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ELECTROCYCLIZATION OF 4-AZIDOCOUMARINS LEADING TO BENZOPYRANO-[3,4-d]-1,2,3-TRIAZOL-4-ONES[1]

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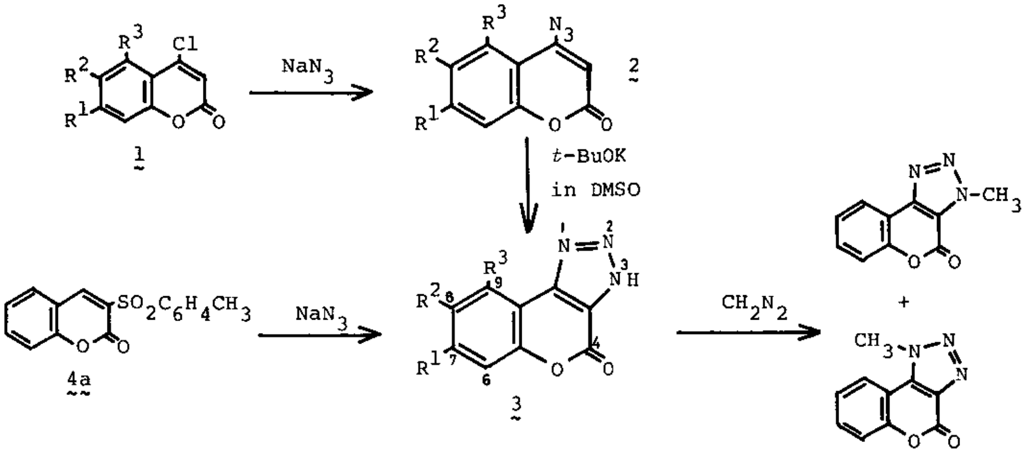
Abstract —— 4-Azidocoumarins 2 as the stable heteroaromatic azides possessing a vinyl azide structure suffered 1,5-dipolar electrocyclization induced by *t*-butoxide leading to the formation of benzopyrano[3,4-d]-1,2,3-triazol-4-ones 3.

An ability of 1,3-dipoles bound to an unsaturated moiety toward intramolecular 1,5-cyclization appears to hold great promise for the preparation of five-membered heterocycles.[2] In this communication we report a novel example of rarely encountered 1,5-dipolar cyclization with respect to a vinyl azide system, *i.e.*, an intramolecular cyclization of 4-azidocoumarins 2 leading to the formation of a benzopyranotriazolone type of compounds 3.



a: $R^1 = R^2 = R^3 = H$
b: $R^1 = CH_3$, $R^2 = R^3 = H$
c: $R^1 = R^3 = H$, $R^2 = CH_3$
d: $R^1 = R^3 = CH_3$, $R^2 = H$
e: $R^1 = CH_3O$, $R^2 = R^3 = H$
f: $R^1 = Cl$, $R^2 = R^3 = H$

Table Benzopyrano[3,4-d]-1,2,3-triazol-4-ones 3

Compound	Yield (%)	Mp (°C)	Ms m/z [M^+]	Ir (KBr) (cm^{-1}) ν(CO)	^{1}H-Nmr (DMSO-d_6) δ (ppm)
3a	41	282-285	187	1756	7.38-8.05(4H,m,C^{6-9}-H)
3b	32	261-264	201	1762	2.41(3H,s,CH_3). 7.41-7.76(3H,m, $C^{6,8,9}$-H)
3c	23	244-246	201	1755	2.42(3H,s,CH_3), 7.44-7.80(3H,m, $C^{6,7,9}$-H)
3d	12	209-211	215	1768	2.37(3H,s,C^7-CH_3), 2.70(3H,s,C^9-CH^3), 7.09(1H,s,C^8-H), 7.14(1H,s, C^6-H)
3e	31	280-282	217	1760	3.88(3H,s,CH_3O), 7.03-7.14(2H,m, $C^{6,8}$-H), 7.92(1H,d,C^9-H)
3f	18	246-248	221	1766	7.49-7.73(2H,m,$C^{6,8}$-H), 8.01(1H,d, C^9-H)

