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A General Synthetic Method for Azolium and Azinium Dinitromethylides†

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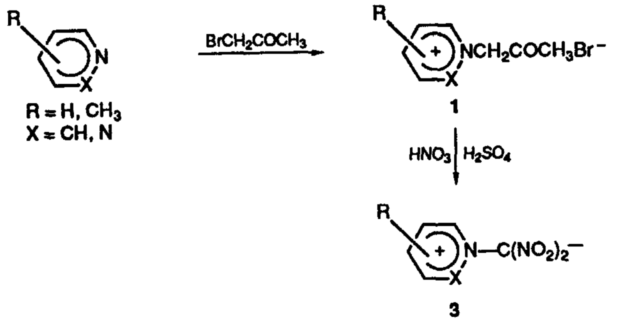
A general scheme for the synthesis of azolium and azinium dinitromethylides, by nitrating *N*-acetonyl derivatives of aromatic *N*-heterocycles with sulfuric acid/nitric acid mixtures, has been developed.

In earlier work on the nitration of the activated methylene unit in carbonyl compounds by sulfuric acid/nitric acid mixtures we developed simple methods for the synthesis of nitro compounds with α-functional groups (derivatives of ketones, carboxylic acids and nitriles).[1,2] It was of interest to demonstrate that the considerable synthetic possibilities of such an approach still exist in the synthesis of rare types of structures which are difficult to obtain, and also to elucidate certain characteristic features of the nitration reaction.

Thus, among the nitro ylides $\overset{+}{X}$–$C(NO_2)_2^-$ (X = S, Se, I, N),[3] which are of interest as reagents for the introduction of a nitrocarbanionic fragment, the nitrogen nitro ylides (X = N) have remained almost uninvestigated because there has been no general method for their synthesis. Only special cases, *e.g.* the preparation of pyridinium dinitromethylides, are known.[3f,4]

We have developed a general approach to the synthesis of the heterocyclic nitrogen dinitromethylides **3** which involves the nitration, using sulfuric acid/nitric acid mixtures of a wide variety of *N*-acetonyl heterocyclic salts nitrogen derivatives (Table 1).‡

Salts **1** based on five-membered heterocycles have been synthesised by the successive alkylation and quaternisation of cyclic compounds using phase-transfer catalytic methods or a high pressure (6–10 kbar) and in a number of instances with the aid of effective alkylating agents (diazoalkanes and alkyl fluorosulfonates).



The nitration stage of salts **1** has been investigated with the aid of UV and NMR spectroscopy.

According to the kinetic data obtained, nitro groups are introduced successively into the methylene unit of the ketones **1**, while hydrolysis involving the removal of the acetyl group is carried out only after the introduction of the second nitro group. It follows from a comparison of the rates of nitration and deuteriation that the process proceeds *via* the highly reactive enolic forms **1′** and **2′**. However, these cannot be detected in sulfuric acid solutions by ^{1}H and ^{13}C NMR spectroscopy: compound **1** exists almost wholly in the ketonic form within the limits of the sensitivity of the NMR method.

Measurements of the rates of deuteriation in D_2SO_4 established that the enolisation of the ketones **1** involves not only the CH_2 unit of compound **1′** but also proceeds at fairly high rates *via* an undesirable pathway involving the CH_3 group of compound **1″**.

As the electron-accepting properties of the ring are

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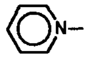
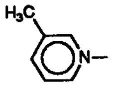
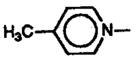
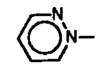
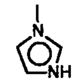
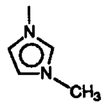
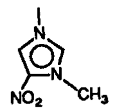
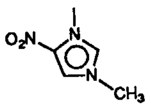
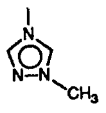
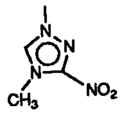
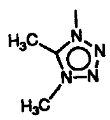
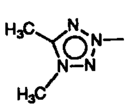
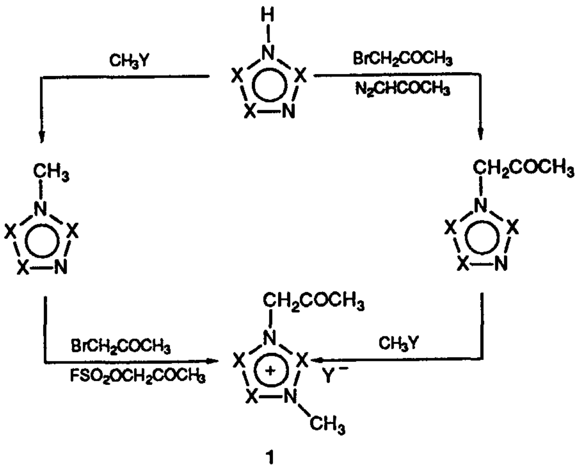
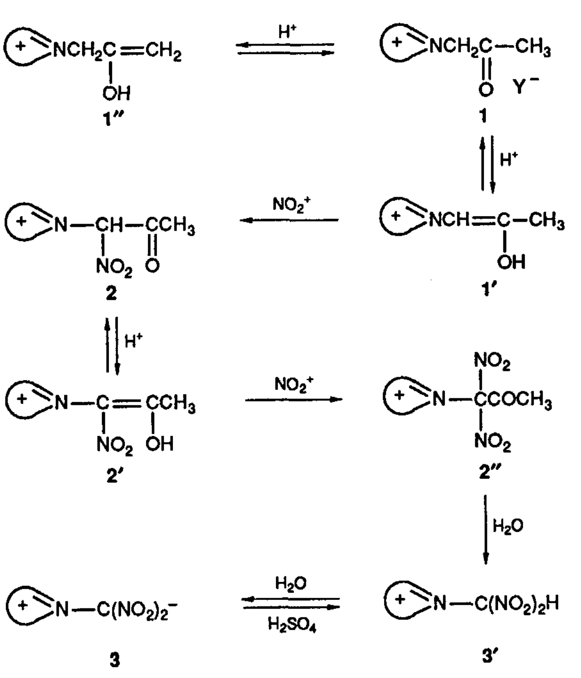
‡ Other *N*-acetonyl derivatives can also be used successfully.

