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Studies in Cycloadditions: Part VII — Condensation of 6-Methoxy-1-vinyl-1-tetralol & 6-Methoxy-1-vinyl-3,4-dihydronaphthalene with *trans*-Cinnamic Acid & *trans*-β-Nitrostyrene*

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Diels-Alder condensation of 6-methoxy-1-vinyl-1-tetralol (I) with *trans*-cinnamic acid (III) at room temperature gives 6-methoxy-1,2,3,4-tetrahydro-1-naphthylideneethyl cinnamate (IV) whereas condensation of its diene II with III in a sealed tube affords the adducts 2-carboxy-1-phenyl-(VI)- and 1-carboxy-2-phenyl-(V)-1,2,3,4,9,10-hexahydro-7-methoxyphenanthrenes and three dimers of diene (II). Similar condensation of tetralol I or diene II with *trans*-β-nitrostyrene gives the adducts 2-nitro-1-phenyl-(XVII)-and 1-nitro-2-phenyl-(XVI)-1,2,3,9,10,10a-hexahydro-7-methoxyphenanthrenes and 1-phenyl-2-nitro-1,2,3,4,9,10-hexahydro-7-methoxyphenanthrene (XVIII).

IN a study of the factors involved in stereo- and regio-selectivities of Diels-Alder reaction[1-4], it was found that in the condensation of *trans*-β-nitrostyrene with diphenylbutadienes, the position of the phenyl rings had a marked effect on the stereochemistry of the products formed. In a related condensation[5] of 6-methoxy-1-vinyl-1-tetralol (I) and 1-vinyl-3,4-dihydronaphthalene (diene II) with methyl *trans*-cinnamate it was found that the major isomer had ester group *meta* oriented to the phenyl group of the diene. These observations led to a deeper study of the condensation of the tetralol I or the diene II with *trans*-β-nitrostyrene and *trans*-cinnamic acid. The results are reported in this communication.

Condensation of I, prepared by the reaction of 6-methoxytetralone and vinylmagnesium bromide, with *trans*-cinnamic acid (III) in benzene at room temperature gave instead of the expected adduct, the ester IV and some polymerized diene; IV*, m.p. 76-77° (benzene-hexane), showed the following spectral data: IR (KBr): 1712 (ester); UV (MeOH)nm (ε): 217 (29540), 223 (27960), 276 (33720); NMR: 98 - 128 (*m*, 2, 3 - CH_2), 150-175 (*m*, 4, 2-CH_2 and 4-CH_2), 228 (*s*, 3, OCH_3), 298 (*d*, 2, OCH_2, J=6·5 Hz), 369 (*t*, 1, =CH.CH_2O, J=6·5 Hz), 391 (*d*, 1, O.CO.CH=C, J=15 Hz), 394-415 (*m*, 2, ArH *o*

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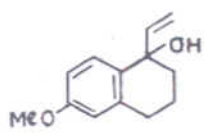
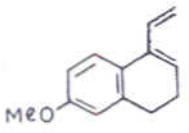
*Satisfactory analytical, IR, NMR data have been obtained for all new compounds. Only those data have been mentioned which have a direct bearing in the discussion of the structure. Purity of these compounds was routinely checked by TLC on silica gel G plates. IR spectra were recorded on Perkin-Elmer infracord 137 and grating infrared 337 and frequency expressed in cm^{-1}. NMR spectra were taken in $CDCl_3$ on a Varian A-60D instrument, the chemical shift values are expressed in Hz units using TMS as internal reference. Mass spectra were run on a Hitachi RMU6 spectrometer.



I



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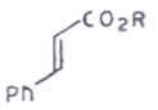

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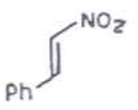
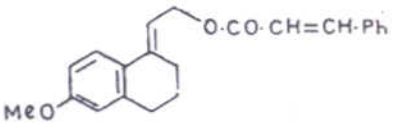
IIIa R=Me



β-Nitrostyrene



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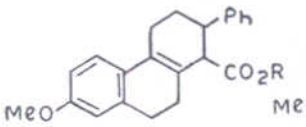