4-Azidocoumarins 2a-f,[3,4] readily obtained from the corresponding 4-chlorocoumarins 1a-f with sodium azide, were stable enough in ordinary solvents ($CHCl_3$, EtOH, THF, DMF, DMSO) even on heating. Coumpounds 2 were also stable in conc. H_2SO_4 at room temperature, whereas they were shown to be labile in the presence of base. It was found that the treatment of 2 with *t*-BuOK in DMF or DMSO readily gave the cyclized isomers 3. Thus, a mixture of 2a[5] (4.0 g, 21 mM) and *t*-BuOK (2.4 g, 21 mM) in DMSO (80 ml) were allowed to be warmed at 50-60°C for 5 h with stirring. Concentration of the reaction mixture followed by neutralization and subsequent extraction with ether gave a solid product, which was subjected to silica gel chromatography affording 1.6 g of 3a, prisms from THF, mp 282-285°C. Mass spectral and microanalysis data suggested that 2a was isomerized into 3a, whose structural elucidation was based on the spectral data. In the ir(KBr) and ^{1}H-nmr(DMSO-d_6) spectra of 3a, the characteristic azide absorption (2124 cm^{-1}) and C^3-H proton singlet signal (δ 6.13 ppm) of 2a dissapeared. On the other hand, quaternary carbon singlet signal at δ 130.3 ppm newly appeared in the ^{13}C-nmr off-resonance spectrum of 3a (DMSO-d_6) in place of doublet C^3 signal (δ 100.2 ppm) of 2a. Finally, the ir, uv, and ^{1}H- and ^{13}C-nmr data[6] of 3a were identical with those of the sample (mp 288-290°C) prepared from 3-(*p*-toluenesulfonyl)coumarin 4 according to the described procedure.[7] Assignment of the N^3-H structure 3 in the Scheme is only tentative, since we could not exactly specify the position of hydrogen on the triazole three nitrogens. However, the treatment of 3a with diazomethane gave the 3 : 1 mixture of the N-methyl derivatives[4] (mp 165-167°C and 182-184°C; ms m/z both 210$[M^+]$), indicating either N^1-H or N^3-H structure of **3a**.[8] Some physical and analytical data of **3a-f**[4] are shown in the Table. The yields were rather unfavorable, presumably due to concomitant reactions through nitrogen elimination to form azirines.[9]

A number of intramolecular cyclization of the vinyldiazomethane derivatives have been described including the facile conversion of 4-diazomethylcoumarins in high yield, recently reported from this laboratory,[10] and the azide group is known to be isoelectronic with the diazomethyl substituent. Neverthless, only two papers have, to our best knowledge, hitherto been recorded on the conversion of a vinyl azide structure, 1-azido-2-(*p*-toluenesulfonyl)ethylene[11] and 6-azido-1,3-dimethyluracil.[12] The present thermal isomerization of **2** leading to the fused 1,2,3-triazoles is assumed to be 1,5-dipolar electrocyclization of a heteroaromatic azide anion induced by base. Mechanistic investigation along with similar cyclization of analogous heteroaromatic azides are now in progress.

REFERENCES AND NOTES

1. Dedicated to Professor Nelson J. Leonard on the occasion of his 70th birthday. A part of this work was presented at the 106th Annual Meeting of the Pharmaceutical Society of Japan, Chiba, April 2, 1986.
2. For reviews, see a) A. Padwa, *Angew. Chem. Int. Ed. Engl.*, 1976. **15**, 123; b) E. C. Taylor and I. J. Turchi, *Chem. Rev.*, 1979, **79**, 181; c) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 947; d) E. N. Marvell, "Thermal Electrocyclic Reactions," Academic Press, New York, 1980, p. 224.
3. **2a**: mp 164-165°C; **2b**: mp 152-154°C; **2c**: mp 140-142°C; **2d**: mp 154-155°C; **2e**: mp 178-180°C; **2f**: mp 179-180°C.
4. Satisfactory microanalysis data were obtained for all new compounds.
5. **2a** was reported to be formed by conversion of chromon-2-carboxylic acid azide: M. Payard, J. Couquelet and A. Paturet, *C. R. Acad. Sci. Ser. C*, 1973, **276**, 1603.
6. Uv(EtOH) λ_{max} nm(log ε): 253(4.07), 265(3.95), 290(3.75); ^{13}C-nmr(DMSO-d_6) δ ppm: 111.3(s), 117.2(d), 123.4(d), 125.0(d), 130.3(s), 131.5(d), 140.9(s), 152.1(s), 154.5(s). For ir and ^{1}H-nmr data, see the Table.
7. G. Beck and D. Günther, *Chem. Ber.*, 1973, **106**, 2758.
8. The presence of ms m/z 173 fragment peak (M-28, primary loss of nitrogen) for

both N-methyl products appears to eliminate the possibility of the N^2-H structure: T. L. Gilchrist and G. E. Gymer, "Advances in Heterocyclic Chemistry," vol. 16, ed. by A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1974, p. 67.

9. See a) G. Smolinsky and C. A. Pryde, "The Chemistry of the Azide Group," ed. by S. Patai, Wiley-Interscience, New York, 1971, p. 563; b) G. La'bbe, *Angew. Chem. Int. Ed. Engl.*, 1975, **14**, 775; c) A. Hassner, "Azides and Nitrenes," ed. by E. F. V. Scriven, Academic Press, New York, 1984, p. 51.
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