Table 1 *N*-Dinitromethylides synthesised

	X^+-$C(NO_2)_2^-$ X	Nitration yield (%)	Nitration conditions T/°C (t/h)	DTA, T/°C onset of decomp. (intense decomp.)	UV spectrum, λ_{max}/nm (ϵ) (in H_2O)	IR spectrum ν/cm^{-1} $C(NO_2)_2^-$ (in KBr)	^1H NMR spectrum δ (ppm) of $CH(NO_2)_2$ (in H_2SO_4)	pK_a of **3'** (in H_2O–H_2SO_4 at 20°C)
a		43	70 (2.0)	128 (130)	344 (17300)	1245, 1494, 1509		−1.7
b		38	70 (0.5)	198 (216)	344 (17600)	1245, 1500		
c		35	70 (2.0)	180 (206)	344 (17800)	1230, 1245, 1495		
d		20	60 (0.5)	94 (130)	338.5 (15800)	1245, 1270, 1482		
e		5	60–70 (1.5)	90 (133)	347 (13700)	1220, 1495		+0.05
f		30	50–60 (1.5)	198 (216)	347 (17200)	1240, 1508	8.04	−0.1
g		48	60–65 (1.2)	161 (167)	342.5 (16500)	1242, 1260, 1495	8.24	−1.0
h		25	50–60 (1.0)	155 (192)	342 (15400)	1235, 1260, 1485, 1497	8.62	−2.25
i		18	65–70 (0.5)	127 (175)	343 (14400)	1225, 1274, 1500	8.33	−0.95
j		32	50–60 (0.7)	72 (105)	332 (15300)	1240, 1280, 1497	8.48	
k		30	70 (0.5)	84 (100)	332 (15600)	1245, 1501	8.70	−3.4
l		35	60–65 (0.8)	198 (200)	332 (16700)	1285, 1305, 1500	8.78	−2.5



X = CH, N
Y = I, CH_3SO_4, FSO_3



enhanced, the rate of CH_2 enolisation, the fraction of the CH_2 enol, and the rate of nitration increase. As the acidity of the medium is reduced (as a result of dilution of the acid with water), the rates of enolisation involving the CH_3 and CH_2 groups diminish, but not in proportion, which results in a sharp increase in the fraction of the CH_2 enols **1′**. The principal reaction condition is associated with this factor: nitration should be carried out as a rule in media containing a large amount of water (in the 75–80% H_2SO_4 concentration range) where the enolisation involving the CH_3 group and the nitration of the latter take place to a lesser extent. Furthermore, in dilute media other side reactions also occur to a lesser extent: the cleavage of the intermediate ketone **2** and the nitration of the $CH(NO_2)_2$ fragment with formation of unstable trinitromethyl compounds. The structure of the ylides **3** was established by IR, UV and ^1H, ^{13}C and ^{15}N NMR spectroscopy.[7,8]

The spectroscopic characteristics of the *gem*-dinitromethyl fragments of the ylides **3** and of their conjugate acids are presented in Table 1. The dinitrocarbanionic fragment in compound **3** has a planar structure and, according to X-ray diffraction data and comparison of its acid – base properties, has rotated relative to the plane of the heterocycle by an angle greater than 70° (*cf.* refs. 4*a* and 4*b*).

The majority of the ylides **3** dissolve without decomposition in sulfuric acid to form azolium and azinium salts **3′**, which involves protonation at the carbon atom of the dinitrocarbanionic fragment.§ The dissociation constant of compound **3′** in water was determined spectrophotometrically from the dependence of the absorption maximum of the $C(NO_2)_2^-$ fragment on the acidity of the medium.

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§ *General method for the synthesis of azolium and azinium dinitromethanides.* The appropriate salt **1** (2 g) was dissolved in 12 ml of sulfuric acid ($d = 1.83$). In the case of the bromides and iodides, the evolved hydrogen halides and traces of bromine were removed at a reduced pressure on a rotary evaporator and the precipitated iodine was filtered off. Whilst cooling with ice (5–10°C), the resulting solutions were treated dropwise with 5 ml of water and then with 5 ml of nitric acid ($d = 1.5$). The reaction mixture was heated under the conditions indicated in Table 1, cooled, and, whilst stirring vigorously, poured into 100 g of finely-ground ice. The segregated deposit (segregation sometimes occurred only after 1–2 h) was filtered off, washed with water, methanol and diethyl ether and dried in air. Analytically pure ylides **3** were obtained. If necessary, they were further purified by reprecipitation from sulfuric acid with water.