Tetrahedron Vol. 40, No. 16, pp. 3113 to 3116, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00
Pergamon Press Ltd.

THE PHOTOCHEMICAL REACTIONS OF α,β:γ,δ-UNSATURATED DIAZO COMPOUNDS AT LOW TEMPERATURE

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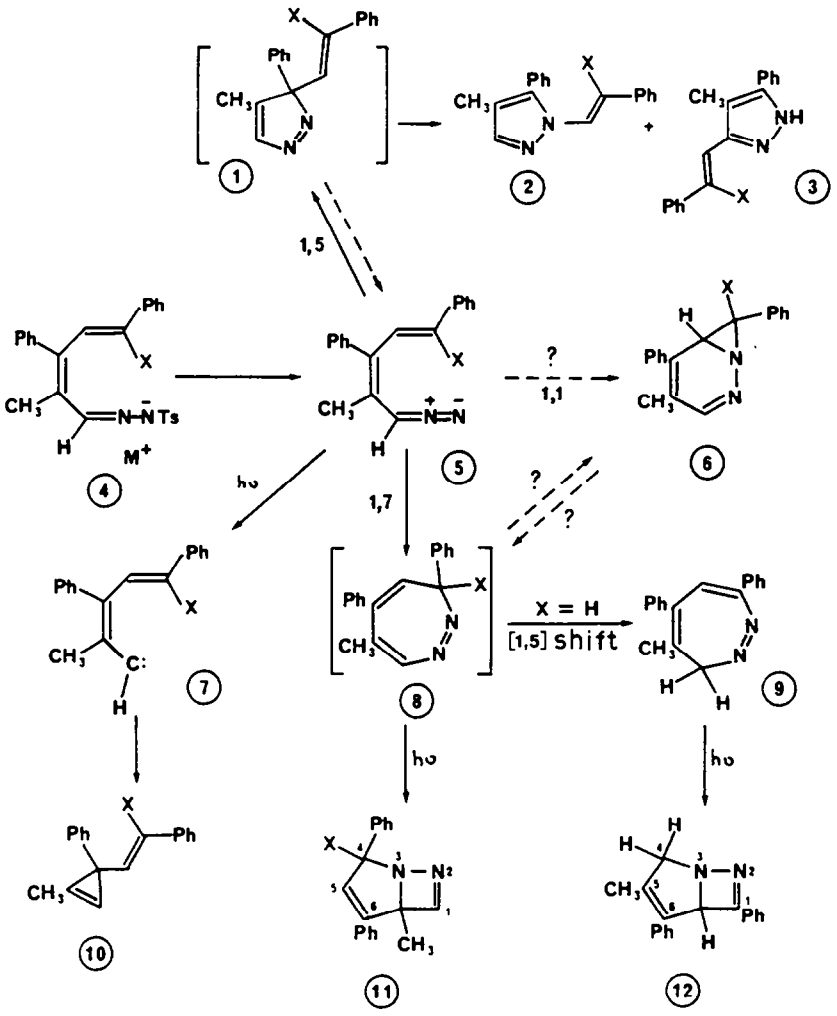
(*Received in UK 4 April* 1984)

Abstract - The α,β:γ,δ-unsaturated tosylhydrazone lithium salts (4) undergo photolysis at -60°C to give vinylcyclopropenes (10) and [1,2]diazeto[1,4-a]pyrroles (11) and/or (12). The formation of (11, X=H) establishes the intermediacy of (8, X=H) in the formation of the 3H-1,2-diazepine (9). The diazoalkene (5, X=Me) showed opposite electrocyclisation periselectivity to its thermal cyclisation and gave (11, X=Me) *via* (8, X=Me), rather than the pyrazoles (2) and (3).

