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PHOTOCONDENSATION OF ARYLACETYLENES WITH ANTHRAQUINONE

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Compounds with a labile system of multiple bonds, obtained by the photocondensation of quinones with tolans [1-3], can, in our opinion, exhibit photochromic properties when functional substituents are inserted into the conjugation chain. In the present paper, besides tolan (II) and phenylacetylene (III), we ran the photocondensation of 4,4'-dimethoxytolan (IV) and p-diethynylbenzene (V) with 9,10-anthraquinone (I).

In the photocondensation of (I) with (IV), immediately after the start of irradiation, an absorption band at 368 nm appears in



Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk. Novosibirsk State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 912-915, April, 1977. Original article submitted December 13, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50. the UV spectrum of the reaction mixture, which corresponds to the initially formed compound (VI), and it is followed in 3-5 min by a band at 408 and 425 nm, which corresponds to the dehydrocyclized product (VII). Two new brightly colored spots with R_f 0.35 for (VI) and 0.47 for (VII) appear simultaneously when the reaction mixture is subjected to TLC (Silufol, CHCl₃). Compounds (VI) and (VII) were isolated in an overall yield of 62% by chromatography on Al₂O₃.

The possibility of dehydrocyclizing (VI) to (VII) was confirmed by the irradiation of pure (VI) under the same conditions. In the NMR spectrum of (VII) the ratio of the intensity of the signals of the aromatic protons to the signals of the protons of the methoxyl groups is smaller than for (VI) by a value of two protons. A conversion of the UV spectrum of product (VI) to the spectrum of (VII) with isobestic points is observed here. The structure of (VI) and (VII) was confirmed by the elemental analysis data and by comparing the UV, IR, and NMR spectra with the spectra of the known compounds (VIII) and (IX) [3, 4].

The photocondensation of the bifuctional acetylenic compound (V) with (I) led to product (X), which simultaneously contains an ethyl and an aldehyde group. The formation of the condensation product at two ethynyl groups was not observed under these conditions. The



yield of (X) is low (7-8%), the same as when (I) is condensed with (III), where the yield of aldehyde (XI) is 5-6% [5]. The low yields are explained by the low reactivity of the terminal acetylenes and the instability of the obtained aldehydes.

The kinetic measurements, which were made employing UV spectroscopy, permit making a qualitative comparison of the reactivity of the studied acetylenes. The observed optical density D of the long-wave absorption band in the UV spectrum increases with time in proportion to the increase in the concentration of the reaction product, which was calculated from the extinction coefficients of authentic samples, measured in benzene. A comparison of the rates of increase in D made it possible to arrange the employed acetylenic compounds in the following order of relative reactivity: 4,4'-dimethoxytolan > tolan > p-diethynylbenzene > phenylacetylene. The UV spectral data for the synthesized products are given in Table 1.

EXPERIMENTAL

Equipment of the condenser type, equiped with either DRSh-250 or DRSh-500 lamps, was used for the photochemical synthesis. The reaction was run in benzene in flasks made from either Pyrex or Jena-G-20 glass, which assured irradiation with λ > 310 nm. The course of the process was followed employing TLC and via the UV spectra. The end of reaction was considered to be the point when the condensation product showed the maximum absorption in the UV spectrum. Further irradiation led to a decrease of this absorption due to photolysis and tarring.

<u>Photocondensation of (I) with (IV).</u> With stirring, a suspension of 2.2 g (0.0106 mole) of (I) and 3.3 g (0.013 mole) of (IV) in 150 ml of benzene was irradiated with light (λ > 310 nm) in a N₂ stream for 50 h. The mixture was evaporated to 50 ml and the unreacted (I) was removed by filtration. The filtrate was subjected to chromatographic separation on an Al₂O₃ column (III activity). The starting (IV) and traces of (I) were eluted first with benzene, and then (VI) and (VII) were eluted in sequence with ether. After evaporation of the ether, the fraction containing (VI) represents a light yellow "solid foam." After washing with hot hexane and recrystallization from a hexane-benzene mixture we obtained 2.6 g (57%) of light yellow needle crystals of (VI), mp 139-140°C. Found: C 80.51; H 5.19%. C₃₀H₂₂O₄. Calculated: C 80.70; H 4.9%. Infrared spectrum (in CHCl₃, ν , cm⁻¹: 1170 (C-O-C), 1670 (C=O),

