

Generation of an *N*-Isocyanatoimine and its Cycloadditions leading to Sterically Stabilised Zwitterions

David W. Jones

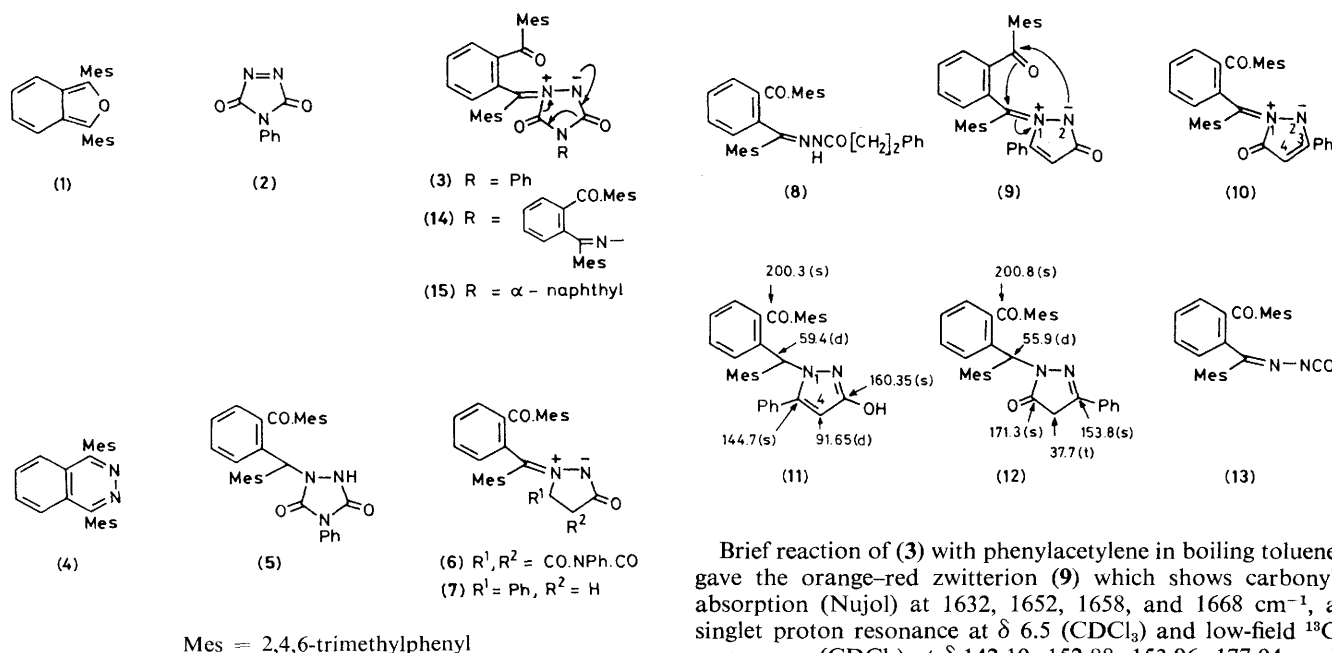
Organic Chemistry Department, The University, Leeds LS2 9JT, U.K.

The reaction between 1,3-dimesitylbenzo[*c*]furan and 4-phenyltriazoline-3,5-dione affords a sterically stabilised zwitterion that at 110 °C decomposes to the *N*-isocyanatoimine (**13**) which adds to olefinic and acetylenic traps to form stable zwitterions of the type (**6**) and (**9**), respectively; (**9**) isomerises to (**10**) at 110 °C.

Although 1,3-diphenylbenzo[*c*]furan is a reactive Diels–Alder diene, 1,3-dimesitylbenzo[*c*]furan (**1**) is inert to several dienophiles even under forcing conditions. Newman¹ therefore proposed that the observed additions to 1-mesityl-3-phenylbenzo[*c*]furan were two-step processes involving diradical or zwitterionic intermediates. We describe the ‘foiled’ Diels–Alder addition of (**1**) to 4-phenyltriazoline-3,5-dione (**2**). This

gives the zwitterion (**3**) which is clearly derived from the kind of dipolar Diels–Alder intermediate envisaged by Newman.