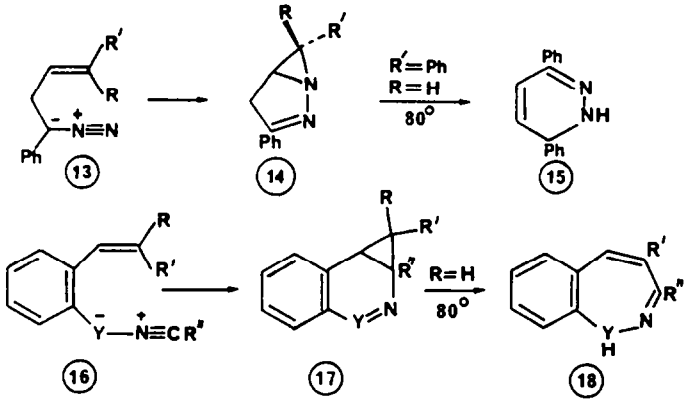
We recently reported on the periselectivity of the thermal cyclisation reactions of a range of α,β:γ,δ-unsaturated diazo compounds e.g. (5, X=H) and (5, X=Me), carried out at *ca* 80°C.[1] Reactants such as (5, X=H) which have a *cis* hydrogen atom at the cyclisation site reacted exclusively by 1,7-ring closure to give the 3H-1,2-diazepine (9) *via* the presumed but undetected intermediate (8, X=H). However similar diazo compounds e.g. (5, X=Me) having a *cis* methyl group reacted only *via* 1,5-ring closure and subsequent vinyl group and hydrogen migrations to give the pyrazoles (2, X=Me) and (3, X=Me). This difference in periselectivity was attributed to a steric effect of the methyl group which raised the activation energy for the 1,7-cyclisation.[2]

This paper is concerned with reactions of the same diazo compounds but in this case generated at -60°C by the photolysis of the tosylhydrazone lithium salts (4; M=Li, X=H or Me). This was undertaken for several reasons: (i) to find out whether the electrocyclisation periselectivity shown by (5) would be affected either by the photochemical nature of the reaction or by the low reaction temperature, (ii) in the hope of finding positive evidence for the intermediate (8), and (iii) to discover whether (5) would react *via* a '1,1-cycloaddition' to give (6) at low temperature. The last point was of particular interest because it has recently been shown that some diazo compounds e.g. (13) cyclise at room temperature by a formal 1,1-cycloaddition to give the 1,2-diazabicyclo[3,1,0]hexenes (14).[3,4] This product however is thermally unstable and undergoes further reaction at 80°C to give (15).[3] It has also been reported that the unsaturated nitrilium betaines (16, Y=N or CH) - isoelectronic with (5) - also cyclise by a formal 1,1-process at room temperature to give the bridged systems (17).[5,6,7] These are also thermally unstable and rearrange at 80°C to give the seven-membered heterocycles (18). At present it is not clear whether these highly stereospecific 1,1-cycloadditions involve concerted formation of the two new bonds or proceed in a stepwise process *via* an intermediate. This notwithstanding, these results obviously raised the questions of whether the diazo system (5) would also undergo 1,1-cycloaddition at low temperature and whether this might be the primary process in the thermal cyclisation at 80°C i.e. (5) ▸ (6) → (8) ▸ (9)?

An essential element in this study was the knowledge that the 3H-1,2-diazepines e.g. (9) undergo rapid and quantitative photoisomerisation to give the diazeto[1,4-a]pyrroles (12).[8,9]



Thus in the low temperature photochemical reactions of the diazo compounds two distinct and distinguishable reaction paths can be envisaged: (i) Direct cyclisation by 1,7-electrocyclisation to give the diazepine (8) - previously postulated as an intermediate in the 'thermal' cyclisation. This product would be quickly "trapped" by photoisomerisation and isolated as the diazetopyrrole (11). (ii) Formation of the diazanorcaradiene (6). This product could however - if thermally unstable - undergo ring expansion to give (8) after conclusion of the photolysis, during the warming up from -60°C and work-up at room temperature. In this case therefore either the diazanorcaradiene itself or the diazepine (9) would be isolated (hydrogen shifts in the 3H-1,2-diazepine system are known to be fast at room temperature[10]).

