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THERMOLYSES OF STRAINED 1,2,5-OXADIAZOLES AND 1,2,5-THIADIAZOLES OF THIANORBORNANE SERIES[1]

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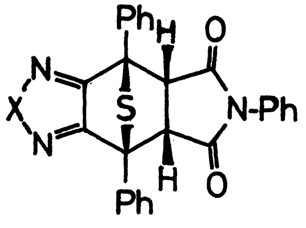
Thermolysis of stereoisomeric 4-oxa-13-thia-3,5,10-triaza-1,7,10-triphenyltetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]trideca-2,5-diene-9,11-diones, which are cycloadducts of 4,6-diphenylthieno[3.4-c]-1,2,5-oxadiazole to N-phenylmaleimide, under mild conditions results in ring cleavage of the oxadiazole ring to nitrile and nitrile oxide moieties which can be trapped as 1,3-cycloadducts to dimethyl acetylenedicarboxylate. On the other hand, analogous strained adducts obtained from 4,6-diphenylthieno[3.4-c]-1,2,5-thiadiazole and N-phenylmaleimide undergo a retro-cycloaddition reaction.

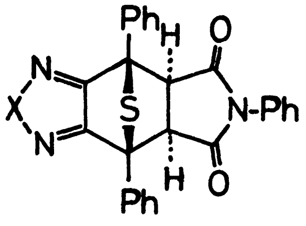
Upon thermolysis (≥300°C)[2] and photolysis[3] 3,4-diphenyl-1,2,5-oxadiazole has been shown to yield benzonitrile and benzonitrile oxide. Recently, it has been demonstrated that thermolysis of strained 1,2,5-oxadiazole N-oxides of the norbornane series results in fragmentation of the oxadiazole ring under rather mild conditions.[4,5]

Previously,[6] we have reported the preparation of strained 1,2,5-oxadiazoles of the thianorbornane series by the reaction of 4,6-diphenylthieno[3.4-c]-1,2,5-oxadiazole, a nonclassical 10π-electron condensed thiophene, with olefins.

In the present paper we wish to report that thermolysis of such strained oxadiazoles, 4-oxa-13-thia-3,5,10-triaza-1,7,10-triphenyltetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]trideca-2,5-diene-9,11-diones 1 and 2



1 (X=O)
3 (X=S)



2 (X=O)
4 (X=S)

under mild conditions results in ring cleavage to the nitrile and nitrile oxide moieties which can be trapped in good yields as 1,3-dipolar cycloadducts to dimethyl acetylenedicarboxylate (DMAD). In this context, thermolysis of analogous strained 1,2,5-thiadiazole derivatives 3 and 4[7] is also described.

