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SYNTHESIS OF *ANHYDRO*-3-PHENYL-5-DICYANOMETHYL-1,2,3-OXADIAZOLIUM HYDROXIDE. AN *EXO*-METHYLENE ANALOG OF SYDNONE

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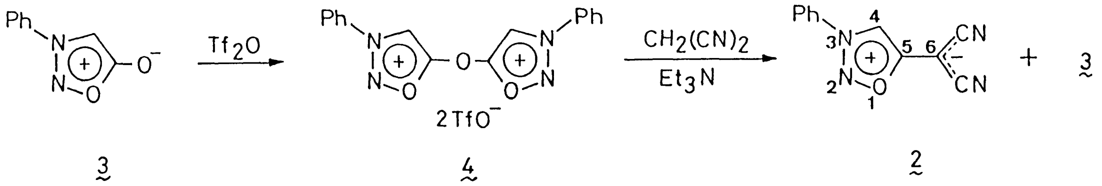
As the first *exo*-methylene analog of sydnone, the title compound was synthesized by the treatment of 3-phenylsydnone with trifluoromethanesulfonic anhydride followed by the reaction with malononitrile-triethylamine. The electronic structure is discussed on the basis of the spectroscopic evidences.

Sydnone is known as a representative of meso-ionic compounds and the chemistry of sydnone and the related meso-ionic heterocycles has widely been studied.[1)] However, the *exo*-methylene analog of sydnone, in which the carbonyl oxygen is replaced by a carbanionoid group, has been hitherto unknown. This novel cross-conjugated electron system is of interest not only as a model to examine the aromaticity of the sydnone system but also as a meso-ionic analog of heptafulvene.[2)] Here, we describe the synthesis of the first example of the *exo*-methylene analog of sydnone.

As an accessible approach to the *exo*-methylene analog of sydnone, base-induced condensation of 3-phenyl-5-ethoxy-1,2,3-oxadiazolium tetrafluoroborate (**1**)[3)] with active methylene compounds seemed to be appropriate. Because, several meso-ionic compounds in which the negative charge is associated with a carbanionoid group have been prepared in this manner.[2)] However, all attempts to synthesize *anhydro*-3-phenyl-5-dicyanomethyl-1,2,3-oxadiazolium hydroxide (**2**) by the reaction of **1** and malononitrile under various conditions gave no evidence for the formation of the desired product. The synthesis of **2** was eventually achieved by the following method.

To a stirred solution of 3-phenylsydnone (**3**) in dichloromethane was added trifluoromethanesulfonic anhydride at room temperature. The white precipitate of the dicationic ether salt (**4**) deposited within 5 min. Although the extreme moisture-sensitivity prevented the full characterization, the structure of **4** was deduced by the IR and ^{19}F NMR spectra.[4)] Further reaction of **4** with malononitrile in the presence of triethylamine at -78 °C for 30 min gave an orange reaction mixture. Purification by column chromatography on silica gel followed by recrystallization from acetonitrile-ether gave orange cubes of **2**, mp 219 °C (decomp), in 22% yield.



3 **4** **2**

The meso-ion (2) is stable to air and the elemental analysis agreed with the proposed structure; Found: C,63.15;H,2.66:N,26.61%. Calcd for $C_{11}H_6N_4O$: C,62.85; H,2.88;N,26.66%. The mass spectrum showed an intense molecular ion peak at m/z 210 indicating the large stability of this electronic system. The IR spectrum revealed a strong absorption at 1594 cm^{-1} which can be assigned to the stretching mode of the *exo*-cyclic carbon-carbon bond. The CN stretching vibrations appeared at 2201 and 2175 cm^{-1}. The ^1H NMR spectrum of 2 in $CDCl_3$ showed a complex multiplet of the phenyl protons at δ 7.88 - 7.74 and a sharp singlet of the 1,2,3-oxadiazolium ring proton at δ 7.69. The latter signal is much more deshielded than the corresponding proton of 3-phenylsydnone (3) (δ 6.78),[5] suggesting the lower electron density on the five-membered ring of 2. This fact is also supported by the ^{13}C NMR analysis. As summarized in Table 1, the C-4 carbon of 2 resonates at lower magnetic field (109.8 ppm) than that of 3 (94.9 ppm). On the contrary, the *exo*-methylene carbon (C-6) resonates at very high field (33.9 ppm) due to the high electron density on this carbon. These spectral properties suggest the significant contribution of the dipolar canonical structure (2) to the resonance hybrid. It is worthy to note that the chemical shift of the *exo*-methylene carbon of 8,8-dicyanoheptafulvene, the isoelectronic system with 2, is 70.1 ppm.[6] In the electronic spectrum of 2 measured in acetonitrile, three absorption maxima were observed: λ_{max} 220 nm (log ε 3.78), 268 (4.49), and 417 (3.99). The longest-wavelength band shows a pronounced solvatochromy: 417 nm (MeCN), 421 (EtOH), 432 (CH_2Cl_2), and 442 (Et_2O), in agreement with the formulation of the meso-ionic structure (2).

Table 1. ^{13}C NMR chemical shifts[a] of 2 and 3

	C-4	C-5	Phenyl				C-6	CN
			ipso	ortho	meta	para		
2	109.8	174.2	132.5	130.3	122.4	133.3	33.9	115.6
3	94.9	168.5	134.5	130.1	121.5	132.4	—	——

a) In d_6-DMSO.

References

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3) K.T.Potts, E.Houghton, and S.Husain, J. Chem. Soc., Chem. Commun., 1970, 1025.
4) Similar dicationic ether salts have been prepared by the reaction of activated ketones with trifluoromethanesulfonic anhydride [P.J.Stang, G.Maas, D.L.Smith, and J.A.McCloskey, J. Am. Chem. Soc., 103, 4837 (1981)], but the present work is the first example using a meso-ionic compound as activated ketone.
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