Reactions of Grignard Reagents with 2,4,6-Tri-t-butylnitrosobenzene: 1,4- and 1,6-Conjugate Addition to the Nitroso-group

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Summary The reaction of 2,4,6-tri-t-butylnitrosobenzene with Grignard reagents affords products of 1,2-, 1,4-, or 1,6-addition to the nitroso-group, depending on the Grignard reagent used.

ALTHOUGH the formation of *NN*-disubstituted hydroxylamines and secondary amines in the reactions of Grignard reagents with nitrosobenzenes has been demonstrated,[1] there has been no report of conjugate addition to a nitroso-group.

We present here the first example of such reactions in nitrosobenzene systems.

Reaction of 2,4,6-tri-t-butylnitrosobenzene[2] with a large excess of RMgX in ether for 1 h at 0°, followed by dry-column chromatography (silica gel, carbon tetrachloride) gave compounds (I)—(V) (Table).

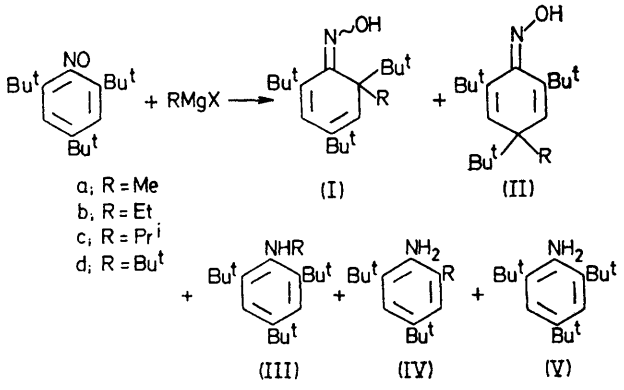
TABLE

RMgX	Reaction yields/%[a] (I)	(II)	(III)	(IV)	(V)[3]
MeMgI ..	46	4	—	—	2
EtMgBr ..	26	30	—	—	8
Pr^{i}MgBr ..	2	54	6	3	—
Bu^{t}MgCl ..	—	trace[b]	43	—	38

[a] Recrystallized from methanol except for (Ia) where n-hexane was used. [b] Identified by n.m.r. and i.r.

The structures of the products were confirmed by their analytical and spectral data (n.m.r., i.r., u.v., and mass).

The oximes (I) and (II) represent 1,4- and 1,6-conjugate addition of the Grignard reagent to the nitrosobenzene, respectively. The formation of (IIIc) and (IIId) is noteworthy in view of the vigorous conditions required for the preparation of the methyl and ethyl derivatives, previously



the only known *N*-alkylated 2,4,6-tri-t-butylanilines;[4] this reaction might thus provide a method for the synthesis of 2,4,6-tri-t-butylanilines with a bulky alkyl group on the nitrogen.

The oximes (I) and (II) are thought to be produced *via* an attack of the anionic species onto the *ortho*- and the *para*-positions respectively, while the *N*-alkylanilines (III) are formed *via* the following pathway involving an electron transfer from the Grignard reagent onto the nitroso-group.

$$Ar\text{–}N{=}O + RMgX \rightarrow [Ar\text{–}\dot{N}\text{–}O\text{–}MgX + R\cdot] \rightarrow$$

$$Ar(R)NOMgX \xrightarrow{RMgX} Ar(R)NMgX \rightarrow (III)$$

(Ar: 2,4,6-$Bu^t_3C_6H_2$)

The aniline (IVc) is presumably formed by elimination of isobutylene from (Ic) followed by reduction with the Grignard reagent.

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[1] G. A. Russell, E. G. Janzen, and E. J. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807; K. Maruyama, *Bull. Chem. Soc. Japan*, 1964, **37**, 1013.
[2] R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 3611; R. Okazaki, T. Hosogai, M. Hashimoto, and N. Inamoto, *ibid.*, 1969, **42**, 3559.
[3] P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Amer. Chem. Soc.*, 1954, **76**, 2349.
[4] J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Rec. Trav. chim.*, 1958, **77**, 491; see also Y. Okamoto and H. Shimizu, *J. Amer. Chem. Soc.*, 1968, **90**, 6145.