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CYCLOADDITION OF SINGLET OXYGEN AND TRIAZOLINEDIONE (TAD) WITH SPIROCYCLOPENTADIENYL-1,3,5-CYCLOHEPTATRIENES[1]: TROPILIDENE VERSUS NORCARADIENE REACTIVITY

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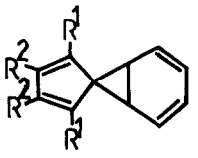
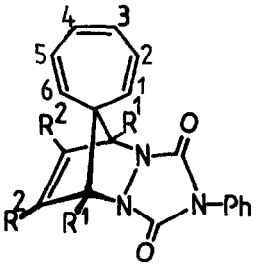
SUMMARY: 4-Methyl-1,2,4-triazoline-3,5-dione (MTAD) gives with 7-spirofluorenyl-1,3,5-cycloheptatriene (1d) initially the norcaradiene-type urazole (N3d) which at ambient temperatures rearranges into (6d), while $^1O_2$ gives the tropilidene-type endoperoxide (T4d).

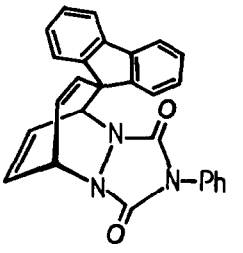
Triazolinediones (TAD) give only norcaradiene-type (N) products with 1,3,5-cycloheptatrienes[1] irrespective of the electronic nature of 7-substituents. On the other hand, singlet oxygen affords both the tropilidene-type (T) and the norcaradiene-type (N) products.[2] For example, while $^1O_2$ gives exclusively the T-product with 7-methoxy-1,3,5-cycloheptatriene and exclusively the N-product with 7-cyano-1,3,5-cycloheptatriene, TAD leads only to N-products. Since usually the T ⇌ N equilibrium lies on the side of the T-isomer[3], we expected that the spirocycloheptatrienes (1), for which significant amounts



$R^1=R^2=H$ (N1a)
R^1=Ph; R^2=H (N1b)
$R^1=R_2$=Cl (N1c)

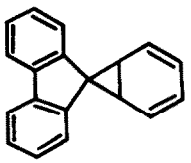


$R^1=R^2=H$ (2a)
R^1=Ph; R^2=H (2b)
$R^1=R^2$=Cl (2c)

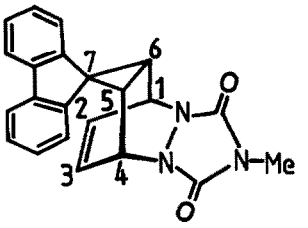


(T3b)

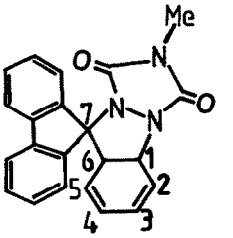
of the N-isomer are present even at room temperature[4], should all give preferentially N-cycloadducts with TAD and $^1O_2$. However, the parent spirosystem (N1a) cycloadded with 4-phenyl-1,2,4-triazolinedione (PTAD)[5] exclusively at the cyclopentadienyl moiety. Analogously we confirmed that the diphenyl and tetrachloro derivatives (N1b) and (N1c) also gave with PTAD the adducts (2b)



(N1d)



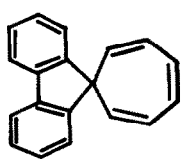
(N3d)



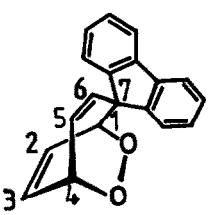
(6d)

and (2c), respectively.[6] On the basis of spectroscopic data alone it was difficult to differentiate with certainity TAD cycloaddition at the cyclopentadiene versus cycloheptatriene moiety and an X-ray analysis was run, proving beyond doubt that (2b) had been formed. By spectral analogy the same structures were assigned to (2a,c). The reaction of spirocycloheptatrienes (1a-c) with $^1O_2$ gave only complex mixtures of nonperoxidic products even at -50°C (presumably decomposition products from cycloaddition with the cyclopentadienyl moiety).