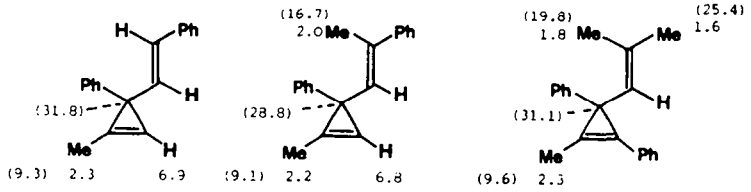


In the event the photolysis of (4, X=H) at -60°C followed by work-up at room temperature gave the vinylcyclopropene (10, X=H; 41%) and the two isomeric diazetopyrroles (11, X=H; 25%) and (12, 10%), but no diazanorcaradiene or diazepines. This is consistent with pathway (i) as discussed above. It would appear that at this low temperature the rate of the sigmatropic hydrogen shift is slower than the rate of photoisomerisation of (8, X=H) so that this previously undetected primary product is effectively trapped as (11, X=H).

The photolysis of the analogue with a cis methyl group (4, X=Me) also failed to give any diazanorcaradiene or diazepine but interestingly did give (11, X=Me; 25%) as well as the cyclopropene (10, X=Me; 37%). The formation of (8, X=Me), as the precursor to (11, X=Me), and not the pyrazoles (2 and 3, X=Me) thus shows completely opposite periselectivity to that observed in the thermal reaction at 80°C.

The success of this photochemical 1,7 cyclisation of (5, X=Me) may be due to reaction of the diazo compound in an excited electronic or vibrational state. The high yields of the carbene-derived products (10, X=H and X=Me), which were not isolated in the thermal reaction,[1] support the suggestion that excitation of the diazo group does occur. However the isolation of a product from the 1,7 cyclisation of (5, X=Me) may also be due in large part to poorer competition from 1,5 cyclisation as a product forming pathway under the low temperature photochemical conditions. The 1,5-electrocyclisation of α,ß-unsaturated diazo compounds to give 3H-pyrazoles e.g. (1) is known to be photochemically reversible[11] and in addition the sigmatropic vinyl and hydrogen shifts which led to (2) and (3) at 80°C will be very slow at -60°C.

The structures of the diazeto[1,4-a]pyrroles (11) and (12) were assigned by comparison of their ^{1}H and ^{13}C n.m.r. spectra, and mass spectrometry fragmentation patterns with data from compounds of the same type prepared by the photoisomerisation of 3H-1,2-diazepines[8] and 1H-2,3-benzodiazepines.[9] Compound (12) formed in the photochemical decomposition of the tosylhydrazone salt was identical with the sample prepared by the photoisomerisation of a sample of the diazepine (9) isolated from the thermal cyclisation of (5, X=H) at 80°C. The vinylcyclopropenes were also identified by comparison of their ^{1}H and ^{13}C n.m.r. spectra with data reported for similar compounds.[12] Some of the chemical shifts for (10, X=H and X=Me) and a comparison compound are shown in structures (19), (20), and (21) (δ values, carbon in parenthesis).



(19) (20) (21)

These results have thus demonstrated the intermediacy of (8, X=H) in the formation of (9) and also shown that diazo compounds (5) with a cis methyl group can undergo 1,7-cyclisation. The failure to find any evidence for the diazanorcaradiene (6) is also interesting and it must be concluded either that such species are not formed or are thermally or photochemically unstable at -60°C.

EXPERIMENTAL

N.m.r. spectra were obtained using the following instruments: Bruker WP80 (^{1}H, 80 MHz) and, Bruker WP200 (^{1}H, 200 MHz; ^{13}C, 50 MHz), and are recorded as δ values for solutions in deuteriochloroform unless otherwise stated. Merck Kieselgel 60 was used for flash chromatography. Tetrahydrofuran (T.H.F.) was dried and distilled over calcium hydride.

