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TRANSANNULAR PHENOMENA IN CYCLIC DIACETYLENES

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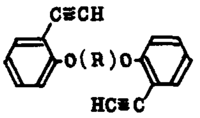
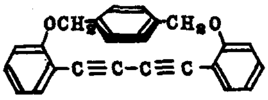
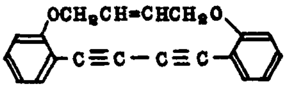
Recently we have shown that the oxidative coupling of α,ω-diacetylenes of type I with cupric acetate in pyridine[1] leads to the cyclic diacetylenes[2]. We have studied the synthesis of the same type of cyclic diacetylenes bearing π-electron system in R to investigate the possibility of transannular interaction with the diacetylenic function.



I



II_p



III_t , III_c

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[1] **G. Eglinton and A. R. Galbraith, *Chem. & Ind.* 1956, 737 ; *J. Chem. Soc.* 1959, 889.**

[2] **F. Toda and M. Nakagawa, *Chem. & Ind.* 1959, 458 ; *Bull. Chem. Soc. Japan* 33, 223 (1960).**

The oxidative coupling of 1,4-bis-(o-ethynylphenoxymethyl)-benzene (I, R= p-xylylene group, m.p. 93~94°C) which was derived from sodium o-ethynylphenoxide and p-xylylene dibromide gave the cyclic monomer, II_p (m.p. 274~275°C, hydrogenated to $C_{24}H_{24}O_2$, m.p. 195~197°C, Mol. wt., 381, calcd., 344). Similarily, the oxidative coupling of the terminal diacetylene (I, R= trans-2-butenylene group, m.p. 118~119°C) which was obtained by the reaction of sodium o-ethynylphenoxide with trans-1,4-dichloro-2-butene yielded the cyclic diacetylene, III_t (m.p. 130°C (decom.), hydrogenated to $C_{20}H_{24}O_2$, m.p. 63.5°C, Mol. wt., 303, calcd., 296). The corresponding o-xylylene isomer, II_o (m.p. 148.5°C (decom.), hydrogenated to $C_{24}H_{24}O_2$, m.p. 180°C, Mol. wt., 346, calcd., 344) and the cis-2-butenylene isomer, III_c

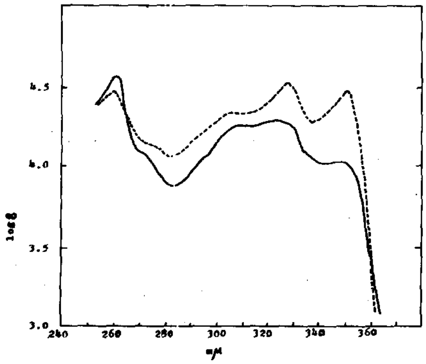

Fig. 1. The U.V. spectra of II_p(——) and IV(-----).

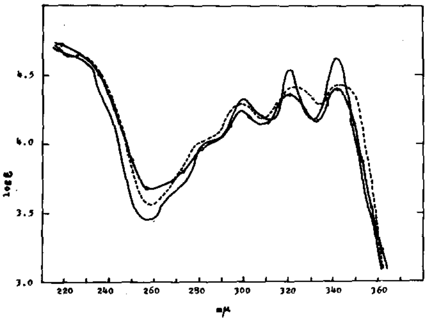

Fig. 2. The U.V. spectra of II_o(–o–o–), III_t(-----) and III_c(——).

(m.p. 154°C (decom.), reduction product was proved to be identical with that of III_t) were prepared according to a similar sequence of reactions.

The ultraviolet spectrum of II_p showed broad and flat absorption peaks as compared with the well defined sharp peaks in the spectrum of o,o´-dibenzyloxydiphenyldiacetylene (IV) as illustrated in Fig. 1. Also the absorption bands arising from the out-of-plane deformation of the adjecent two hydrogen atoms in the p-disubstituted benzene nucleus appeared at 814 cm^{-1} and 796 cm^{-1} in the infrared spectrum of 1,4-bis-(o-ethynylphenoxymethyl)-benzene (I, R= p-xylylene), whereas the corresponding absorption shifted to 776 cm^{-1} in the case of II_p. The same type of an anomalous ultraviolet spectrum was observed in the case of III_t, but could not be seen in the spectra of II_o and III_c (Fig. 2)*.

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* The ultraviolet spectra of III_t, III_c and II_o showed hypsochromic shift of absorption peaks as compared with those of the open chain analogues. This phenomenon could be ascribed to a large ring strain involved in these cycles. Also the presence of a strong absorption minimum at ca. 260 mμ could be attributed to a proximity effect of methylene groups in the bridging chain to the diyne unit. The detailed account of the spectral properties of this series of compounds will be published in near future.

An examination of the scale models of these diacetylenic cycles reveals that the p-xylylene group in II_p and the trans-ethylenic linkage in III_t are held closely to the diyne unit, on the other hand the o-xylylene group in II_o and the cis-ethylenic linkage in III_c are fixed fairly apart from the diacetylenic bond in the cycles. From these observations, it seems to be highly probable that the anomalousness in the spectra of II_p and III_t is associated with a transannular interaction of π-electrons in the bridging chain with those of the diyne function.

The details of this investigation will be published elsewhere in near future.