Compound	λι (ε.10-3)	λ2(ε.10-3)	λ ₃ (ε.10 ⁻³)	λ.4 (ε · 10-3)	24 (e·10-3) *	λ.₅ (ε · 103)	2.6 (E · 10-3)	λι (ε.10-3)	$\lambda_{\rm s}(\epsilon\cdot 10^{-3})$
EEEEEEEEEEEE	$\begin{array}{c} 232 (55,4)\\ 232 (45,8)\\ 231 (42,4)\\ 231 (42,4)\\ 241 (40,3)\\ 230 (25,6)\\ 225 (24,0)\\ \end{array}$	$\begin{array}{c} 279 \left(33,5 \right) \\ 279 \left(34,6 \right) \\ 252 \left(34,7 \right) \\ 248 \left(42,0 \right) \\ 254 \left(23,1 \right) \\ 259 \left(20 \right) \end{array}$	295 (35,4) 295 (35,4) 278 (37,3) 282 (30,7,3) 280 (12,9) 290 (12,9) 290 (12,4)	$\begin{array}{c} 370(13,0)\\ 293(32,2)\\ 356(9,4)\\ 352(13,9)\\ 352(7,3)\\ 350(7,3)\\ 350(7,3)\end{array}$	$368 (10, 2) \\ 354 (\overline{9}, 1) \\ 355 (9, 2) \\ 351 (9, 2) \\$	307(28,4) 302(14,9) -	320 (19,2) 320 (12,8) -	387 <u>(</u> 10,1) 385 (<u>12</u> ,4) 	$424 \frac{1}{(7,5)}$ $397 \frac{1}{(7,5)}$

UV Spectral Data for Condensation Products of Anthraquinone with Acetylenic Compounds in Ethanol TABLE 1.

*Solvent = benzene

2800-3000 (-CH₃). NMR spectrum (in CD₃COCD₃): four multiplet signals of aromatic protons in the 6.40-8.10 ppm region with an intensity ratio of 2:4:6:4, and two singlets of the protons of the methoxy groups at 3.60 and 3.65 ppm. After removal of the ether from the fraction containing (VII), the residue was recrystallized from a benzene hexane mixture to give 0.2 g (5%) of (VII), which represented orange crystals that strongly fluoresced under a chemiscope and had mp 215-216°. Found: C 81.16; H 4.65%. C₃₀H₂₀O₄. Calculated: C 81.08; H 4.50%. Infrared spectrum (in CHCl₃, v, cm⁻¹): 1170 (C-O-C),1670 (C = O), 2800-300 (-CH₃). TheNMR spectrum (in CD₃COCD₃, δ , ppm) consists of a series of signals in the region of the aromatic protons, with an intensity ratio of 1:1:1:1:1:4:2:1:2, and chemical shifts of 8.86 d, 8.70 d, 8.36 d.d, 8.12 d.d, 7.97 d, 7.73 d, 7.31 m, 7.05 d.d, and 6.68 d, and signals of the methoxy groups at 3.65 and 3.89 ppm.

The photocondensation of (I) with (II) under analogous conditions leads to (VIII) in 39% yield, mp 197°, and (IX), mp 229°; cf. [3]. Infrared spectrum of (VIII) (in $CHCl_3$, v, cm^{-1}): 1670 (C = 0). The NMR spectrum of (VIII) (in CD_3COCD_3 , δ) has three multiplets in the 6.90 and 8.10 ppm regions, with an intensity ratio of 2:3:13, which belong to the aromatic protons. The NMR spectrum of (IX) (in $CDCl_3$, δ , ppm) consists of a series of signals in the region of the aromatic protons, with an intensity ratio of 1:2:1:11, and chemical shifts of 9.00 d, 8.72 d.d, 8.38 d.d, 8.12 d.d, and 7.10-7.90 m.

Photocondensation of (I) with (V). With stirring, a bright yellow suspension of 6.45 g (0.031 mole) of (I) and 3 g (0.032 mole) of (V) in 300 ml of benzene was irradiated for 30 h in a nitrogen stream; the mixture turned dark here. After evaporation, filtration, and chromatographing on Al₂O₃ (III activity) (elution first with benzene and then with ether) we isolated 0.75 g (7.5%) of (X), mp 180-181° (from a benzene-hexane mixture). Found: C 86.12; H 4.42%. C₂₄H₁₄O₂. Calculated: C 86.21; H 4.42%. Infrared spectrum (in CHCl₃, v, cm⁻¹): 1670 (C = 0), 2120 (-C \equiv C-), 2800 (C-H) of aldehyde), 3110 (\equiv C-H). The NMR spectrum (in CD₃COCD₃), δ) has the signals of aromatic protons in the 6.70-8.20 ppm region, the singlet of an acetylenic proton at 3.05 ppm, and an aldehyde proton at 10.4 ppm. In a similar manner, the photocondensation of (I) with (III) gave (X) in 6% yield, mp 85-87°. Infrared spectrum (in CDCl₃, δ) has the signals of aromatic protons in the 6.70-8.20 ppm region, and the signal of the proton of an aldehyde group at 10.4 ppm.

CONCLUSIONS

The photocondensation of anthraquinone with 4,4'-dimethoxytolan proceeds much faster and gives the reaction products in higher yield than does the photocondensation of anthraquinone with phenylacetylene and p-diethynylbenzene.

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