Reprinted from the *Indian Journal of Chemistry* Sec. B Vol. 18, No. 1, July 1979 pp. 71-72

Studies in Cycloadditions : Part VIII—Condensation of 3,4-Dihydro-6-methoxy-1-vinylnaphthalene with *trans*-*p*-Methoxy- & *p*-Nitro-β-nitrostyrenes†

PRABHAKAR M. KELKAR, SHRI NIVAS RASTOGI* & NITYA ANAND
Division of Medicinal Chemistry, Central Drug Research Institute, Lucknow 226 001

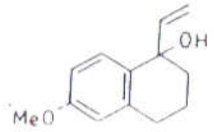
Received 22 January 1979; accepted 8 February 1979

Condensation of 3, 4-dihydro-6-methoxy-1-vinnylnaphthalene (II) with *trans-p*-methoxy- (IV)- and *p*-nitro-β-nitro-(V)-styrenes respectively gives a mixture of adducts from which 1 -[*p*-methoxy-(VII)-and *p*-nitro-(X)]phenyl-2-nitro- and 2-[*p*-methoxy-(IX)- and *p*-nitro (XI)]phenyl-1-nitro-1,2,3, 9, 10, 10a-hexahydro-7-methoxy-phenanthrenes have been isolated. This condensation in the presence of $SnCl_4$ or BF_3 etherate catalysts fails to give any adduct. Refluxing of VIII and X in EtOH in the presence of conc. HCl results in the migration of 4, 4a-double bond to furnish the corresponding 4a, 10a-double bonded adducts (XIII) and (XIV). An unreported adduct, 1, 10a-*cis*-1, 2, 3, 9, 10, 10a-hexahydro-7-methoxy-1-nitro-2-phenylphenanthrene (XII) has also been isolated from the cycloaddition of II to *trans*-β-nitrostyrene.

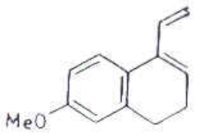
DURING the course of cycloaddition[1] of 6-methoxy-1-vinyl-1-tetralol (I) and its diene (II) to *trans*-β-nitrostyrene (III), it was found that the adduct 1, 2, 3, 9, 10, 10a-hexahydro-7-methoxy-2-nitro-1-phenylphenanthrene (VI) was formed only in small amount while its regio-isomeric adduct, 1-nitro-2-phenyl-(VII) was the main product. The regio orientation of such cycloadditions could possibly be altered by introducing substituents of varying electronic character in the dienophile or by carrying out this condensation in the presence of Lewis acid catalysts. Thus, Diels-Alder condensation of diene (II) with dienophiles *trans-p*-methoxy-β-nitrostyrene (IV) and *trans*-β, *p*-dinitrostyrene (V) was carried out and results are reported in this communication.

The dienophiles (IV) and (V), prepared according to literature methods[2,3], were condensed with II in refluxing C_6H_6. Condensation of V and II proceeded smoothly to give the adduct in good yield, presumably due to presence of electron withdrawing nitro group in the dienophile, a factor known to favour such reactions. Contrary to this, the condensation of II with IV gave poor yield of the adduct possibly as a result of inactivation of dienophile due to presence of electron donating methoxy group. However, the condensation of II and IV in refluxing toluene furnished better yield of the adduct. Fractional crystallisation of these adduct mixtures followed by chromatographic separation over silica gel column gave adducts (VIII to XI) which were characterised on the basis of their spectral data given below.

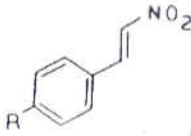
VIII, m.p. 151-52° (C_6H_6-hexane); IR : 1372, 1543 (NO_2); UV : 219 (19320), 264(14310) ; NMR: 226 [*s*, 6, $(OCH_3)_2$], 295 (complex *m*, 1, $-C_2HNO_2$), 365 (hump, 1, olefinic C_4-H). 449.5 (*d*, 1, arom. $C_5-H, J=8$Hz); Mass : *m/e* 365 (M^+), 335 (M^+-30), 318 (M^+-47), 121(C_8H_9O). IX, m.p. 202° (C_6H_6); IR : 1364, 1549 (NO_2); UV : 219(19320), 265(14310); NMR : 226[*s*, 6, $(OCH_3)_2$], 282(*d* of *d*, 1,—C_1-HNO$_2$,



