

CYCLOPROPYLCARBINYL ANIONS

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In a prior study,¹ competing Sommelet-Hauser rearrangements were used to compare carbanions derived from the cyclopropylcarbinyll group with saturated and unsaturated carbanions. Although the cyclopropane ring appeared to stabilize the adjacent negative charge, no ring-opened products were detected.

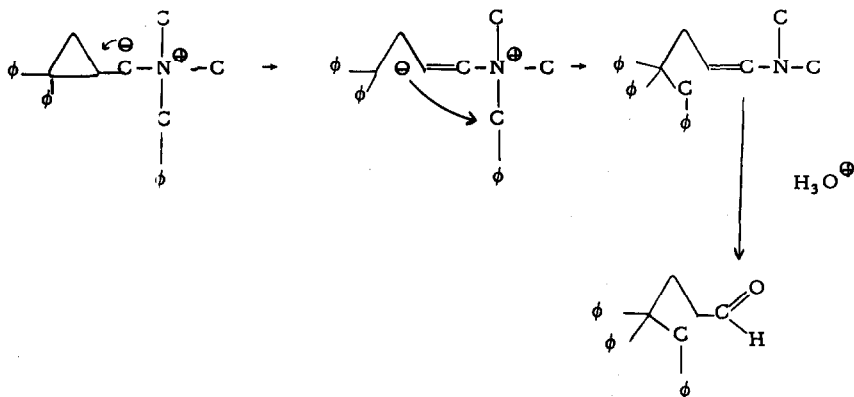
Another investigation, concerned with difluoramino-induced deamination of amines,² showed that whereas primary aliphatic amines were converted to alkanes, cyclopropylcarbinyllamine was converted to the olefin butene-1. These reductive deaminations may well proceed through an alkylidimide or azamine intermediate which can give rise to a carbanion by loss of a proton and molecular nitrogen.

To acquire more knowledge concerning isomerization (ring opening) of cyclopropylcarbinyll systems having negative charge built up on the carbon atom adjacent to the ring, we investigated a number of reactions (Table I) which may involve cyclopropylcarbinyll anions or closely related structures.

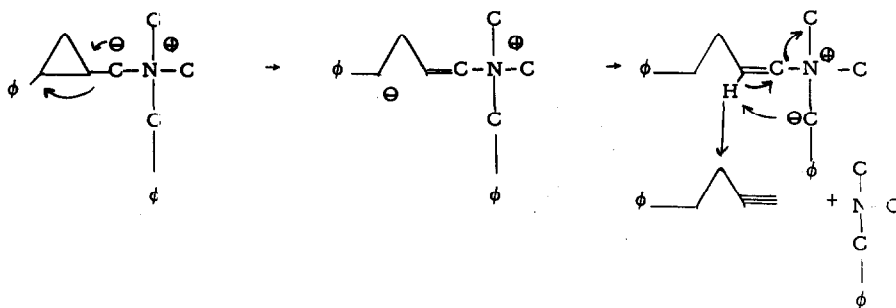
Cleavage of the three-membered ring is not important in reaction 1 (Table I) for the products shown are isolated in nearly quantitative yield.¹ The aldehyde which constitutes a major product from reaction 2 may arise by the steps outlined, which, of course, have as a necessary feature ring opening.³

¹ C. L. Bumgardner, J. Am. Chem. Soc., 85, 73 (1963).

² C. L. Bumgardner, K. J. Martin and J. P. Freeman, ibid., 85, 97 (1963).



Interestingly, reaction 3 gives in addition to rearranged amines, two types of ring opened products, an aldehyde, likely coming about in the manner described above and an acetylene, 4-phenylbutyne, which may be formed as indicated.



³ This conversion can be viewed as a homoallylic example of the rearrangement which leads to aldehyde ii from ylid i. See ref. 1 and others contained therein.

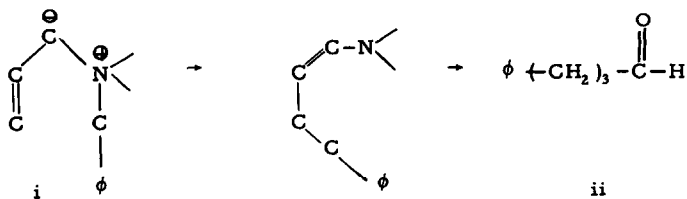


TABLE I

Series	Reaction	Possible Intermediate	Products	Ring Opening
(1)				No
(2)				Yes
(3)				Yes
(4)				Yes
(5)				Yes
				No
(6)				Yes
				No
(7)				Yes
				No
				Yes
				No
(8)				

