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CYCLOADDITION REACTION OF SYDNONE AND MALEIMIDE

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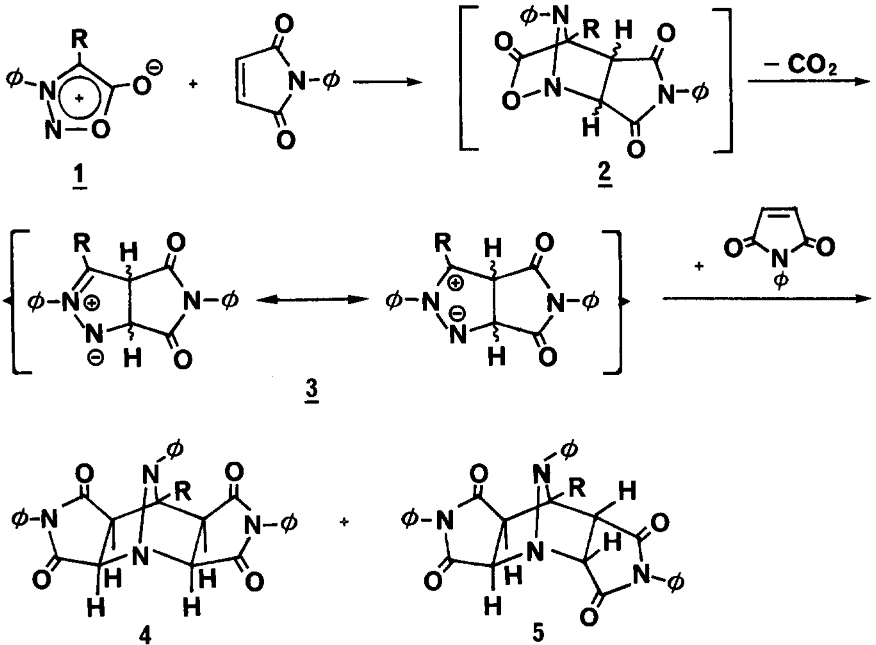
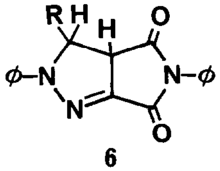
SUMMARY: The cycloaddition of sydnone to maleimide afforded exclusively two isomeric 1:2-adducts. This bifunctional character of sydnone allows its reaction with bismaleimides to form novel polyimides.

The 1,3-dipolar cycloaddition of mesoionic sydnones (1) to olefinic double bonds to form substituted Δ^2-pyrazolines or pyrazoles has been extensively studied.[1] The reaction involves the initial formation of an unstable 1:1 primary adduct which eliminates carbon dioxide and followed either by a 1,3-proton shift to form a Δ^2-pyrazoline, or by a further elimination of a neutral molecule to form a pyrazole as the final stable product. Only in one case, the reaction of 3-phenyl sydnone and acenaphthylene, a bisadduct was formed in addition to pyrazoline. The bisadduct is the result of the reaction of one mole of sydnone with two moles of acenaphthylene.[2] The intramolecular double cycloaddition of azomethine-imine derived from sydnone to the two double bonds of a diene to give low to moderate yields of double adducts also have been reported.[3]

It is now found that the addition of 3-phenyl sydnone (1, R=H) to N-phenylmaleimide affords exclusively bisadducts in practically quantitative yield regardless of the ratio of the reactants. Upon heating of a toluene solution of 10 mmol of 3-phenylsydnone and 25 mmol of N-phenylmaleimide at 95°, carbon dioxide was generated and after 6 hours two isomeric bisadducts, 7-phenyl-1,7-diaza-bicyclo[2.2.1]heptane-exo-2,3-exo-5,6-tetracarboxylic acid bisphenylimide (4, R=H)[4] and 7-phenyl-1,7-diaza-bicyclo[2.2.1] heptane-endo-2,3-exo-5,6-tetracarboxylic acid bisphenylimide (5, R=H)[5] in 87:13 ratio were isolated in 99% yield. No other products, such as the endo,endo-bisadduct or the expected pyrazoline 6 (R=H) were obtained. Also not formed was the tetrazine 7 (R=H), which is the dimer of azomethine-imine 3. Examples of such dimerization of azomethine-imine to 1,2,4,5-tetrazine derivative have been reported.[6] The configurations of the two isomeric bisadducts were determined by ^{1}H nmr: The spectrum of the endo,exo-adduct 5 (R=H) showed a 5.6 Hz coupling of the bridgehead proton (H4) with the exo-proton (H3) but no coupling with the endo-proton (H5) of the diazanorbonane ring. Whereas in the spectrum of the exo,exo-isomer 4 (R=H), the bridge head proton (H4) was not coupled with the two endo-protons (H3 and H5) and therefore appeared as a singlet.[7]





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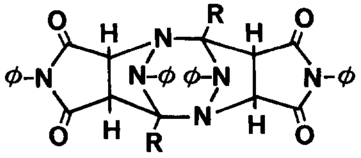

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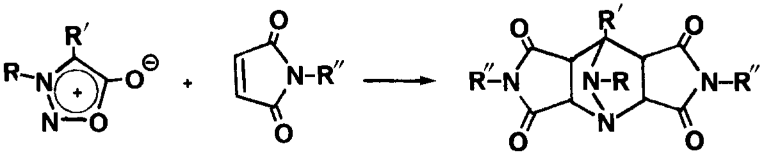
It was surprising to find that when this reaction was carried out with large excess of 3-phenyl sydnone instead of excess of maleimide (3-phenyl sydnone: N-phenylmaleimide = 2:1), the products were still 4 (R=H) and 5 (R=H), again no pyrazoline 6 (R=H) was formed. This result indicates that the second cycloaddition, the trapping of the intermediate azomethine-imine 3 (R=H) by the highly reactive maleimide, is extremely fast. It is faster than both the first cycloaddition to form the primary adduct 2 (R=H) and the energetically unfavorable 1,3-proton shift of 3 (R=H) to form pyrazoline 6 (R=H) with a strained double bond.

