CHEMISTRY LETTERS, pp. 155-157, 1977. Published by the Chemical Society of Japan

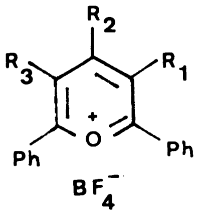
REACTIONS OF PHENYLPYRYLIUM FLUOROBORATES WITH PYRIDINIUM-N-IMINE

Takashi TODA, Hisayo MORINO, Yoshizo SUZUKI,* and Toshio MUKAI
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba, Aramaki, Sendai 980

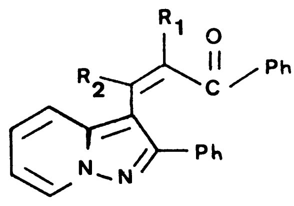
Reactions of phenylpyrylium fluoroborates with pyridinium-N-imine afforded 3-substituted 2-phenyl-pyrazolo[1,5-a]pyridine derivatives.

Although numerous reactions of pyrylium salts with anionoid reagents have been studied,[1] the reactions with ylides are scarecely known in literatures.[2,3] In connection with this, we have reported the reactions of phenylpyrylium fluoroborates with dimethylsulfonium phenacilide.[4] As a part of this series of studies, we wish to report the reaction of phenylpyrylium salts with pyridinium-N-imine.

Reactions of di-, tri- and tetra-phenylpyrylium fluoroborates (1-3)[5,6] with pyridinium-N-imine[7] afforded corresponding 3-substituted 2-phenyl-pyrazolo[1,5-a]-pyridine derivatives (6, 7, and 8; mp 139°, 151°, and 165°) in yields of 32, 40, and 15 %, respectively. In a typical experiment, triethylamine (0.61 g, 3 mmol) was added dropwise under water cooling to a solution of 2 (1.2 g, 3 mmol) and N-aminopyridinium iodide (0.81 g, 3.6 mmol) in acetonitrile (5 ml). After 3 hr stirring,



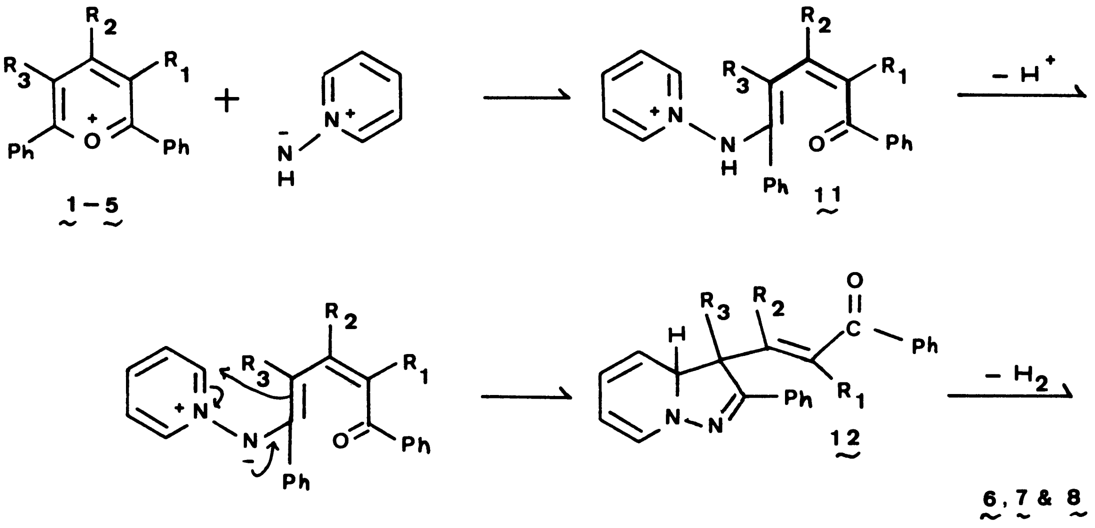
1. $R_1=R_2=R_3=H$
2. $R_1=R_3=H$; $R_2=Ph$
3. $R_1=R_2=Ph$; $R_3=H$
4. $R_1=R_3=Ph$; $R_2=H$
5. $R_1=R_2=R_3=Ph$



