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REPLACEMENT OF DIPOLAROPHILE OF 1,3-CYCLOADDUCT

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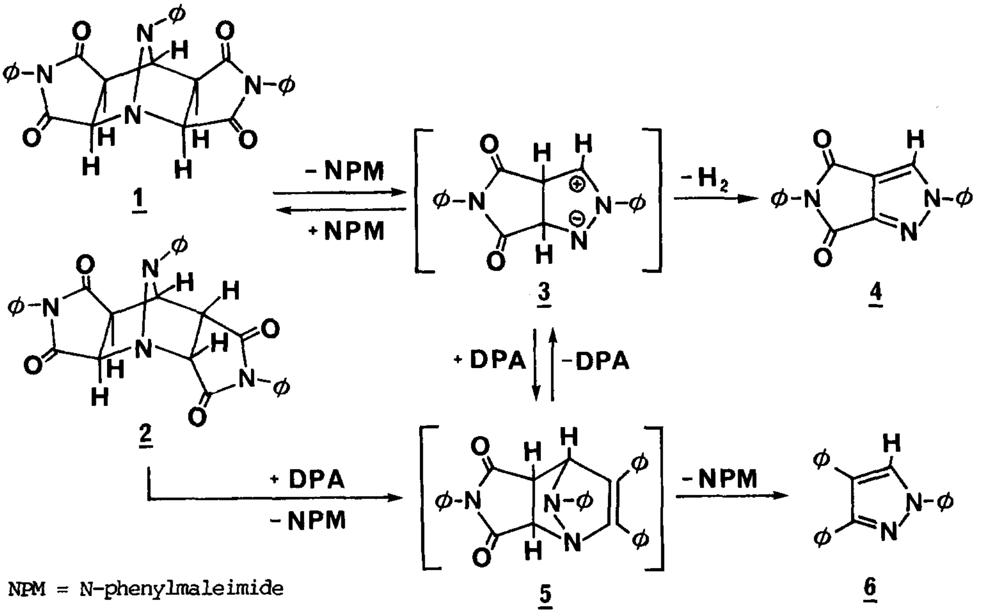
Summary: Novel double 1,3-cycloreversion and the replacement of dipolarophile of the bisadducts of 3-phenyl sydnone and N-phenylmaleimide are described.

The double 1,3-cycloaddition of 3-phenylsydnone to two molecules of N-phenylmaleimide to form carbon dioxide and two isomeric bisadducts, the bisphenylimide of isomeric 7-phenyl-1,7-diaza-bicyclo [2.2.1] heptane-2,3,5,6-tetracarboxylic acid, (1 and 2) has been discussed in the previous report.[1] This communication describes the reversibility of this cycloaddition and the further reaction of the regenerated azomethine-imine (3) of this cycloreversion.

Upon heating of bisadduct 1 or 2 at 310° under 0.1 mm Hg, a retro-1,3-cycloaddition took place to give a distillate which contained 95% yield of N-phenylmaleimide and 70% yield of 2,5-diphenyl pyrrolo [3,4-c] pyrazole-(2H,5H)-4,6-dione (4)[2]. In this thermal reaction the intermediate (3) which was regenerated from the cycloreversion has eliminated a molecule of hydrogen to form pyrazole 4. Many examples of similar aromatizations of cyclic azomethine-imines to pyrazole derivatives by the elimination of a neutral molecule such as hydrogen have been reported.[3]

When the thermal cleavage of 1 or 2 was carried out in the presence of diphenylacetylene and under atmospheric pressure, in addition to 4 and some minor unidentified products, another pyrazole derivative, 1,3,4-triphenylpyrazole (6)[4] was formed. It was identified by comparison with the reaction product of 3-phenylsydnone and diphenylacetylene.[5] In this reaction, the regenerated N-phenylmaleimide remained in the reaction mixture and polymerized to a yellow solid. Pyrazole 6 became a major product when 1 or a mixture of 1 and 2 was heated with 20 equivalents of diphenylacetylene at 150° for 40 min. A 52% yield of 6 and a 17% yield of 4 were isolated by column chromatography.[6] The formation of 6 is believed to be the result of another 1,3-cycloreversion reaction, the elimination of N-phenylmaleimide from intermediate 5, which in turn, is a cycloadduct of 3 and diphenylacetylene.



NPM = N-phenylmaleimide

DPA = Diphenylacetylene

The formation of 6 by the reaction of diphenylacetylene and the bisadduct is a unique example of a trans-1,3-cycloaddition reaction, in which the dipolarophile moeity of a 1,3-adduct is replaced by another dipolarophile. The fact that bisadducts 1 and 2 are stable up to around 300° and do not undergo detectable change at 150°, the mechanistic aspect of the formation of 6 and 4 at 150° is being studied and will be discussed in the future.

References and Notes:

1. See the preceding communication.
2. Pyrazole 4: mp 240-241°(DMF/chloroform); $C_{17}H_{11}N_3O_2$(289.28) calc. C 70.58 H 3.83 N 14.53; found C 69.75 H 3.96 N 14.30; ^{1}H nmr (DMSO-d6) δ 9.1 (s, H3), 7.4-8.1 (M, aromatic 10H); IR(KBr) 3060, 1790, 1775, 1490, 1355 and 755 cm^{-1}.
3. Huisgen, R., Gotthardt, H., Chem. Ber. (1968) 101, 839; Huisgen, R., Grashey, R., Gotthardt, H., ibid. 829; Vasil'eva, V.F., Yashunskii, V.G., Shchukina, M.N., Zh.Obshch. Khim. (1960) 30, 698; ibid. (1961) 31, 1051; ibid. (1964) 33, 3706.
4. Pyrazole 6: mp 96-97°; $C_{21}H_{16}N_2$(296.36) calc. C 85.10 H 5.44 N 9.45; found C 85.02 H 5.57 N 9.42; ^{1}H nmr ($CDCl_3$) δ 7.96 (s, H5), 7.15-7.83 (m, aromatic 15H).
5. Bacchetti, T., Salvatori, T., Palladino, N., Chemica e Ind. (Milan) (1964) 46,1337; Husigen, R., Gotthardt, H., Grashey, R., Chem. Ber. (1968) 101, 536.
6. Silica gel column; mixture of toluene and hexanes as eluting solvent.

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