. M. Borgnaes.

[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≡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.

TABLE I

ISOMERIZATION OF ISOPROPYLMAGNESIUM BROMIDE

$\frac{TiCl_4}{RMgBr}$	$\frac{CH_3CH_2CH_2D}{TiCl_4}$	$\frac{CH_3CH_2CH_2D}{(CH_3)_2CHD}$
2.2×10^{-3}	21.5	0.065
2.2×10^{-2}	6.9	0.299
4.4×10^{-2}	4.6	0.609
10^{-1}	2.5	2.1

erization of the Grignard reagent brought about by the titanium tetrachloride.

$$(CH_3)_2CHMgBr \xrightarrow{TiCl_4} CH_3CH_2CH_2MgBr \tag{2}$$

Small amounts (10^{-1} to 10^{-3} moles per mole of Grignard reagent) of titanium tetrachloride were added at 0° to a solution of isopropyl magnesium bromide in diethyl ether and the mixture was stirred for one hour and decomposed with deuterium oxide. Infrared analysis of the C_3 hydrocarbons showed that both 1-deuteropropane and 2-deuteropropane were formed.

In Table I is shown the effect of varying titanium tetrachloride concentration on the ratio of "rearranged" to "unrearranged" deuteropropanes. In all cases several moles of rearranged product were formed for each mole of titanium tetrachloride. No rearrangement could be detected when titanium tetrachloride was omitted, and *n*-propylmagnesium bromide did not rearrange even in the presence of titanium tetrachloride.

It appears likely that the rearrangement proceeds by an elimination-addition mechanism as in the isomerization of alkylboranes.[2] The first step is the formation of an alkyltitanium compound, followed by elimination of the elements of Ti-H (shown for convenience as $TiHCl_3$ but probably a part of the solid Ziegler-type complex) and terminal addition to the olefin. The fact that more than one molecule of rearranged product is formed for each mole of titanium tetrachloride requires that the alkyltitanium compound can exchange with the Grignard reagent.

TABLE II

REACTIONS OF GRIGNARD REAGENTS PREPARED BY OLEFIN EXCHANGE

Olefin	Reagent	Product
1-Pentene	HCHO	1-Hexanol (45%)
4-Methyl-1-pentene	CH_3CHO	6-Methyl-2-heptanol (37%)
1-Hexene	Cyclohexanone	1-Hexylcyclohexanol (24%)
1-Octene	CO_2, CH_3OH	Methyl pelargonate (40%)
1-Octene	$HC(OC_2H_5)_3$	Pelargonaldehyde (19%)
Allyl benzene	CO_2	δ-Phenylbutyric acid (62%)
Vinylcyclohexane	CO_2	β-Cyclohexylpropionic acid (51%)
4-Vinylcyclohexene	CO_2	β-(Δ^3-Cyclohexenyl)propionic acid (28%)
4-Vinylcyclohexene	O_2	β-(Δ^3-Cyclohexenyl)ethanol (40%)
p-Methoxystyrene	CO_2	*p*-Methoxyhydratropic acid (22%)

$$(CH_3)_2CHMgBr + TiCl_4 \longrightarrow (CH_3)_2CHTiCl_3 + MgBrCl \tag{3}$$

$$(CH_3)_2CHTiCl_3 \longrightarrow CH_3CH{=}CH_2 + TiCl_3H \tag{4}$$

$$CH_3CH{=}CH_2 + TiCl_3H \rightleftarrows CH_3CH_2CH_2TiCl_3 \tag{5}$$

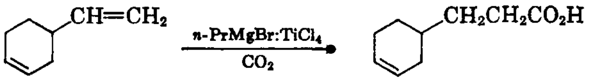
$$CH_3CH_2CH_2TiCl_3 + RMgBr \rightleftarrows CH_3CH_2CH_2MgBr + RTiCl_3 \tag{6}$$

If an olefin other than that derived from the original alkyl group is present it should compete for the TiH in (5), displacing propylene and producing the Grignard reagent derived from the added olefin.

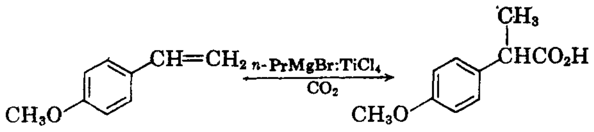
$$RCH{=}CH_2 + PrMgBr \xrightarrow{TiCl_4} RCH_2CH_2MgBr + CH_3CH{=}CH_2 \tag{7}$$

This olefin exchange reaction provides a novel method for the synthesis of Grignard reagents, one which should be of preparative value, using as it does olefins and readily available alkyl halides. In Table II are shown the products and yields obtained when a number of olefins were refluxed for eighteen hours with a mixture of *n*-propylmagnesium bromide and titanium tetrachloride (mole ratio olefin: $C_3H_7Br:TiCl_4$ = 1:1:0.03) and the product then allowed to undergo typical Grignard reactions.

The expected products were obtained in 20–50% yields. These are preliminary results and undoubtedly do not represent the maximum attainable. Under the conditions employed, internal double bonds do not react; thus β-Δ^3-cyclohexenyl)-propionic acid was obtained from 4-vinylcyclohexene:



The products from the aliphatic olefins were those corresponding to the terminal Grignard reagent, but *p*-methoxystyrene yielded *p*-methoxyhydratropic acid, rather than the expected *p*-methoxyhydrocinnamic acid.



Further investigation of the scope and limitations of the titanium-catalyzed olefin exchange reaction is in progress.

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[2] H. C. Brown and B. L. Subba Rao, *J. Org. Chem.*, 22, 1136 (1957); *J. Am. Chem. Soc.*, 81, 6434 (1959).