Trapping Evidence for 1,2-Dinitrospiropentene

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Photolysis of 1,2-diiodo-1,2-dinitrospiropentanes **1a** and/or **1b** in the presence of furan afforded the formal Diels–Alder adduct **2** of 1,2-dinitrospiropentene.

Spiropentene and its derivatives are rare compounds characterised by low stability.[1] This is true primarily owing to high strain energy: spiropentene itself has been estimated to have 380 kJ mol^{-1} of strain energy.[2] 1,2-Dinitroalkenes are relatively sensitive compounds especially prone to conjugate attack by nucleophiles.[3] The parent dinitroalkene, 1,2-dinitroethylene, is unstable and can only be stored for a short time in the cold. Furthermore, whilst a few 3-nitrocyclopropenes have been reported,[4] 1-nitrocyclopropenes are unknown. Thus the questions arise, 'Would 1,2-dinitrospiropentene be a viable chemical entity?' 'Indeed, is any strained-ring dinitroalkene a viable entity?'

We recently reported[5] the preparation and characterization of the *cis*-**1a** and *trans*-**1b** isomers of 1,2-diiodo-1,2-dinitrospiropentane. Removal of two iodine atoms from either **1a** or **1b** was envisioned as a route to 1,2-dinitrospiropentene and products derived from it (Scheme 1).

Irradiation† of a methylene chloride solution containing furan and either pure **1a**, pure **1b**, or a **1a–b** mixture gave the cycloadduct **2** which was isolated as a single isomer by preparative TLC. Repeated reactions run on the isomer mixture gave workable quantities of pure **2**, albeit in only 3% yield. Iodine and low yields of unidentified furan-derived sideproducts were also produced in these reactions. Conditions have not been optimised for the synthesis of cycloadduct **2**, but it was noted that none of **2** could be obtained from photolysis of **1a–b** in neat furan.

Cycloadduct **2** has been characterised by the usual spectral techniques.‡ The stereochemical assignment is based on comparison of the ^{1}H NMR spectrum with the known[1] spiropentene–furan cycloadducts **5a** and **6a** and the known[6] 2-cyclopropenecarboxaldehyde–furan cycloadducts **5b** and **6b**. Cycloadduct **2** exhibited olefinic-H absorption at δ 7.08 in much better agreement with the *exo*-isomer **5a** (δ 6.46) than the *endo*-isomer **6a** (δ 6.05). Virtually no coupling was apparent between the olefinic-H and the bridgehead-H of **2**, merely a slight broadening which could be sharpened by decoupling. The ^{13}C NMR spectrum of **2** is also consistent with the stereochemical assignment. Olefinic-C absorption was observed at δ 138.91 in better agreement with the exo-isomer **5b** (δ 138.4) than the *endo*-isomer **6b** (δ 131.5).[6] Finally, there is precedence for the assigned *endo*-orientation of the nitro groups in cycloadduct **2**: nitroethylene and furan have been reported to form predominantly the *endo*-cycloadduct (55% yield; only a minor amount of the *exo*-cycloadduct was noted).[7]

The formation of cycloadduct **2** is hypothesised to involve the intermediacy of 1,2-dinitrospiropentene. Initial photodissociation of diiodides **1a–b** would be expected to produce the free radical **3**. Interconversion of **1a** and **1b** was observed under the reaction conditions, consistent with the presence of radical **3**. Loss of the second iodine atom from **3** would then produce 1,2-dinitrospiropentene. Elimination of iodine does not appear to be a simple cage process because the *cis*-isomer **1a** showed no greater tendency to form cycloadduct **2** than did the *trans*-isomer **1b**.

There is literature precedence for each step of the proposed process. Simple α-iodonitro compounds can apparently photodissociate to afford iodine and α-nitro radicals.[8] Loss of a β-iodo atom from a free radical is well known, occurring in the iodine-catalysed isomerization of alkenes.[9] Finally, the reaction[1] of spiropentene with furan closely parallels the proposed reaction of 1,2-dinitrospiropentene with furan.

An alternate route to cycloadduct **2** which does not proceed *via* the spiropentene **4** has been considered. Addition of free radical **3** to furan could produce the radical **7**. However, it is not clear how radical **7** might cyclise to afford the cycloadduct **2**. Either **7** would have to undergo a ring closure for which there is no precedent or to survive sufficiently long to undergo a second photolysis followed by ring closure. It is therefore concluded that cycloadduct **2** likely arises *via* Diels–Alder reaction of spiropentene **4**.

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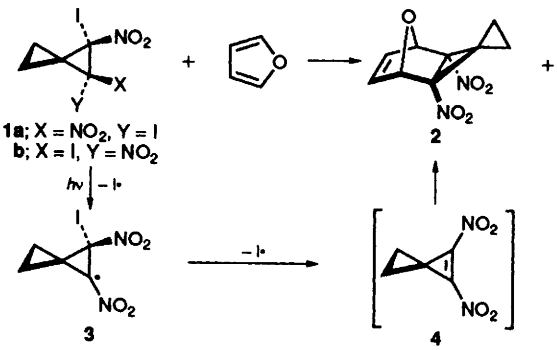
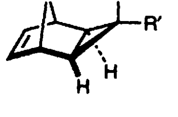
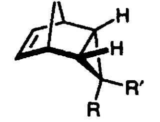


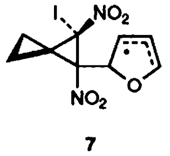
Scheme 1



5a; R, R' = $-CH_2CH_2-$
b; R = H, R' = CHO



6a; R, R' = $-CH_2CH_2-$
b; R = H, R' = CHO



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Footnotes

† Photolyses were conducted using a sunlamp.

‡ Data for **2**: mp 136–136.5 °C; IR (KBr) ν/cm^{-1} 1548, 1345 (NO_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.08 (s, 2 H), 5.27 (s, 2 H), 1.79 (apparent t, 2 H, *J* 8.7 Hz), 1.53 (apparent t, 2 H, *J* 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 138.91 (=CH), 79.08 (OCH), 10.22 (CH_2), 9.60 (CH_2), quat C's were not observed; MS *m/z* 224 (M^+), 178 ($M^+ - NO_2$), 131 ($M^+ - HN_2O_4$).

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