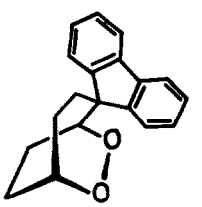
Of considerable greater interest was the cycloheptatriene (1d), in which the spirofluorenyl group obliges cycloaddition with the cycloheptatrienyl ring. Thus, the reaction of MTAD with (1d) in CH_2Cl_2 at room temperature afforded the urazole (6d)[7] in 70% yield as shown by X-ray analysis. However, when the



(T1d)



(T4d)



(T5d)

MTAD cycloaddition was run at -10°C and monitored by ^1H- and ^{13}C-NMR, cycloadduct (N3d) was obtained.[7] After warm-up to 25°C (N3d) rearranged into (6d).

The mechanism of the (N3d) → (6d) rearrangement presumably involves heterolysis of a lateral cyclopropane bond in (N3d), e.g. C_5-C_7, with subsequent fission of the C_4-N bond and fusion of the C_7-N bond to give (6d). The driving force must come from the large strain due to interaction between the peri-hydrogen of the spirofluorenyl group with the C_2-C_3 double bond in (N3d), as suggested by Dreiding models.

The singlet oxygenation of (1d) was performed in CCl_4 at 0°C, using tetraphenylprophyrin as sensitizer. The endoperoxide (T4d)[8] was obtained in 80% yield and diimide reduction afforded the saturated peroxide (T5d) in 36% yield. X-ray analysis of (T4d) confirms beyond doubt the tropolilidine structure of this endoperoxide.

Again we see the divergent cycloaddition behavior between the TAD and $^1O_2$ dienophiles, but for the spirocycloheptatriene substrate (1d) the reasons are steric rather than electronic in nature. Although a large amount (ca. 20%)[4] of the norcaradiene valence isomer (N1d) persists even at 37°C, $^1O_2$ affords exclusively the tropilidene adduct (T4d). In the case of TAD, the (4+2)-cycloaddition route seems to be predestined to give initially the (N3d) product. Therefore, planarity of the dienic moiety is essential for TAD even at the expense of severe steric compression.

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6. (2b): 88% yield, mp 176-177°C (granular solid from CH_2Cl_2/C_5H_{12}). Satisfactory elemental composition for $C_{31}H_{23}N_3O_2$. IR ($CHCl_3$) ν(cm^{-1}) 3050, 3090, 1780, 1725, 1600. ^1H NMR (90 MHz, $CDCl_3$) δ(ppm): 5.13, 5.80 (b.d, 2H, $H_{1,6}$), 5.5 (t, 2H, $H_{2,5}$), 5.96-6.00 (m, 2H, $H_{3,4}$), 6.7 (s, 2H, cyclopentene) and 6.7 (m, 15H, aromatic); J (Hz) 11.10 ($H_{1,2}$) and 3.6 ($H_{2,3}$). ^{13}C NMR (22.25 MHz, $CDCl_3$) δ(ppm): 73.71 (s), 85.64 (s), 120.02, 122.43, 125.24,

127.68, 128.00, 128.34, 129.06, 129.70, 131.50, 132.05, 134.25, 157.37.

(2c): 85% yield, mp 165-167°C (needles from CH_2Cl_2/C_5H_{12}). Satisfactory elemental composition for $C_{19}H_{11}Cl_4N_3O_2$. IR ($CHCl_3$) ν(cm^{-1}): 3050, 3000, 1750, 1590 and 1500. ^1H NMR (90 MHz, $CDCl_3$) δ(ppm): 4.90, 5.60 (m, 2H, $H_{1,6}$), 6.5 (m, 4H, $H_{2,3,4,5}$), 7.4 (m, 5H, phenyl); ^{13}C NMR (22.25 MHz, $CDCl_3$) δ(ppm): 92.42, 115.51, 119.97, 125.01, 125.71, 128.71, 129.33, 129.46, 130.24, 130.76, 131.05, 131.05, 131.78, 132.13.

