

ABNORMAL REACTIONS OF GRIGNARD REAGENTS  
WITH 2,4,6-TRI-*t*-BUTYLNITROBENZENE

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The reactions of 2,4,6-tri-*t*-butylnitrobenzene with the Grignard reagents give rise to products derived from an attack of the latter onto the ortho- and the para-positions to the nitro-group.

In continuation of our work on poly-*t*-butylbenzene derivatives,<sup>1)</sup> we have found abnormal reactions of the Grignard reagent with 2,4,6-tri-*t*-butylnitrobenzene (1) leading to the products derived from an attack of the Grignard reagent onto the ortho- and the para-positions of the nitro-group. A recent communication by Barclay *et al.* on the hydride reduction of 1<sup>2)</sup> describing the formation of a similar product (6, R=H) prompts us to report our preliminary results.

Addition of an ethereal solution of 1 to a large excess of the Grignard reagent in ether (0°C, 2-6 hr), followed by dry-column chromatography on silica gel, gave compounds 2-5.<sup>3)</sup> The yields are listed in Table.

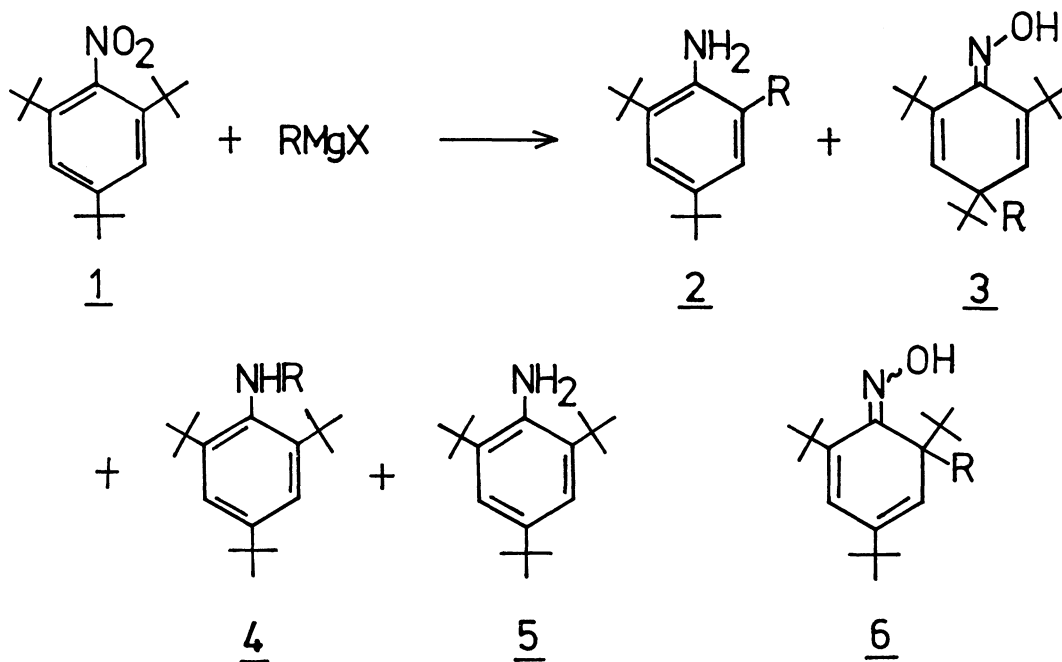


Table  
Yields (%) of the reaction products

| RMgX     | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> |
|----------|----------|----------|----------|----------|
| MeMgI    | 18       | --       | 2        | 40       |
| EtMgBr   | 11       | 15       | 4        | 41       |
| i-PrMgBr | 6        | 21       | 16       | 40       |
| t-BuMgCl | --       | --       | 28       | 49       |

The formation of oxime 3, which shows the Grignard reagent attacked the para-position of the nitro-group, is unprecedented in the reactions of the Grignard reagent with nitroarenes.<sup>6)</sup> The formation of a most unusual product 2, apparently resulted from substitution-reduction with the Grignard reagent, is presumably accounted for by elimination of isobutylene from an initially formed oxime 6 followed by reduction with the Grignard reagent.

We believe that the direct formation of secondary amines 4, especially of N-isopropyl and N-t-butyl derivatives, from the readily available nitrobenzene 1 is of synthetic significance, despite the relatively low yields, considering the difficulties reported for alkylation of 2,4,6-tri-t-butylaniline.<sup>5)</sup>

#### References

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- 2) L.R.C. Barclay, I.T. McMaster, and J.K. Burgers, Tetrahedron Lett., 1973, 3947.
- 3) The identity of the products was established by their analytical and spectral data or by comparison of the spectral data with those reported.<sup>1e,4,5)</sup>
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