As required by this equation, benzyldimethylamine was obtained also.⁴ The aldehyde and acetylene were separated by distillation and the structures assigned on the basis of infrared and n. m. r. spectra.⁵

Reaction 4, a thermal amine oxide rearrangement, is pictured as proceeding through an ion pair intermediate in accordance with Schöllkopf's recent findings,⁶ although a homoallylic amine oxide rearrangement is plausible.⁷ Isolation of the hydroxylamine was achieved by gas phase chromatography and the structure established by elemental analyses, infrared and n. m. r. spectroscopy. Thermal decomposition of trans-(2-phenylcyclopropyl) methyl dimethylamine oxide has been reported to yield trans-1-N, N-dimethylaminomethyl-2-phenylcyclopropane.⁵ Although we find this amine (resulting from deoxygenation of the amine oxide) to be the main product, the hydroxylamine derivative also is produced by rearrangement.

Reaction 5 recalls² that reductive deamination via difluoramine leads to olefinic isomers resulting from ring opening. In contrast, Wolff-Kishner reduction of cyclopropane carboxaldehyde has been reported to give methylcyclopropane⁸ although the same intermediate

⁴ Elimination of benzyldimethylamine is pictured as occurring via an α',β -process since this mode of elimination is observed in olefin-forming reactions. C. L. Bumgardner, J. Org. Chem., 27, 1035 (1962). J. Am. Chem. Soc., 83, 4420 (1961).

⁵ J. Smejkal and J. Farkas, Collection Czech. Chem. Commun., 28, 404 (1963) have found that treatment of trans-(2-phenylcyclopropyl)methyltrimethylammonium iodide with potassium amide in ammonia also gives 4-phenylbutyne.

⁶ U. Schöllkopf, Angew. Chem., 75, 219 (1963).

⁷ For rearrangement of benzylic and allylic amine oxides see A. C. Cope and P. H. Towle, J. Am. Chem. Soc., 71, 3423 (1949). A. C. Cope and C. L. Bumgardner, ibid., 78, 2812 (1956).

⁸ E. Renk, P. Shafer, W. H. Graham, R. D. Mazur and J. D. Roberts, J. Am. Chem. Soc., 83, 1987 (1961).

alkyldiimide is presumably involved.⁹ A similar pattern is displayed in reaction series 6 where difluoramine deamination produces olefin and Wolff-Kishner reduction gives the cyclopropane.

Reaction series 7 underscores the importance of substitution (cf. reaction 1 with 2 and 3) for Wolff-Kishner reduction of the 2-phenyl derivative gives a mixture of olefinic and cyclopropyl isomers. This appears to be the first instance of ring cleavage during Wolff-Kishner reduction. In contrast the 1-phenyl derivative provides only the cyclic isomer. Deamination with difluoramine produces exclusively the olefin, 4-phenylbutene, consistent with similar deaminations collected in reactions 5 and 6. The products in series 7 were separated by gas phase chromatography and identified by their infrared spectra.¹⁰

Application of Wolff-Kishner reduction to the unsaturated bicyclic ketone in reaction 8 results in a mixture of the olefinic hydrocarbon and the tricyclic isomer containing a cyclopropane ring. Here Wolff-Kishner reduction generates a three-membered ring, reminiscent of the action of magnesium on *endo*-dihydronorbornyl halides,¹¹ and butyl lithium on norbornadiene.¹²

⁹ D. J. Cram, M. V. Sahyun and G. R. Knox, *ibid.*, 84, 1734 (1962).

¹⁰ Although it is tempting to explain the difference between the Wolff-Kishner reaction and difluoramine deamination on the basis of a cyclic breakdown of the alkyldiimide intermediate in the latter reaction and carbanoid decomposition under Wolff-Kishner conditions, more data are needed to warrant a definite conclusion. A forthcoming publication will discuss in more detail the relationship between Wolff-Kishner reduction and HNF_2 -deamination.

¹¹ J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, 72, 3116 (1950).

¹² G. Wittig and E. Hahn, *Angew. Chem.*, 72, 781 (1960).

The results in Table I show that cyclopropyl ring opening (isomerization of cyclopropylcarbinyl anions) is a function of both the nature of the reaction and the substituents attached to the small ring.¹³

¹³ For related studies see: (a) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt and J. D. Roberts, J. Am. Chem. Soc., 82, 2647 (1960). (b) P. T. Lansbury and V. A. Pattison, ibid., 85, 1886 (1963).

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