The orange crystalline product (**3**) is formed rapidly in high yield (>90%) by mixing equimolar quantities of the reactants at or below 20 °C; it shows carbonyl absorption (Nujol) at 1723 and 1804 cm^{−1} similar to that observed for the unstable zwitterions formed from diazoalkanes and (**2**)² as well as

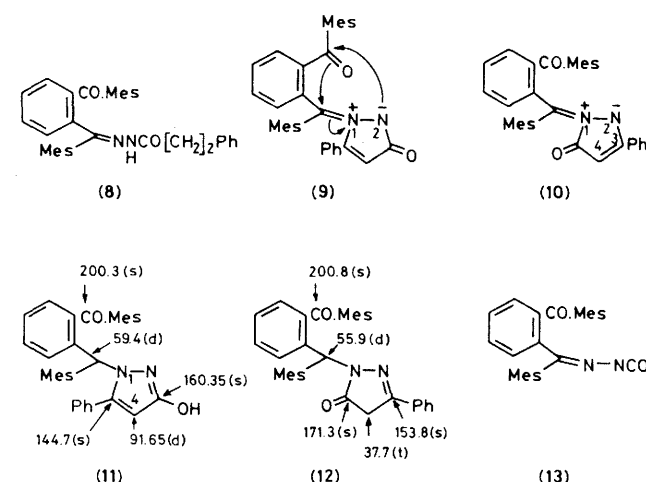


absorption for the diaryl ketone (1670 cm^{-1}). The ^{13}C -spectrum of (3) (CDCl_3 , -50°C) showed resonance for the diaryl ketone (δ 199.25 p.p.m.) as well as peaks at δ 157.11, 153.7, and 149.89 p.p.m.† for the imide carbonyls and the iminium carbon, but apart from methyl resonances (δ 19.44–21.56 p.p.m.) includes no resonance above δ 125 p.p.m.; the observed shifts show that the ketone oxygen is not intimately involved in stabilising the positive charge at the iminium carbon.

Presumably because of extreme steric protection of the iminium carbon, (3) fails to show the chemical reactions characteristic of related 1,3-dipoles.² Reactions with both nucleophiles and dipolarophiles take an unusual course. Thus with sodium methoxide in methanol (3) gives the phthalazine (4) and methyl phenylcarbamate, and acid hydrolysis of (3) ($\text{HCl}-\text{H}_2\text{O}-\text{HOAc}$) gives (4) and only a little *o*-dimesitylbenzene. These reactions are understandable if nucleophilic attack upon (3) occurs at the carbonyl of the acyl-iminium system rather than at the iminium carbon itself. In contrast, reduction of (3) with sodium dithionite proceeds readily to give the expected urazole (5).

Reaction of (3) with *N*-phenylmaleimide in boiling toluene did not produce the expected product of 1,3-dipolar addition. Instead a new yellow azomethine imine (6) resulted. Similar products were formed from cyclo-octa-1,5-diene, norbornadiene, and styrene. The styrene product (7) showed carbonyl absorption at $1670\text{ (br.) cm}^{-1}$, proton resonances (CDCl_3) at δ 2.72 (1H, dd, J 16.6 and 4 Hz), 3.21 (1H, dd, J 16.6 and 10 Hz), and 5.20 (1H, dd, J 10 and 4 Hz), and carbon resonances (CDCl_3) at 40.66 (CH_2), 72.09 (CH), 142.99 ($>\text{C}=\text{N}^+$), 182.39 ($>\text{C}=\text{O}$), and 198.08 p.p.m. ($>\text{C}=\text{O}$). Reduction of (7) (H_2 -Pd/C-EtOAc) gave the hydrogenolysis product (8) which was hydrolysed ($\text{KOH}-\text{EtOH}-\text{H}_2\text{O}$) to the phthalazine (4) and β -phenylpropionic acid.