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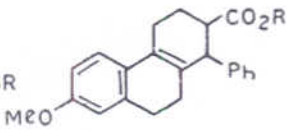
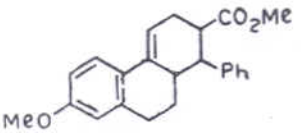
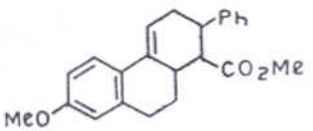
VII R=Me



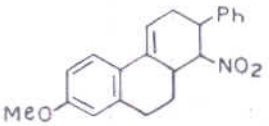
VI R=H
VIII R=Me



IX



X



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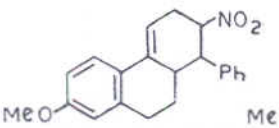

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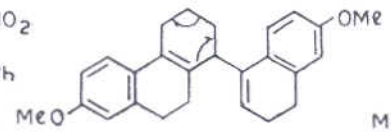

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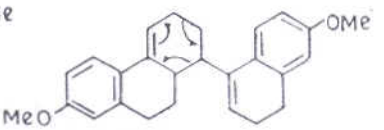

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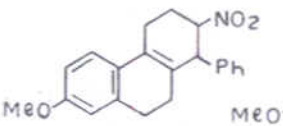
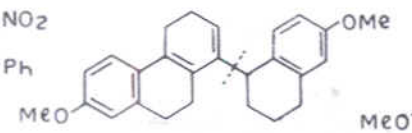
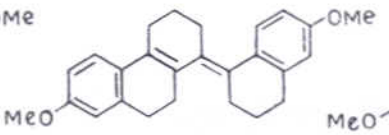


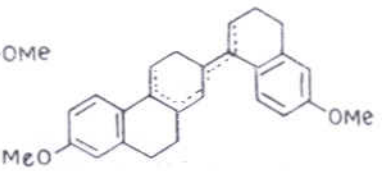
XVIII



XIII



XIV



XV

to OCH_3), 468 (*d*, 1, $-CH=CH$.Ph, $J=15$ Hz), 438-463 (*m*, 6, C_6H_5 and Ar*H* *m* to OCH_3); M^+ 334. Treatment of II, obtained from the tetralol (I) with III in a sealed tube at 150°, gave a mixture of the acids, V and VI as these on esterification with MeOH-H_2SO_4 furnished methyl esters VII and VIII respectively which were identical with the esters obtained by condensation of tetralol I or diene II with methyl *trans*-cinnamate (IIIa). The latter reaction as reported[1] earlier furnished a mixture consisting of varying amounts of all possible adducts with major proportion of adduct VII and dimerized products. By solvent-temperature study, the optimum temperature conditions to obtain all the isomeric adducts was found to be $105° \pm 2°$. Below this temperature in benzene and toluene only partial reaction took place and some unreacted diene and teralol could be detected in NMR and TLC, while above this temperature in refluxing toluene, xylene or *o*-dichlorobenzene, predominantly double bond isomerized adducts were obtained.

The structures of adducts VII and VIII have been discussed in our earlier paper[1]. The third adduct, m.p. 133-34°, which was isolated in about 90% purity from the same reaction had the following spectral characteristics: IR (KBr): 1730 (COOMe); UV (MeOH) nm (ϵ): 263 (17540); NMR; 201 and 214 (two *s*, 3, O-CH_3) due to the presence of a mixture of two isomers in the ratio of 10:1, 226 (*s*, 3, OCH_3), 373 (*bh*, 1, olefinic C*H*), 452 (*d*, 1, Ar*H* *m* to OCH_3, $J=8$ Hz) suggesting the presence of 4,4a-double bond. As 1-C*H* and 2-C*H* appeared along with aliphatic protons and also from its NMR in the presence of Eu(fod)$_3$ it has not become possible to pick up the coupling pattern of these two and hence to assign any particular structure out of the two possible adducts IX and X. Besides the separation of these adducts from this Diels-Alder reaction we also isolated three dimers A, B and C having melting points 134°, 168° and 143° respectively. Nazarov *et al.*[6] had earlier reported the isolation of three dimers of same melting points from another Diels-Alder condensation. Later Kuo *et al.*[7] also obtained two dimers A and B by warming tetralol I in AcOH and tentatively proposed their structures as XI and XII respectively on the basis of UV and NMR data and Alder-Stein rule[8]; they, however, did not obtain the dimer C. The dimers A and B now obtained had the same UV and NMR data as reported by Kuo *et al.*[7]. In addition to this data we also determined mass spectra of these dimers in which A and B showed strong fragments of *m/e* 186 besides the molecular ion peak at M^+ 372. If we consider A and B as XI and XII as proposed by Kuo *et al.*[3] then the formation of the fragment *m/e* 186 may be depicted by retro-Diels-Alder of XII and fragmenta-