The photolyses were carried out under nitrogen through pyrex using a 100 watt medium pressure lamp (Applied Photophysics). The reactor was of the immersion type and in the low temperature experiments the reaction vessel was kept in a bath of the coolant, and ethanol at the reaction temperature was circulated through the annular jacket around the lamp. The preparation of the tosylhydrazones is described elsewhere.

Photolytic decomposition of tosylhydrazone lithium salts

(i) E,E-3,5-Diphenyl-2-methylpenta-2,4-dienal tosylhydrazone (4,X=H). Methyllithium (1.5M in

ether, 0.94 ml, 1.41 mmol) was added with stirring, under dry nitrogen to a solution of E,E-3,5-diphenyl-2-methylpenta-2,4,dienal tosylhydrazone (534 mg, 1.28 mmol) in dry T.H.F. (70 ml) at -60°C in a pyrex photochemical reactor. The resulting solution was stirred for 1 h and then irradiated under dry nitrogen at -60°C for 4 h. The mixture was allowed to warm to room temperature and water (25 ml) added. Most of the T.H.F. was removed under reduced pressure and dichloromethane (100 ml) added. The aqueous layer was separated, extracted with dichloromethane (2 x 25 ml) and the combined organic layers were washed with water (2 x 20 ml) and dried. Evaporation of the solvent under reduced pressure gave a brown oil which was purified by flash chromatography (silica, ether:petrol, 1:9) to give: (a) E-1-Methyl-3-phenyl-3-(2-phenylethenyl)-cyclopropene (10, X=H) as a clear oil (121 mg, 41%), (Found: m/z, 232.123215. $C_{18}H_{16}$ requires m/z, 232.125194; δ_H (200 MHz) 2.26(3H, d, J 1.3 Hz, 1-Me), 6.27(1H, d, J 16 Hz, 1'-H), 6.92(1H, d, J 16 Hz, 2'-H), 6.90(1H, br, q, J 1.3 Hz, 1-H), 7.18-7.62(10H, m, aromatic); δ_C (50 MHz) 9.25 (Me), 31.75 (C-3), 102.78, 121.40 (quat), 125.34, 125.83, 126.57, 127.10, 128.06, 128.37, 128.68, 137.45, 137.94 (quat), 146.88 (quat), (b) 4,6a-Dihydro-6a-methyl-4,6-diphenyl[1,2]diazeto-[1,4-a]pyrrole (11, X=H) as an oil (84 mg, 25%), (Found: m/z 260.132386. $C_{18}H_{16}N_2$ requires m/z 260.131342); δ_H (80 MHz) 1.67(3H, s, 6a-Me), 5.24(1H, d, J 2.5 Hz, 4-H), 6.04(1H, d, J 2.5 Hz, 5-H), 7.19-7.43(10H, m, aromatic), 8.61(1H, s, 1-H); δ_C (50 MHz) 18.03 (Me), 69.69 (C-4), 91.89 (quat) (C-6a), 126.22, 126.71, 127.00, 127.27, 128.11, 128.58, 133.57 (quat), 141.81 (quat), 143.31 (quat), 177.15 (C-1); m/z 260 (12), 233 (100), 192 (49), 157 (48), 156 (28), 115 (45%), (c) 4,6a-Dihydro-5-methyl-1,6-diphenyl[1,2]diazeto[1,4-a]pyrrole (12, X=H) (32 mg, 10%). This was identical by t.l.c. and ^1H n.m.r. to the product formed by the photolysis of 4-methyl-5,7-diphenyl-3H-1,2-diazepine (9).