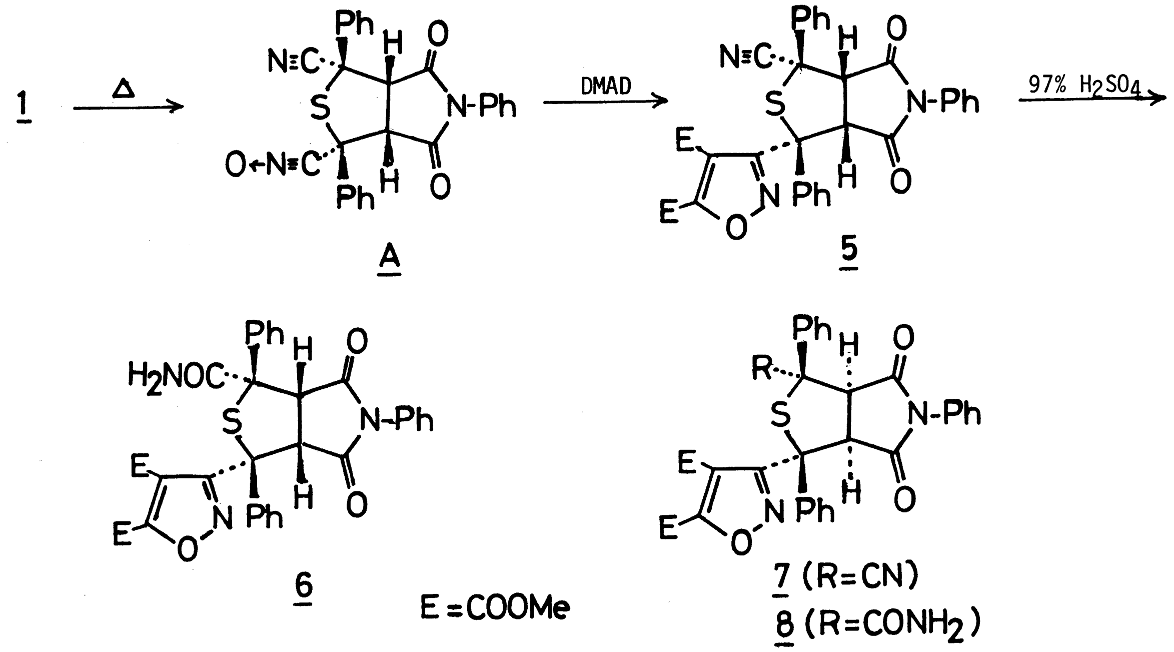
When a solution of equimolar amounts of the endo-adduct 1 and DMAD in xylene was refluxed under nitrogen for 8 h, the 1:1 adduct 5, mp 191.5-192.5°C, as colorless prisms (from EtOH) was obtained in 74% yield.[8]

5: IR (KBr) 2220 (very weak), 1780, 1720 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.42, 3.95 (each s, 3H), 4.91, 5.08 (each d, 1H, J=11 Hz), 7.2-8.0 (m, 15H); MS m/e 593 (M^+).

The presence of cyano group in 5 was confirmed by the result of hydrolysis. Hydrolysis of 5 by using 97% sulfuric acid (at 40°C, 1 h) was ultimately attained, the corresponding carbamoyl derivative 6, mp 257-258°C (dec.), as colorless needles (from MeOH) being formed in 80% yield.

6: IR (KBr) 3500, 3400, 1740, 1720, 1690 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.45, 3.90 (each s, 3H), 4.43, 4.99 (each d, 1H, J=10 Hz), 6.2-6.5 (broad, 2H, exchanged with D_2O), 6.9-7.9 (m, 15H); MS m/e 611 (M^+).

On the basis of above spectral data and of the chemical conversion, 5 was deduced to be 1-cyano-3-[3-{4,5-bis(methoxycarbonyl)isoxazolyl}]-syn-cis-syn-1,3,5-triphenylperhydrothieno[3.4-c]pyrrole-4,6-dione which would be formed through a 1,3-dipolar cycloaddition process of the nitrile oxide moiety in A to DMAD (Scheme 1). The suggested structure for 5 was confirmed by its X-ray diffraction study.[9]



Scheme 1

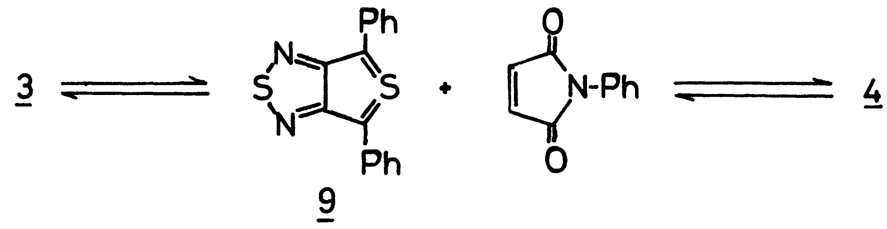
Similarly, the exo-adduct 2 reacted with DMAD under similar conditions (16 h) to give 92% yield of the anti-cis-anti isomer 7, mp 251-253°C (dec.), as colorless needles (from MeOH). Hydrolysis of 7 with 97% sulfuric acid afforded 81% yield of the corresponding carbamoyl derivative 8, mp 204-205°C, as colorless prisms (from MeOH).