7. (6d): 70% yield, mp 215-217°C (plates from CH_2Cl_2/C_5H_{12}). Satisfactory elemental composition for $C_{22}H_{17}N_3O_2$. IR (CH_2Cl_2) ν(cm^{-1}): 3050, 3015, 1775, 1720 and 1600. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 3.00 (s, 3H, N-CH_3), 3.95 (d, 1H, H_6), 4.80 (d, 1H, H_1), 5.25 (d, 1H, H_5), 5.88 (m, 1H, H_4); 6.09 (m, 1H, H_3), 6.7 (d, 1H, H_2) and 7.25-7.76 (m, 8H, fluorene); J (Hz) 18.0 ($H_{1,6}$), 5.0 ($H_{3,4}$), 9.50 ($H_{2,3}$, $H_{5,4}$), 2.25 ($H_{1,2}$). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ(ppm): 25.33 (q), 56.48 (d), 60.12 (d), 71.91 (s), 120.45, 120.75, 123.24, 124.24, 124.72, 126.24, 127.01, 127.92, 128.55, 129.79, 139.89, 140.66, 141.68, 142.65, 152.29, 156.89.

(N3d): ^1H NMR (90 MHz, $CDCl_3$, 0°C) δ(ppm): 2.55 (t', 2H, cyclopropyl), 2.95 (s, 3H, -NCH_3), 5.35 (m, 2H, bridge head), 6.53 (t', 2H, olefinic) and 6.8-7.9 (m, 8H, fluorene); J (Hz) 2.0 ($H_{1,6}$) and 4.0 ($H_{1,2}$); primed notation means second order splitting. ^{13}C NMR (100.6 MHz, $CDCl_3$, -20°C) δ(ppm): 25.75 (d), 31.91 (q), 38.67 (s), 53.93 (d), 119, 120, 124, 126, 127, 128, 129, 130, 135, 137, 143, 148, 158.

8. (T4d): 80% yield, mp 150-152° (needles from CH_2Cl_2/C_5H_{12}). Satisfactory elemental composition for $C_{19}H_{14}O_2$. IR (KBr pellet) ν(cm^{-1}): 3050, 3025, 1600 and 1100. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.16 (d, 1H, H_1), 4.90 (t, 1H, H_4), 5.23 (d, 1H, H_6), 6.34, 6.45 (m, 2H, $H_{5,2}$), 7.03 (t, 1H, H_3) and 7.2-8.0 (m, 8H, fluorene); J (Hz) 7.2 ($H_{1,2}$), 9.0 ($H_{2,3}$), 1.95 ($H_{1,6}$), 6.98 ($H_{4,5}$) and 10.5 ($H_{5,6}$). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ(ppm): 61.87 (s), 73.79 (d), 81.63 (d), 119.69, 120.16, 125.85, 126.91, 127.49, 128.12, 128.60, 130.75.

(T5d): 36% yield, mp 119-120°C (plates from CH_2Cl_2/C_5H_{12}). Satisfactory elemental analysis for $C_{19}H_{18}O_2$. IR (CH_2Cl_2) ν(cm^{-1}): 3010, 2990, 2975, 2945, 1600 and 1050. ^1H NMR (90 MHz, $CDCl_3$) δ(ppm): 1.65-2.90 (m, 8H, $H_{2,3,5,6}$), 3.60 (b.s, 1H, H_1), 4.80 (m, 1H, H_4), 7.10-8.30 (m, 8H, fluorene). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ(ppm): 19.11 (t), 20.04 (t), 30 93 (t), 33.40 (t), 59.99 (s), 76.5 (d), 81.46 (d), 119 45, 124.48, 127, 128.03, 139.37, 140.99.

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