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THE REACTION OF 1-AZIRINES WITH CYCLOPROPENYL CATIONS. PYRIDINE FORMATION.

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The recent accessability of 1-azirines has prompted a number of investigations into the chemistry of these highly strained "aza-cyclopropenes."[1,2] For any new heterocyclic system reactivity comparisons with the carbocyclic analog are of general significance; however, the available data on the 1-azirine system is largely divergent from this point.[3] The preliminary results described in this communication provide a pertinent example of cyclopropene mimicry by 1-azirines while at the same time offering further insight into the mechanism of an interesting cyclopropene rearrangement.

Stehouwer and Longone have previously reported[4] that reaction of 1,2-diphenyl cyclopropenyl cation 1a (X = BF_4) with cyclopropene, 1,2-diphenylcyclopropene and 2,3-diphenylcyclopropenecarboxylic acid afforded the benzene derivatives 2. The exclusive formation of the 1,2,4,5-isomer 2 (R^1=R^3=H; R^2=Ph) led these authors to propose the mechanism outlined in path a (N = R^2-C) of the Scheme. If the same pathway were operative in reaction of azirines 3 with cations 1a or 1b then the analogous pyridines 4 would be anticipated products. Indeed azirines 3a-c react with triphenylcyclopropenyl bromide (1b; X = Br) to afford pyridine derivatives 4a-c in good to modest yield (see Table). Structures were confirmed by comparisor with authentic samples.

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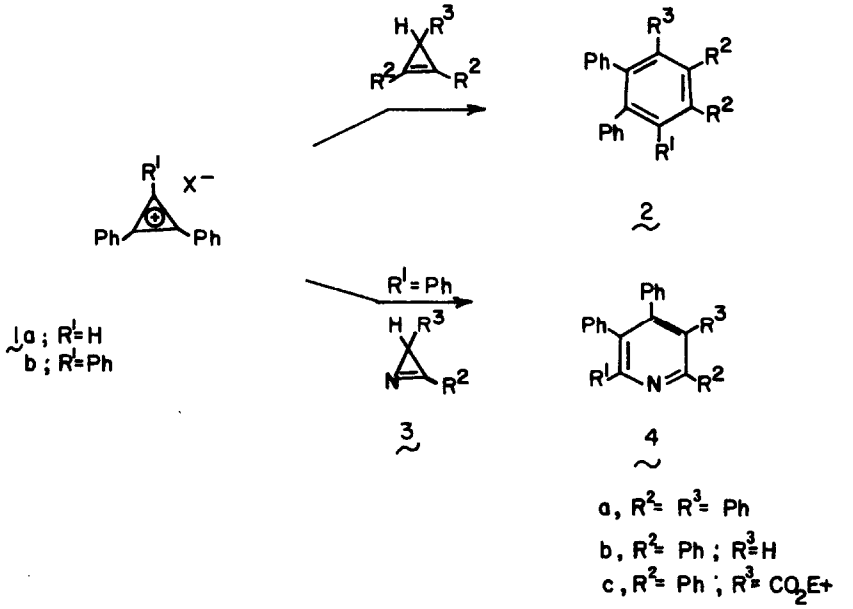


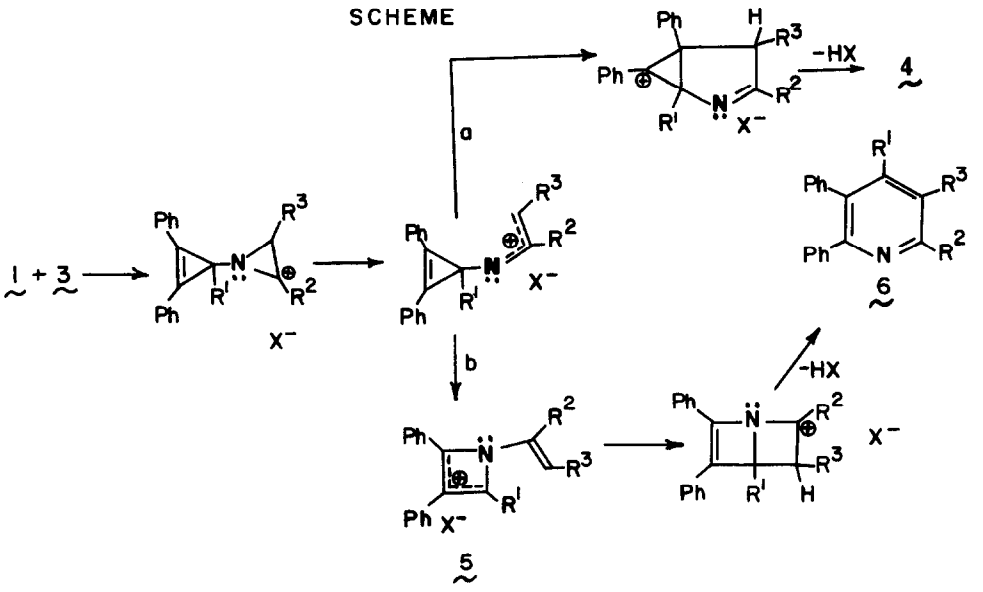
Table. Reaction of Azirines 3 with Triphenylcyclopropenyl Bromide (1b; X=Br)