6. $R_1=R_2=H$
7. $R_1=H$; $R_2=Ph$
8. $R_1=R_2=Ph$

the reaction mixture was poured into cold water and extracted with ether. The usual work-up and separation by column chromatograph afforded pyrazolopyridine 7 (0.48 g). The structures of 6, 7, and 8 are deduced from the following evidences. Elemental analyses[8] and mass spectra (M^+; 324, 400, and 476) indicate correct molecular formulas for each compounds. Characteristic peaks which can be assigned to a proton at C_7 position of pyrazolo[1,5-a]pyridine derivatives[9] are observed at δ 8.5-8.8 (d; J=ca 7 Hz) in their nmr spectra. Their ir spectra show acylophenone type carbonyl bands ($\nu_{C=O}^{KBr}$; 1650, 1655, and 1645 cm^{-1}, respectively)[3] and are consistent with the assigned structures. Catalytic reduction of 6 gave a dihydroketone 9 (mp 143°: $\nu_{C=O}^{KBr}$; 1680 cm^{-1}) and a tetrahydro alcohol (10, mp 118°). Uv spectrum of 10 [nm (log ε): 238.5 (4.51), 261.5 (4.44), and 290 (4.01)] is very similar to that of 3-methyl-2-phenyl-pyrazolo[1,5-a]pyridine.[10] Also, nmr spectral pattern of the methylene moiety of 9 at δ 3.30 is almost superimposable with that of dihydrochalcon's methylene which appears at δ 3.05.

The formation of 6, 7 and 8 can be explained in the following scheme. Imine anion attacks at the C_2 position of the pyrylium salts to give intermediates (11) and the subsequent intramolecular 1,5-dipolar cyclization affords dihydro-compounds (12) of pyrazolo[1,5-a]pyridine. Dehydrogenation of 12 occurs readily because of the formation of hetero-aromatic system. Analogous examples of 1,5-dipolar cyclization have been reported.[11]



Upon reaction with pyridinium-N-imine, 4 did not give any clear products, and 5 yielded only a small amount of pentaphenylpyridine (mp 240°).[12]

Under similar conditions, reactions of 2 with N-p-toluenesulfonyldimethylsulfilimine[13] and with N-ethoxycarbonylimidopyridine[14] failed and the starting substances were recovered completely.

References and notes

* Department of Chemistry, Faculty of Education, Iwate University, Ueda, Morioka 020.

1) K. Dimroth and K.H. Wolf, "Newer Method of Preparative Organic Chemistry," Vol. III, pp 357-423, ed. by W. Foerst, Academic Press, 1964, New York; H.C. van der Plas, "Ring Transformation of Heterocycles," Vol. II, Chapter 4, Academic Press, 1973, New York.

2) G. Märkl, Angew. Chem., 74, 696 (1962); K. Dimroth, K.H. Wolf, and H. Wache, ibid., 75, 860 (1963).

3) A.R. Katritzky, S.Q. Abbas Rizvi, and J.W. Swinski, Heterocycles, 3, 379 (1975); idem., J. Chem. Soc. Perkin I, 1975, 2489.

4) Y. Suzuki, T. Toda, and T. Mukai, Heterocycles, 4, 739 (1976).

5) R. Lombard and J.-P. Stephan, Bull. Soc. Chim. France, 1958, 1458; M. Simalty, J. Carretto, and R. Funitto, ibid., 1966, 2959.

6) J.A. van Allan and G.A. Reynolds, J. Org. Chem., 33, 1102 (1968).

7) R. Gösl and A. Meuwsen, "Organic Syntheses," Coll. Vol. V, p 43 (1973).

8) Satisfactory elemental analyses were obtained for all new compounds.

9) B.H. Lynch and B. P-L. Lem, J. Heterocyclic Chem., 11, 223 (1974).

10) K.T. Potts, U.P. Singh, and J. Battacharyya, J. Org. Chem., 33, 3766 (1968).

11) Y. Tamura, N. Tsujimoto, Y. Sumida, and M. Ikeda, Tetrahedron, 28, 21 (1972); T. Sasaki, K. Kanematsu, and A. Kakehi, J. Org. Chem., 37, 3106 (1972).

12) E. Knoevenagel and R. Weisgerber, Ber., 26, 436 (1893).

13) C. King, J. Org. Chem., 25, 352 (1960).

14) K. Hafner, D. Zinser, and K.-L. Moritz, Tetrahedron Letters, 1964, 1733.

(Received December 4, 1976)