Thermolysis of Geminal Diazido Compounds

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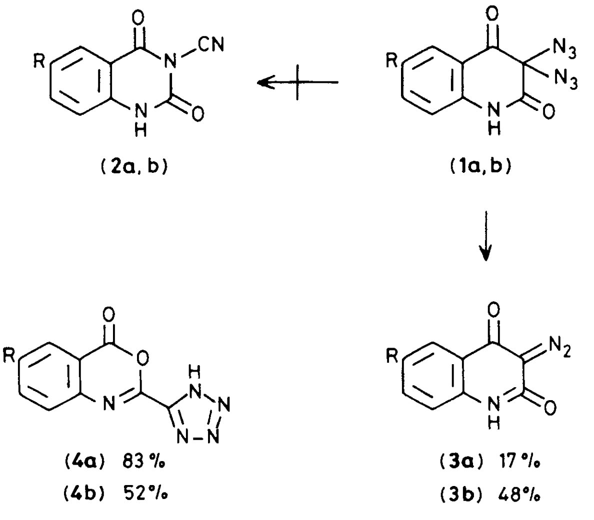
Thermal decomposition of 3,3-diazidotetrahydroquinoline-2,4-diones (**1**) yields 3-diazotetrahydroquinoline-2,4-diones (**3**) as side products and not 3-cyanotetrahydroquinazoline-2,4-diones, as previously assumed.

The thermal decomposition of 3,3-diazido-6-chloro-tetrahydroquinoline-2,4-dione (**1b**) was reported in 1976 and the compound obtained was assigned the structure of a 6-chloro-3-cyanotetrahydroquinazoline-2,4-dione (**2b**).[1] Very recently LeCount[2] described the synthesis of (**2a**) starting with 2-amino-3,1-benzoxazin-4-one and sodium cyanamide. From a comparison of his spectroscopic data of (**2a**) and those reported for the compound previously believed to be (**2b**) LeCount concluded that the proposed structure is incorrect. Unfortunately, LeCount was unable to repeat the published[1] decomposition of (**1b**) in order to permit a more exact comparison. We are now in a position to clarify the situation.



(2a, b) (1a, b)

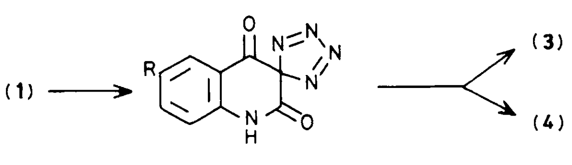
(4a) 83% (3a) 17%

(4b) 52% (3b) 48%

a; R = H
b; R = Cl

More than ten years ago we had already studied the pyrolysis of geminal diazido compounds of type (**1**).[3] However, we found tetrazolo-benzoxazinones (**4**) to be the major products of this reaction. Later we found also the 'cyanoquinazolines' as side products of this reaction.[4,5] In view of the recent results of LeCount[2] we have re-examined the structure of the side products of the pyrolysis of the geminal diazides (**1**) and have now identified these compounds as the isomeric 3-diazoquinoline-2,4-diones (**3a,b**). Compound (**3a**) has been known for many years[6] and has been used for the preparation of azo dyes (by coupling with phenolic compounds)[3,7] and their copper complexes.[7] The diazo compounds (**3a,b**) were readily obtained by the method of Regitz[6] from the corresponding 4-hydroxyquinoline-2(1*H*)-ones and tosyl azide in the presence of triethylamine, and are identical in all respects (t.l.c., m.p. and mixed m.p., i.r., ^{1}H and ^{13}C n.m.r.) with the products isolated from the pyrolysis of (**1a**) and (**1b**), respectively.

From the spectroscopic data presented in Table 1 it is obvious that the two isomeric systems (**2**) and (**3**) can now



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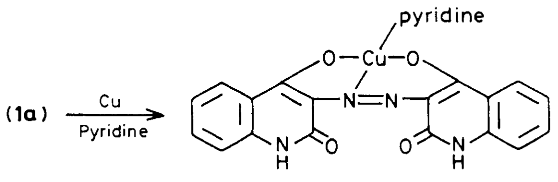

(6)

Table 1. Comparison of physical and spectroscopic data of the isomeric compounds (**2**) and (**3**).

Compound	M.p./°C (solvent)	I.r. (Nujol, cm^{-1})	^{13}C N.m.r. in $(CD_3)_2SO$ δ/p.p.m.
(**2a**)	258—260 (ethanol)	2310 (CN), 1720, 1710 (10)	104.0 (C=N), 112.6, 116.5, 124.0 128.0, 137.2, 139.6, 146.9, 160.2[a]
(**3a**)	224—226 decomp. (butan-1-ol)	2160 (CN_2), 1670, 1635 sh, 1610	78.5 (CN_2), 116.7, 118.6, 122.4, 125.0, 134.9, 140.3, 159.0 (2-CO), 175.8 (4-CO)
(**3b**)	245 decomp. (butan-1-ol)	2170 (CN_2), 1670, 1635 sh, 1610	79.3 (CN_2), 119.0, 119.8, 124.4, 126.9, 134.7, 139.2, 159.0 (2-CO), 174.8 (4-CO)[b]

[a] Data for (**2a**) from ref. 2. [b] See footnote †.

easily be distinguished not only by their i.r. carbonyl absorption, but also by the very characteristic ^{13}C n.m.r. resonance of the diazo carbon atom at δ *ca.* 80 p.p.m., which is in good agreement with values from the literature, *e.g.* for 5-diazobarbituric acid or 2-diazocyclohexane-1,3-dione.†[8]

Although the decomposition of geminal diazides has been studied with several different structural systems in recent years, the formation of diazo compounds, most probably *via* a 5*H*-tetrazole derivative, such as (**5**), has not yet been reported. We think that this mechanism may be also operative with other geminal diazides, at least as a side pathway. Also the reaction conditions may influence the course of the reaction. An indication of this can be seen in the fact that the decomposition of (**1a**) in boiling pyridine in the presence of copper affords the complex (**6**) in 90% yield [compared with a 17% yield of (**3a**) in boiling toluene]; this complex was previously obtained from (**3a**) under the same conditions and in about the same yield.[7]

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† The ^{13}C n.m.r. data for (**3b**) in ref. 1 are in good agreement with the values given in Table 1, with two exceptions: we have not found a band at δ 184.5 p.p.m., and on the other side the important resonance of the diazo carbon at δ 79.3 p.p.m. is missing (obviously attributed to an impurity of chloroform). Furthermore, the ^{13}C n.m.r. signal for the CN_2 carbon atom is usually less intense owing to the long relaxation time!