(ii) E,E-3,5-Diphenyl-2-methylhexa-2,4-dienal tosylhydrazone. Methyllithium (1.5M in ether, 0.46 ml, 0.69 mmol) was added with stirring, under dry nitrogen to a solution of E,E-3,5-diphenyl-2-methylhexa-2,4-dienal tosylhydrazone (295 mg, 0.69 mmol) in T.H.F. (70 ml) at -60°C in a pyrex photochemical reactor. The resulting solution was stirred for 1 h and then irradiated under dry nitrogen at -60°C for 6 h. The mixture was allowed to warm to room temperature and water (20 ml) added. A work-up similar to that above followed by preparative t.l.c. (alumina, 10 vol % ether in petroleum) gave: (a) E-1-Methyl-3-phenyl-3-(2-phenylpropenyl)cyclopropene (10, X=Me) as an oil (62 mg, 37%). (Found: m/z 246.140302. $C_{19}H_{18}$ requires m/z 246.140844); δ_H (200 MHz) 2.02 (3H, d, J 1 Hz, 2'-Me), 2.21(3H, d, J 1 Hz, 1-Me), 6.23(1H, br, q, J 1 Hz, 1'-H), 6.82(1H, br, q, 3-H), 7.21-7.51(10H, m, aromatic); δ_C (50 MHz) 9.09 (C-1 Me), 16.69 (Me), 28.8 (C-3), 103.87, 120,10 (quat), 124.74, 125.52, 126.27, 126.62, 127.86, 128.07, 131.22, 137.33 (quat), 143.56 (quat), 147.91 (quat), (b) 4,6a-Dihydro-4,6a-dimethyl-4,6-diphenyl[1,2]diazeto[1,4a]pyrrole (11, X=Me) (48mg, 25%) as an oil (Found: m/z 274.144532. $C_{19}H_{18}N_2$ requires m/z 274.146991; δ_H (200 MHz) 1.65(3H, s, 6a-Me), 1.73(3H, s, 4-Me), 6.26(1H, s, 5-H), 7.20-7.61(10H, m, aromatic), 8.48(1H, s, 1-H); δ_C (50 MHz) 17.57 (Me), 31.62 (C-4 Me), 70.52 (quat, C-4), 90.99 (quat, C-6a), 126.61, 126.70, 127.51, 127.99, 128.21, 128.65, 130.77, 133.76 (quat), 139.35 (quat), 143.25 (quat), 175.98 (C-1); m/z 274 (8), 259 (100), 232 (81), 247 (47%).

Photolysis of 4-methyl-5,7-diphenyl-3H- 1,2-diazepine (9)

A solution of 4-methyl-5,7-diphenyl-3H- 1,2-diazepine (371 mg, 1.43 mmol) in dry T.H.F. (70 ml) was photolysed at -70°C for 30 min. T.l.c. showed only one product and this was isolated by flash chromatography (silica, ether:petrol 40/60, 1:1) to give 4,6a-dihydro-5-methyl-1,6-diphenyl[1,2]diazeto[1,4-a]pyrrole (12) (310 mg, 83%) m.p. 86-87°C (from ethanol/pentane) (Found: C, 82.85; H, 6.0; N, 11.0. $C_{18}H_{16}N_2$ requires C, 83.0; H, 6.2; N, 10.8%); δ_H (200 MHz) 1.76(3H, d, J 1.5 Hz, 5-Me), 4.11 (2H, br, s, 4-H_2), 6.16 (1H, br, m, 6a-H), 7.13-7.43 (10H, m, phenyl); δ_C (20 MHz) 12.96 (Me), 62.33 (C-4), 85.59 (C-6a), 124.48, 127.37, 128.05, 128.21, 128.40, 129.31, 130.20, 131.27 (quat), 134.01 (quat), 134.73 (quat), 182.74 (quat, C-1); m/z 260 (10), 157 (100), 156 (47), 116 (16), 115 (25), 103 (22%).

Acknowledgment. We thank the S.E.R.C. and the University of Edinburgh for support (I.R.R.).

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