HETERODIENE SYNTHESIS

III.* REACTION OF ACETYLENEDICARBOXYLIC ACID ESTER WITH FORMAZANS

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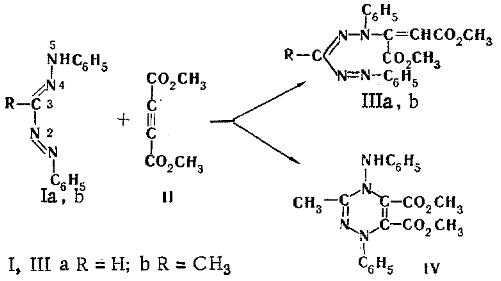
Both 1,4,-cycloaddition with the formation of a 1,4-dihydro-1,2,4-triazene derivative and electrophilic addition of acetyldicarboxylic acid ester to the secondary nitrogen atom occur during the reaction of acetylenedicarboxylic acid ester with 1,5-diphenyl-3-methyl-3-methylformazan. In the case of 1,5.diphenylformazan, the reaction proceeds only in the second direction.

Dienes with one and two nitrogen atoms which form nitrogen-containing heterocycles by reaction with dieneophiles are described in [1-3]. The diene system of formazans (−N=N−C=N−) apparently should also react with dienophiles via a 1,4-cycloaddition scheme.

Different products, depending on the C-3 substituent, were obtained by the reaction of formazans Ia and b with acetylenedicarboxylic acid esters (II). Ia forms only IIIa with II according to the well-known scheme [4] for the addition of acetylenes, activated by acceptor groups, to nucleophilic reagents.

In addition to IIIb, Ib gives a higher yield of a 1,4-cycloaddition product viz., a 1,4-dihydro-1,2,4-triazine derivative (IV).



I, III a R = H; b R = CH_3

It may be assumed that the methyl group attached to C-3 of Ib affects the polarization of the dienes; this promotes a competitive Diels−Alder reaction and sets up more favorable steric conditions.

III are crystalline, colored compounds: IIIa is ruby-red, IIIb is orange-red. The product of the diene synthesis of IV is a colorless, crystalline substance. IV has somewhat low analytical results since it begins to decompose to the starting materials during recrystallization on heating the solvent.

The structure of the compounds obtained were proved by the IR absorption spectra. The appearance of bands at 1730 cm^{-1} in the spectrum of IIIa and b, as compared with the starting Ia and b, and the disappearance of bands above 3100 cm^{-1} indicate the addition of the carbonyl-containing group to nitrogen.

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*See [3] for Communication II.

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Valence vibrations of the N−H bond, which forms intermolecular hydrogen bonds and is manifested as a band at 3280 cm^{-1}, are observed in the spectrum of a solid sample of IV. A carbon tetrachloride solution of IV displays two bands from the valence vibrations of the N−H bond. The band at 3405 cm^{-1} corresponds to the amino group which forms an intramolecular hydrogen bond, while the frequency at 3495 cm^{-1} corresponds to vibration of the free NH group.

The UV spectra also confirm different structures for the products of reaction of Ia and b with II. Addition products IIIa and b have absorption maxima at 392 and 377 nm in contrast to the starting Ia and b which have maxima at 425 and 410 nm. The significant shift without a change in the character of the curve and the disruption of the interval of the absorption maxima should apparently be explained by a similar effect of the unsaturated ester residue in Ia and b with preservation of the formazan structure of the molecules (IIIa and b). In addition, the absorption in the more remote short-wave region for IV (λ_{max} 266 nm) and the absolutely different character of the curve confirm the conclusions of IR spectroscopy and are explained by significant changes with disruption of the conjugated system of the formazans due to the formation of a 1,2,4-dihydrotriazine derivative (IV).

EXPERIMENTAL

Reaction of Dimethyl Acetylenedicarboxylate with1,5-Diphenylformazan. 1,5-Diphenyl-5-(1,2-dimethoxycarbonylvinyl)formazan (IIIa). A solution of 1.7 g (0.0075 mole) of Ia [5] and 1.1 g (0.0075 mole) of II in 15 ml of absolute benzene was refluxed for 1-3 h or allowed to stand at room temperature for 12 days. The solvent was removed in vacuo, 5 ml of methanol was added to the thick, oily residue, and the mixture was thoroughly stirred and allowed to stand overnight. The resulting ruby-red crystals of IIIa were filtered to give (by refluxing) 0.63 g (23%) (on standing) 1.35 g (50%) of a product with mp 119 deg (methanol). Found %: C 62.61; H 4.94; N 15.00. $C_{19}H_{18}N_4O_4$. Calc. %: C 62.28; H 4.95; N 15.29.

Reaction of Dimethyl Acetylenedicarboxylate with 1,5-Diphenyl-3-Methylformazan. 1,5-Diphenyl-3-methyl-5-(1,2-dimethoxycarbonylvinyl)formazan (IIIb) and 1,4-Dihydro-1-phenyl-3-methyl-4-phenylamine-5,6-dimethoxycarbonyl-1,2,4-triazine (IV). A solution of 1.45 g (0.01 mole) of II and 2.4 g (0.01 mole) of Ib [6] in 10 ml of absolute benzene was gently refluxed for 3 h. The benzene was evaporated in vacuo almost to dryness. The residue was diluted with 7 ml of methanol and allowed to crystallize to give 0.5 g (13%) of fine, orange red prisms of IIIb with mp 162-163 deg (methanol). Found %: N 14.84; $C_{20}H_{20}N_4O_4$. Calc. %: N 14.73.

The mother liquor, after removal of the crystals of IIIb, was evaporated and the residue was washed with petroleum ether and thoroughly stirred with benzene. The resulting precipitate of IV was filtered and washed with benzene to give 0.8 g (21%) of almost colorless prisms with mp 155 deg (dec., methanol). Found %: N 13.96. $C_{20}H_{20}N_4O_4$. Calc. %: N 14.73. Additional amounts of IV could be isolated from the mother liquor.

The IR spectra of KBr pellets and CCl_4 solutions of the compounds were obtained with a UR-20 spectrophotometer. The UV spectra in ethanol were obtained with an SF-4A spectrometer.

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