

REACTIONS OF PHENYLCHLORODIAZIRINE WITH ALKYL LITHIUM REAGENTS

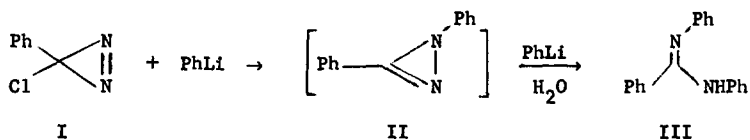
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(Received in USA 21 June 1967)

A variety of studies have demonstrated the unusual stability of the cyclopropenyl cation system.<sup>1</sup> Evidence is also available indicating that its four- $\pi$ -electron relative, the cyclopropenyl anion, is strongly destabilized.<sup>2,3</sup> Among the numerous heterocyclic ions which have been prepared, the diazirinium ion is of particular interest. This heterocyclic ion is isoelectronic with the cyclopropenyl cation and consequently would be predicted to be stable according to Hückel's  $4n + 2$  rule.<sup>4</sup> In fact, recent work by Graham suggests its existence under solvolytic conditions.<sup>5</sup> We felt it desirable to obtain additional data on the stability of the related heterocyclic four- $\pi$ -electron conjugated system. Accordingly we set out to examine metal exchange reactions of 3-halodiazirines in the hope of documenting the transient existence of the anion.

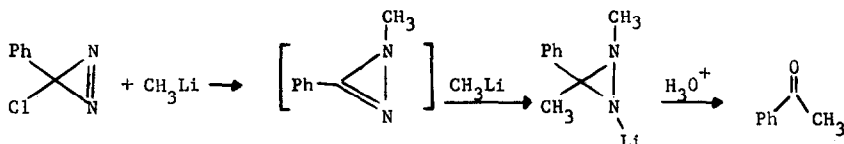
Treatment of phenylchlorodiazirine<sup>5</sup> (I) with phenyllithium in ether afforded in excellent yield a product whose structure was demonstrated to be diphenylbenzamidine (III). The assignment was supported by spectroscopic data, hydrolysis to aniline and benzanilide, and by comparison with an authentic sample prepared by a procedure described by Hill and Cox.<sup>6</sup> Isolation of the amidine suggests that the reaction occurs by attack of phenyllithium on the N-N double bond followed by chloride ion loss and subsequent reaction of the initially formed intermediate with excess phenyllithium.



Previous reports by Schmitz<sup>7</sup> have demonstrated the facile addition of related organometallic

compounds to diazirines and provides reasonable chemical analogy for the first step. Evidently, intermediate II undergoes further reaction with phenyllithium at a faster rate than does starting material. This explanation accounts for the large amount (53%) of starting material that can be recovered when equivalent quantities of phenyllithium were used. When a two-mole excess of phenyllithium was employed, a near quantitative yield of III could be obtained. Experiments designed to trap II with dimethylacetylene dicarboxylate or with substituted butadienes were unsuccessful.

The reaction course followed by treating I with methyllithium in ether proved to be dramatically different. The major product obtained in this case was identified as acetophenone. Careful examination of the residue revealed no detectable amounts of dimethylbenzamide. This result may be rationalized by the following sequence.



The major difference in reaction of I with the two lithium compounds used seems to be related to the direction of addition across the carbon-nitrogen double bond of the initial intermediate. If phenyllithium simply adds across the carbon-nitrogen double bond in the observed direction, then the only phenyl group with which the anion is conjugated is one which is also present in the starting material and which could function just as well in the methyllithium reaction. It therefore appears that attack by phenyllithium is accompanied by ring opening, since the amidine anion which results does indeed have the extra phenyl stabilization in this case. In contrast, methyllithium prefers to undergo stepwise addition at the carbon atom end since the related amidine anion would be devoid of this overlap. The formation of acetophenone may be readily explained by a hydrolytic fission of the diazide upon acid hydrolysis.<sup>8</sup>

**Acknowledgement:** We gratefully acknowledge support of this work by the Public Health Service - Grant GM 13990-01.

References

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4. For a discussion see: A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", John Wiley and Sons, Inc., New York, N.Y., 1961, p. 256.
5. W. H. Graham, J. Am. Chem. Soc., 87, 4396 (1965).
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7. E. Schmitz, "Advances in Heterocyclic Chemistry", A. R. Katritzky, Ed.; Academic Press; New York, 1965, Vol. II, p. 129.
8. The hydrolytic fission of diaziridines to carbonyl compounds is a general reaction of this ring system.