Azirine	Solvent	T,°C	Pyridine	Yield	m.p. (°C)	Ref.
3a	$ClCH_2CH_2Cl$	83	4a	45%	243-244.5	a
3b	CH_2Cl_2	0	4b	83.5%	182-183	b
3c	$ClCH_2CH_2Cl$	83	4c	16%	243-244	c

[a]W. Dilthey, W. Schommer, W. Hoschen, and H. Dierichs, Ber., 68, 1159 (1935). [b]E. Knoevenagel and H. Schmidt, Ann., 281, 25 (1894). [c]Converted to 4b by hydrolysis and decarboxylation.

In view of the symmetrical structure of cation 1b an alternative mechanism (path b in Scheme) involving ring expansion to an N-vinylazetyl cation 5 followed by further conversion to pyridine 6 cannot be excluded. Accordingly we investigated the reaction of 2,3-diphenyl-1-azirine (3a) with diphenylcyclopropenyl bromide (1a; X = Br).[5] Addition of 3a to a cold suspension of 1a (X = Br) in acetonitrile resulted in exclusive formation of 2,3,5,6-tetraphenylpyridine

SCHEME



(6, $R^2=R^3=Ph$; $R^1=H$), m.p. 238-239° (lit.[6] 232-233°), in 40% yield. Assignment of structure was supported by the nmr spectrum [($CDCl_3$) δ 7.74 (1H, s), 7.6-7.1 (m, 20H)] and confirmed by comparison with authentic material.[6] Careful analysis (tlc) of the reaction mixture indicated total absence of the 2,3,4,5-tetraphenyl isomer 4 ($R^2=R^3=Ph$; $R^1=H$)[7].

The exclusive formation of the 2,3,5,6-tetraphenylpyridine cannot be accomodated by the formally analogous mechanism of Stehouwer and Longone (path a) unless allylic attack by the azirinyl nitrogen at a phenyl bearing carbon of covalent diphenylcyclopropenyl bromide is invoked. Since the latter possibility is rendered highly unlikely by literature precedence[8] mechanistic path b may be operative. Cyclopropenylcarbinyl-cyclobutenyl cation type ring expansions have been proposed for a number of cyclopropene rearrangements[9] including the thermal and silver-catalyzed conversion of bis-cyclopropenyls to Dewar-benzene derivatives.[10] Further mechanistic investigations of these and related cyclopropene rearrangements are in progress.[11]

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2. (a) D.J. Anderson and A. Hassner, *J. Amer. Chem. Soc.*, 93, 4339 (1971); *J. Org. Chem.*, 38, 2565 (1973); (b) V. Nair, *ibid.*, 37, 802, 2508 (1972); (c) A. Hassner and D.J. Anderson, *J. Amer. Chem. Soc.*, 94, 8255 (1972); (d) A. Hassner and A. Kascheres, *J. Org. Chem.*, 37, 2328 (1972).

3. The recently observed (4+2) cycloaddition reactions of 1-azirines[2a-c] constitute the closest previous parallel to cyclopropene reactivity.

4. D.M. Stehouwer and D.T. Longone, *Tetrahedron Lett.*, 5311 (1969).

5. Treatment of the perchlorate (1a, X=ClO_4) and hexafluorophosphate (1a, X=PF_6) salts with 1-azirines gave only traces of the corresponding pyridine products, despite apparently instantaneous reactions. The nature of the products from these reactions and the effect of the counter ion on reaction course are under investigation.

6. H. Carpenter, *Ann.*, 302, 223 (1898).

7. 2,3,4,5-Tetraphenylpyridine, m.p. 185-186°, was prepared by reaction of ethyl cyanoformate with tetracyclone followed by hydrolysis and subsequent decarboxylation.

8. Ultraviolet spectral analysis of 1b (X = Br) in acetonitrile revealed no contribution by the covalent form: R. Breslow, J. Lockhart and H. Chang, *J. Amer. Chem. Soc.*, 83, 2375 (1961). Furthermore, nucleophilic attack on a disubstituted cyclopropenyl cation occurs predominatly at the unsubstituted position. For a compilation of examples see I.A. D'yakonov and R.R. Kostikov *Uspekhi Khim*, 36, 1305 (1967) [*Russ. Chem. Rev.*, 36, 557 (1967)].

9. G.L. Closs, in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G.J. Karabatsos, Eds., Academic Press, New York and London, 1966, pp. 94-100.

10. R. Weiss and S. Andrae, *Angew. Chem. Internat. Edit.*, 12, 150, 152 (1973) and references cited therein.

11. It should be noted that a pincol variant of mechanism b is a viable alternative to the previously proposed mechanism[2d] for 4-pyridone formation in the reaction of 1-azirines with diphenylcyclopropenone. This alternative mechanism presumes nucleophilic attack of the azirine at the carbonyl rather than double bond carbon which at the outset appears more reasonable notwithstanding the current confusion in the literature regarding this point.