7: IR (KBr) 2220 (very weak), 1790, 1720 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.49, 3.91 (each s, 3H), 4.52, 5.26 (each d, 1H, J=7.2 Hz), 6.9-8.0 (m, 15H); ^{13}C NMR (DMSO-d_6) δ 55.5, 63.5 (quaternary C), 115.4 (isoxazole ring C-4), 119.9 (C≡N), 155.7, 159.3 (isoxazole ring C-3, C-5), 160.6, 164.5 (ester C=O), 169.3, 170.8 (imide C=O); MS m/e 593 (M$^+$).

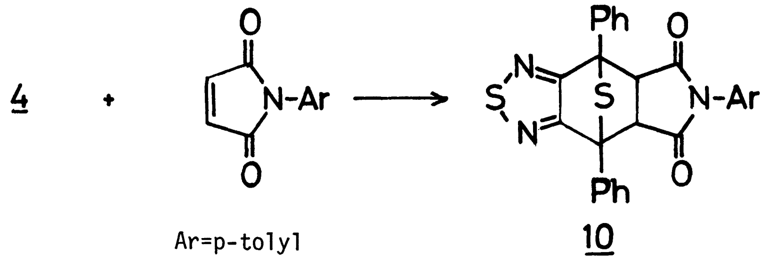
8: IR (KBr) 3500, 3400, 1790, 1720, 1690 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.48, 3.89 (each s, 3H), 4.2-4.5 (broad, 2H, exchanged with D_2O), 5.06, 5.20 (each d, 1H, J=7 Hz), 6.8-7.8 (m, 15H); ^{13}C NMR (DMSO-d_6) δ 62.2, 69.0 (quaternary C), 115.5 (isoxazole ring C-4), 155.7, 159.4 (isoxazole ring C-3, C-5), 159.7, 164.4 (ester C=O), 171.8, 172.7 (imide C=O); MS m/e 611 (M$^+$).

Although cycloadducts of nonclassical 10π-electron condensed thiophenes to olefins have been prepared by several workers,10) further additions to cycloadducts such as mentioned above have not been reported. Therefore, we have investigated thermal behaviour of analogous strained 1,2,5-thiadiazoles 3 and 4.

Thermal interconversion between the endo-adduct 3 and exo-adduct 4 was observed. Upon heating in xylene under reflux, pure 3 or 4 afforded a mixture of 3 and 4, respectively.11) The 3/4 ratio depended on heating time, and seems to be converged to about 4/1 (Scheme 2). This fact indicates that both



Heating time/h (140°C)	From 3 3/4	From 4 3/4
24	8/1	1/1
48	5.5/1	3/1
72	4/1	4/1



Ar=p-tolyl

Scheme 2

the adducts 3 and 4 are subject to a retro-cycloaddition to yield thienothiadiazole 9 and N-phenylmaleimide, which undergo re-cycloaddition. In fact, when a solution of the exo-adduct 4 in xylene was refluxed in the presence of 10 equivalents of N-p-tolylmaleimide for 24 h, a mixture of endo- and exo-adducts 10 of 9 to N-p-tolylmaleimide was formed.[12]

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7) J. D. Bower and R. H. Schlessinger, J. Amer. Chem. Soc., 91, 6891 (1969). However, the reversed assignments of configurations were made for 3 and 4.

8) All compounds in this paper gave satisfactory elemental analyses.

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10) For a recent summary of work in this area see M. P. Cava and M. V. Lakshmikantham, Acc. Chem. Res., 8, 139 (1975).

11) Ratios 3/4 were estimated by ^{1}H NMR spectroscopy in $CDCl_3$. The key signals for 3 and 4 were δ 4.90 and 3.94, respectively.

12) The ^{1}H NMR spectrum of the reaction mixture showed to be a mixture of 4, endo- and exo-adducts 10. A mixture of 4 and exo-10 was isolated in about 50% yield, and the ratio 4/exo-10 in the mixture was estimated by NMR spectroscopy to be 1/4. However, the estimation of endo-10 content was unsuccessful.

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