

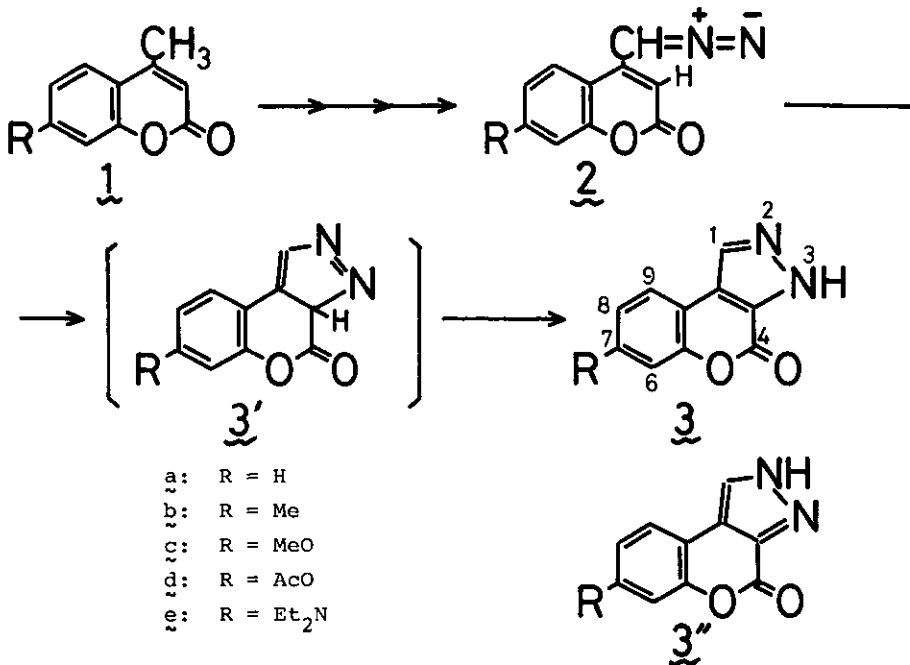
A FACILE INTRAMOLECULAR CYCLIZATION OF 4-DIAZOMETHYLCUMARINS.
 A CONVENIENT ROUTE TO BENZOPYRANO[3,4-c]PYRAZOL-4(3H)-ONES

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Abstract — The 7-substituted 4-diazomethylcoumarins **2** as the stable aryldiazomethanes were rapidly transformed into their cyclized isomers, benzopyrano[3,4-c]pyrazol-4(3H)-ones **3** in high yields in refluxing toluene.

We have recently reported¹ the preparations of the 7-substituted 4-diazomethylcoumarins **2** as a new type of stable aryldiazomethanes which are potentially useful fluorogenic reagents for acids and alcohols.^{1,2} In this communication we wish to report facile thermal cyclization of **2** leading to the formation of the benzopyrano[3,4-c]pyrazol-4(3H)-ones **3**.



Although 2 are extremely stable not always in solid state at room temperature in the open air but also in ordinary solvent (CHCl₃, THF, EtOH, benzene, etc) on reflux, sudden change of the diazo structures of 2 into 3 can be observed at the temperatures above ca. 100°C. Thus, when 1 mM of 2a-e¹ were allowed to be heated in 6 ml of refluxing toluene, yellow color of the solution disappeared and almost colorless crystals of pure 3a-e precipitated within a short period (< 30 min), which were isolated nearly quantitatively (> 85 %) simply by filtration of the reaction mixture on cool. Mass spectral and microanalyses data³ showed that these new crystals are isomers of the starting 2a-e. ¹H-NMR spectra were consistent with the assignment of the benzopyranopyrazole structures of 3. In the NMR spectrum of 3a in DMSO-d₆, for instance, the characteristic diazomethyl proton (δ 5.90) and C³ proton (δ 6.56) singlet signals of 2a disappeared and a new singlet signal attributable to C¹-H (δ 8.63) and a broad singlet NH signal (δ 14.56, exchangeable with D₂O) appeared instead in addition to aromatic proton signals [δ 7.28-7.40(3H, m, C⁶⁻⁸-H), 7.94(1H, d, C⁹-H)]. Furthermore, N-methyl derivative of 3a (needles from isoPrOH, mp 163-164°C) obtained by treatment with diazomethane was identical with the sample prepared by the different route as reported.⁴ Some physical and spectral data of 3a-e are depicted in Table I. All the crystals of 3a-e do not melt below 270°C but tend to be sublimed at higher temperatures. 3c and 3e showed strong fluorescence (emission maximum in EtOH: 402 nm for 3c, 510 nm for 3e).

Table I. Benzopyrano[3,4-c]pyrazol-4(3H)-ones 3

Compound	Yield (%)	Appearance Recryst. Solvent	MS m/e [M ⁺]	IR ν ^{KBr} _{max} cm ⁻¹		¹ H-NMR δ (DMSO-d ₆)	
				NH	CO	C ¹ -H	NH
<u>3a</u>	85	needles (dioxane)	186	3282	1726	8.63	14.56
<u>3b</u>	91	leaves (dioxane)	200	3298	1727	8.56	14.50
<u>3c</u>	90	pale yellow needles (THF)	216	3284	1723	8.52	14.45
<u>3d</u>	95	pale yellow prisms (dioxane)	244	3278	1727 1757	8.71	14.52
<u>3e</u>	86	pale yellow prisms (CH ₃ CN)	257	3290	1724	8.46	14.24

Since the above transformations of 2 proceed rapidly at 100°C or above in dioxane, DMF, BuOH or pyridine as well as in toluene and also at 120-130°C without solvent, but proceed slowly at 90°C and never below 70°C regardless of the solvent used, the isomerization is supposed to be thermo-dependent 1,5-electrocyclic type of ring closure reaction which affords formal 1,3-dipolar cycloaddition product 3' followed by hydrogen migration leading to 3. As the final product we assigned the N³-H structure 3 rather than the tautomeric N²-H structure 3'' on the assumption that 3 is more stable. Possibilities of the other tautomeric structures can be eliminated from the NMR and IR spectral data. In spite of a number of intramolecular cyclization of diazoalkenes using tosylhydrazone precursors indirectly,⁵ those of the isolated pure diazo compounds of heterocyclic system such as 2 are apparently unknown.

4-Diazomethylcoumarins 2 are reported¹ to be easily obtained by three steps from the corresponding 4-methylcoumarins 1, and the isomerizations of 2 are very facile to afford 3 in high yields. Therefore, the present set of transformations starting from 1 through stable diazo intermediates 2 appears to provide a convenient route to benzopyrano[3,4-c]pyrazol-4(3H)-ones 3. Investigations on similar cyclizations of analogous stable aryldiazomethanes are in progress.

REFERENCES AND NOTES

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