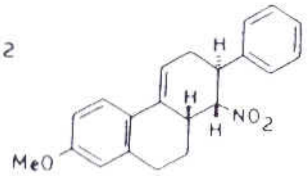
I



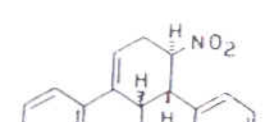
II



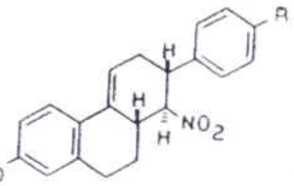
III R = H
IV R = p-MeO
V R = p-NO$_2$



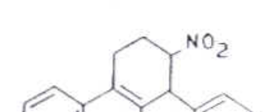
XII



VI R = H
VIII R = p-MeO
X R = p-NO$_2$



VII R = H
IX R = p-MeO
XI R = p-NO$_2$



XIII R = p-MeO
XIV R = p-NO$_2$

---

† CDRI Communication No. 2513

J = 8.5 and 11Hz), 373 (hump, 1, olefinic-C_4H), 452 (d, 1, arom. C_5—H, J=8.5Hz); Mass : m/e 365 (M^+), 335 (M^+—30) 318(M^+—47), 197 (M^+—168 (47+121), 186 (M^+—179). X, m.p. 190°; IR : 1359, 1545 (NO_2); UV : 214(20790), 263(23270); NMR :228 (s, 3, OCH_3), 302 (complex m, 1,-C_2—$H$$NO_2$), 370 (hump, 1, olefinic-C_4H); Mass: m/e 380 (M^+) 333(M^+—47). XI, m.p. 240°; IR : 1374, 1550 (NO_2); UV : 216(25760), 268(33160); Mass : m/e 380 (M^+) (NMR of X could not be recorded because of insolubility).

Surprisingly, no substantial shift in regioselectivity was recorded with any of the three dienophiles (III-V). It may be mentioned here that the other alternative approach to effect regioselectivity using Lewis acid catalysis proved fruitless in the present case as using both $SnCl_4$ at 0° or BF_3 etherate at 0° under standard[4] conditions gave only polymerised product.

An adduct XII with 1, 10a-*cis* stereochemistry was isolated, in addition to three adducts reported earlier[1], from the condensation of diene (II) with III. XII, m.p. 175° (C_6H_6-hexane); IR : 1372, 1550(NO_2) ; UV : 221.5 (13520), 264(19360); NMR : 225(s, 3, OCH_3), 264-317 (complex m, 1, —C_1—HNO_2), 371 (hump, 1, olefinic-C_4—H), 458(d, 1, arom, C_5—H, J = 8Hz) ; Mass: m/e 335 (M^+), 305 (M^+—30), 228 (M^+—47), 186(M^+—149), 197[M^+—138(47+91)], 91($C_7H_7^+$).

Adducts VIII and X when refluxed in the presence of conc. HCl in EtOH gave migrated double bond adducts (XIII) and (XIV) of following physical and spectral data : XIII, m.p. 114° (EtOH); IR : 1372, 1547(NO_2); UV : 230 (13100), 276(18400); NMR : 227 [s, 6, $(OCH_3)_2$], 252(d, 1, C_1—HPh, J=7Hz), 282 (complex m, 1, —C_2—$H.NO_2$); Mass : m/e 365 (M^+), 318(M^+—47), 129(C_8H_9O). XIV, could not be purified but its spectral data was suggestive of migration of double bond.

A similar HCl treatment of other set of adducts VII, IX and XI gave unusual products which are under study.

All adducts described in this communication and the three adducts reported earlier[1] besides showing molecular ion peak showed loss of HNO_2 as indicated by the presence of M^+—47 fragment. In some adducts VII-VIII and XI-XII the loss of CH_2O (M^+—30) was observed. Adducts, VI-VII, IX, XI-XII underwent retro-Diels-Alder reaction as evidenced by the presence of a fragment corresponding to nitrostyrene or diene in their mass spectra. In general, all adducts showed a loss of tropylium cation or substituted tropylium cation presumably arising via benzyl fragment.

IR spectra (ν_{max} in cm^{-1}) were recorded on Perkin-Elmer 137 and 157 infracord instruments; UV (λ_{max} in nm; ϵ values in parentheses) in MeOH on a Perkin-Elmer UV-visible spectrophotometer; NMR (chemical shift in Hz) in $CDCl_3$ on a Varian A60D instrument using TMS internal reference; and mass spectra on a Hitachi RMU-6 spectrometer. The homogeneity of the compounds was routinely checked on silica gel TLC plates. All compounds gave satisfactory elemental analyses.

References

1. Ananthanarayanan, C. V., Kelkar, P. M., Rastogi, S. N & Anand, N., *Indian J. Chem.*, **14B** (1976), 799.

2. Konda, T. & Schinozaki,Y ., *J. pharm. Soc. Japan*, **49** (1929); 267; *Chem. Abstr.*, **24** (1930), 5294.

3. Thiele, *Ber. dt. chem. Ges.*, **32** (1890), 1293.

4. (a) Fray, G. I. & Robinson, R., *J. Am. Chem. Soc.*, **83** (1961), 249.

4. (b) Dickinson, R. A., Kubela, P., Macalpine, G. A., Stojanac, Z. & Valenta, Z., *Can. J. Chem.*, **50** (1972), 2377.