† The peak at δ 149.89 p.p.m. is tentatively assigned to the iminium carbon. This agrees with the shift of that carbon in a closely related zwitterion; we thank Professor M. Regitz for this unpublished information (see ref. 2b).



Brief reaction of (3) with phenylacetylene in boiling toluene gave the orange-red zwitterion (9) which shows carbonyl absorption (Nujol) at 1632, 1652, 1658, and 1668 cm^{-1} , a singlet proton resonance at δ 6.5 (CDCl_3) and low-field ^{13}C resonances (CDCl_3) at δ 142.10, 152.88, 153.96, 177.04, and 199.47 p.p.m. Upon heating (9) in boiling toluene the green zwitterion (10) is formed. This shows carbonyl absorption at 1740 and 1672 cm^{-1} , a singlet proton resonance at δ 4.98 and carbon resonances at δ (CDCl_3) 197.65 (s), 177.69 (s), 170.05 (s), 159.81 (s), and 74.30 (d) p.p.m.‡ Reduction of (9) and (10) [$\text{Na}_2\text{S}_2\text{O}_4-\text{H}_2\text{O}-(\text{CH}_2\text{OMe})_2$] gives the pyrazolones (11) and (12), respectively. ^{13}C -Shifts and assignments are appended to structures (11) and (12) and agree with the available data.^{3§} The pyrazol-3-one (11) is as expected⁴ formed by base-catalysed rearrangement ($\text{NaOPr}^n-\text{Pr}^n\text{OH}$) of the styrene adduct (7). Whilst (12) shows carbonyl absorption at 1710 and 1660 cm^{-1} (Nujol) the high-frequency band disappears in dimethyl sulphoxide which favours the OH-tautomer.⁵

It is likely that formation of (6), (7), and (9) from (3) involves initial expulsion of phenyl isocyanate (3; arrows) to give the *N*-isocyanatoimine (13) which then adds an olefin or an acetylene molecule to give the mono-adducts of type (6) or (9). Azines are known to undergo 'criss-cross' addition involving two molecules of a dipolarophile.⁶ For (6), (7), and (9) steric effects presumably block the addition of a second molecule of the olefin or acetylene. In agreement with the intermediacy of (13) the mass spectrum of (3) includes a strong ($M - \text{PhNCO}$) peak and heating (3) ($> 200^\circ\text{C}$) gives the phthalazine (4) in high yield; the reaction leading from (13) to (4) is merely an intramolecular version of the long-known reaction of ketones with isocyanates.⁷ In boiling toluene in the absence of a trap (3) is converted to a small extent into the dimer (14) of (13). Moreover both (3) and (14) react with α -naphthyl isocyanate in boiling toluene to give (15).

An attractive route for the conversion of (9) into (10) involves complete formation of the benzo[c]furan-3,4-diazacyclopentadienone adduct *e.g.* as indicated in (9; arrows) followed by a partial reverse Diels-Alder addition cleaving the

‡ The high-field position of C-4 in (10) (δ 74.30 p.p.m.) is attributable to electron supply from N-2; cf. the shift of C-4 in (11).

§ The spectrum of (12) was measured in CDCl_3 and that of (11) in $(\text{CD}_3)_2\text{SO}$ containing C_6D_6 . The high-field position of the benzydrylic carbons in (11) and (12) is accompanied by a deshielding of the benzydryl protons (*ca.* δ 7.8 p.p.m., CDCl_3). Both effects may be due in part to the close proximity of the benzydryl proton and the oxygen atom of the diaryl ketone.

remaining bond to N-1. Alternative mechanisms, *e.g.* one involving a diaziridine intermediate, are also possible.

The results described here and elsewhere⁸ suggest that *N*-isocyanatoimines are reactive molecules which participate readily in cycloaddition and electrocyclic reactions; their generation by reverse cycloaddition is one way in which they may be further studied. Although the reactions of furans with aza-dienophiles apparently proceed normally,^{9a} the present results suggest that reappraisal of some of the earlier work may be necessary. Nitrosocarbonyl compounds react reversibly with furans to give products of furan ring-opening easily rationalised *via* zwitterion intermediates.^{9b}

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