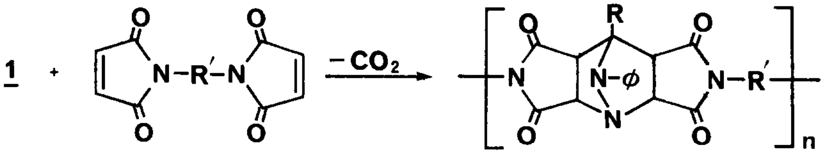
In an attempt to suppress the formation of the bisadducts by steric effect, a reaction of 3,4-diphenyl sydnone (1, R=C_6H_5) with N-phenylmaleimide was carried out, hoping that the replacement of the hydrogen at C3 of intermediate 3 (R=C_6H_5) and those at the bridge head of bisadducts 4 (R=C_6H_5) and 5 (R=C_6H_5) by a phenyl group would create sufficient steric hindrance to slow down or even prevent the second cycloaddition. However, these steric effects failed to suppress the formation of the bisadducts and to promote that of the pyrazoline 6 (R=C_6H_5). Although the addition reaction was slow at 110°, the products were again 4 (R=C_6H_5) and 5 (R=C_6H_5).

This double cycloaddition of sydnone to maleimide to form two isomeric bisadducts appears to be a general reaction. Preliminary results indicate that the reaction of several sydnones with maleimides, as listed in the following table, all gave high yields of two bisadducts.



R	R'	R''	% Yield of endo,exo- and exo,exo-bisadducts
C_6H_5	H	C_6H_5	99
C_6H_5	H	p-$C_6H_4CH_3$	96
C_6H_5	H	CH_3	96
C_6H_5	H	H	94
C_6H_5	C_6H_5	C_6H_5	84
n-C_3H_7	C_2H_5	C_6H_5	81

The bifunctional character of sydnone in this reaction allows its reaction with bismaleimides (8) to form polyimides (9), which have good thermal stability and mechanical properties. This novel polymerization reaction will be discussed in a separate paper.



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1. Gotthardt, H., Huisgen, R., Chem. Ber. (1968) 101, 552; Huisgen, R., Grashey, R., Gotthardt, H., ibid. 829; Huisgen, R., Gotthardt, H., ibid, 839; Vasil'eva, V.F., Yashunskii, V.G., Shchukina, M.N., Zh. Obshch. Khim (1960) 30, 698; ibid. (1961) 31, 1051; ibid. (1964) 33, 3706.

2. Huisgen, R., Gotthardt, H., Grashey, R., Angew. Chem. Intern. Ed. (1962) 1, 49; also the first paper in 1.

3. Weintraub, P.M., Chem. Comm. (1970) 760; Haneda, A., Imagawa, T., Kawanisi, M., Bull. Chem. Soc. Japan, (1976) 49, 748.

4. Bisadduct 4 (R=H): mp 286-287°; $C_{27}H_{20}N_4O_4$ (464.46) calc. C 69.81 H 4.34 N 12.06; found C 69.91 H 4.37 N 12.17; ^{1}H nmr (DMSO-d6/$CDCl_3$) δ 3.55 (d, $J_{3,2}$ and $J_{5,6}$ = 6.4 Hz, H3, 5), 4.50 (d, $J_{2,3}$ and $J_{6,5}$ = 6.4 Hz, H2,6), 5.53 (s, H4), 6.56 - 7.35 (m, aromatic); IR (KBr) 3060, 1780, 1720, 1595, 1495, 1380 and 1200 cm^{-1}.

5. Bisadduct 5 (R=H): mp 271-272.5°; $C_{27}H_{20}N_4O_4$ (464.46) calc. C 69.81 H 4.34 N 12.06; found C 69.34 H 4.46 N 11.89; ^{1}H nmr (DMSO-d_6/$CDCl_3$) δ 3.35 (d, $J_{5,6}$=6.4 H_z, H5), 3.68 (dd, $J_{2,3}$=8.6 Hz $J_{3,4}$=5.6 H_z H3), 4.32 (d, $J_{6,5}$=6.4 Hz H6), 4.60 (d, $J_{2,3}$=8.6 Hz H2), 5.37 (d, $J_{4,3}$=5.6 Hz H4), 7.0 - 7.5 (m, aromatic); IR(KBr) 3060, 1780, 1720, 1595, 1490, 1375 and 1195 cm^{-1}.

6. Schmitz, E., Chem. Ber., (1958) 91, 1495; Huisgen, R., Grashey, R., Laur, P., Leitermann, H., Angew. Chem (1960) 72, 416; Grashey, R., Huisgen, R., Sun, K.K., Moriarty, R.M., J. Org. Chem (1965) 30, 74.

7. The nmr assignments of the bisadducts are based on the conformational determination of similar ring systems, such as bicyclo [2.2.1] heptane and its heterocyclic analogues. See references cited in Section 6.6 of "Application of ^{1}H Nuclear Magnetic Resonance Spectroscopy to the Conformational Analysis of Cyclic Compounds". Kowalewski, V.J., in "Progress in NMR Spectroscopy" Vol. 5, Emsley, J.W., Feeney, J., Sutcliffe, L.H., ed., Pergamon Press, 1969.

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