tion of XI in the manner shown by half arrows in their structures. The dimer C of which a structure is yet to be proposed showed no carbonyl absorption in its IR, and its NMR spectrum showed one proton triplet at 350 (J=7 Hz) indicating the presence of one olefinic proton and one deshielded aliphatic proton at 208 as a hump which appeared to be that for a benzylic-cum-allylic proton. On the basis of this data and in analogy with the structures of dimers A and B, and keeping in view the other possibilities of placement of double bond the product C could have structure XIII, formed obviously through an intermediate XIV, which has so far not been isolated. In the mass spectral fragmentation of XIII, there was no fragment of m/e 186 and the major fragments were at m/e 211 and 161, in addition to the molecular ion peak at M^+ 372, which could arise as a result of fragmentation across the broken line.

Though the spectroscopic data fits well with the proposed structures XI, XII and XIII for dimers it does not exclude the possibility of alternative structures for these dimers such as XV which would have similar spectral characteristics. Thus to assign unequivocally the structures of these dimers an unambiguous synthesis would be needed.

In a similar Diels-Alder addition of tetralol I or diene II with *trans*-β-nitrostyrene under refluxing benzene for 36 hr gave an adduct mixture with the adduct XVI as the main reaction product containing no unreacted diene or its dimer as observed from the NMR of the crude reaction product. By repeated crystallization of this mixture from $CHCl_3$-benzene and benzene-hexane followed by chromatographic purification over silica gel column, it became possible to isolate three pure adducts XVI, XVII and XVIII the structures of which were assigned on the basis of their spectral data given below: XVI, m.p. 198° ($CHCl_3$-benzene); IR (KBr): 1546 and 1376 (NO_2); UV (MeOH) nm (ε): 217·5 (23850), 264·5 (23850); NMR: 229 (*s*, 3, OCH_3), 288 (*d* of *d*, 1, 1-C*H*-NO_2, J=9·5 and 10·5 Hz), 377 (*bh*, 1,4-C*H*=C, $W^{\frac{1}{2}}$=12 Hz), 455 (*d*, 1, 5-Ar*H*, J=8·5 Hz); M^+ 335. XVII, m.p. 177° (benzene-hexane); IR (KBr): 1565 and 1372 (NO_2); UV (MeOH) nm (ε): 216 (20390), 264 (18210); NMR: 229 (*s*, 3, OCH_3), 290-322 (complex, centred around 307, 1, 2-C*H*-ON_2), 372 (*bh*, 1, 4-C*H*=C, $W^{\frac{1}{2}}$=11 Hz), 457 (*d*, 1, 5-Ar*H* J=8·5 Hz). XVIII, m.p. 120° (benzene-hexane); IR (KBr): 1541 and 1367 (NO_2); UV (MeOH) nm (ε): 220 (15620), 275 (14930); NMR: 228 (*s*, 3, OCH_3), 256 (*bd*, 1, 1-C*H*Ph, J=7 Hz), 272-297 (*m*, centred around 285, 1, 2-C*H*-NO_2); M^+ 335.

Adduct XVII on refluxing with conc. HCl in EtOH resulted migration of the double bond giving a product identical in all respect with adduct XVIII. This transformation further substantiated their structural assignments. However, an adduct having 1-nitro-2-phenyl group with double bond at 4a, 10a-position was not isolated from β-nitrostyrene reaction and also this adduct could not be obtained by isomerization of the double bond in adduct XVI by refluxing with conc. HCl in ethanol.

Interestingly, corresponding adducts V and VII were the main products isolated from the condensation of I or II with *trans*-cinnamic acid and methyl *trans*-cinnamate.

References

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