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# THE PHOTOCHEMISTRY OF *trans*-*trans*-*o*-PHENYLENEDIACRYLATE[1]

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We have prepared diethyl *o*-phenylenediacrylate, a substituted *o*-divinylbenzene, by a Wittig reaction, and have found that its photochemistry differs significantly from that reported for *o*-divinylbenzenes (1,2) and other susbtituted divinyl arenes (3), and the formally analogous 1,3,5-hexatrienes.

A solution of carbethoxymethylenetriphenylphosphorane (4) in benzene was added to a solution of phthaladehyde (in benzene) and heated at reflux for 18 hours to give, after purification, a 58% yield of *trans*-*trans*-*o*-phenylenediacrylate (I), m.p. (from ether) 77.5-78° (lit. (5) m.p. 81°); $\lambda_{max}^{CH_3CN}$: 258 mμ (ε 31,800), 292 mμ (ε 25,800); ν(KBr) 3070, 2990, 2940, 2910, 1720, 1630, 1430, 1310, 1180, 980, and 770 $cm^{-1}$. The nmr (60MHz) spectrum of I showed the expected AB pattern for *trans* olefinic protons centered at $\tau$2.0 and 3.7 (*J*=16Hz), and peaks centered at $\tau$2.57 (aromatic), 5.74 (methylene), and 8.68 (methyl), in a ratio of 1:1:2:2:3.

Irradiations of 0.5% (0.018M) solutions (nitrogen purged) of I in acetronitrile at 2537 and 3500Å (Rayonet Photochemical Reactor) and with an unfiltered 550-w Hanovia mercury arc lamp were monitored by quantitative thin-layer chromatography[2] on aliquots. Separation of the complex mixture of products was extremely difficult. In a typical preparative experiment 20 ml of a 5% (0.18M) solution was irradiated with 3500Å light for about 30 hr then applied to 40 tlc plates (silica gel G; E. Merck) which were developed three times (benzene + 1% EtOH). The zones were collected, combined and eluted.

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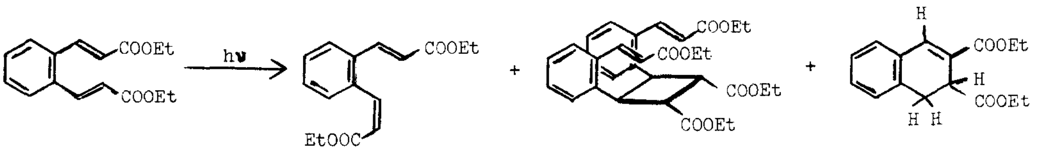
[1] Taken in part from the Ph.D. Thesis of W.H. Ploder.

[2] The method, based on the relationship of spot size to weight of substance and using calibration curves for each compound, is described by Nybom (6). The relative experimental error is ±10%.

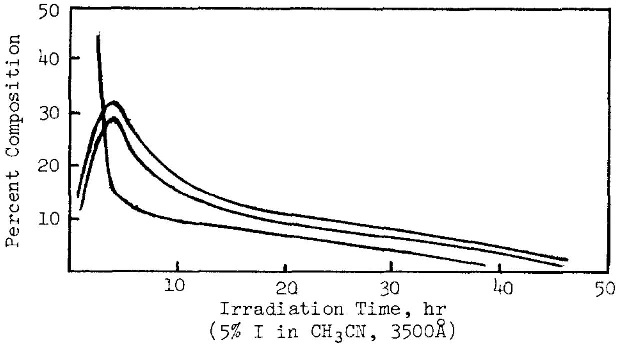


I II III IV

+ V (see below) + others

The appearance of the major photoproducts II and III with time is given in Fig. 1. Prolonged irradiation completely consumed I and only higher molecular weight material (crystalline solid from EtOH) remained, having the same elemental analysis as I and molecular weight of the order of 7000-10,000 by vapor pressure osmometer measurement.

Fig. 1



Compound II, which can be obtained in about 90% yield (3 hr irradiation of 0.5% soln ($CH_3CN$), at 2537Å), is a colorless oil with the same elemental analysis as I and molecular weight 269 (theory 274) by vapor pressure osmometer measurement. $\lambda_{max}^{CH_3CN}$: 261 mμ (ε 21,600), 285 mμ (ε 21,200); the nmr (100MHz) spectrum showed two methyl groups centered at τ8.69 and 8.9, two methylene groups centered at τ5.76 and 5.96, aromatic protons centered at τ2.7 (m,4), and two AB quartets: doublets centered at τ2.21 and 3.67 (2,*J*=16Hz, trans), and doublets centered at τ2.78 and 3.88 (2,*J*=12Hz, cis). Spin decoupling experiments confirmed the assignments.

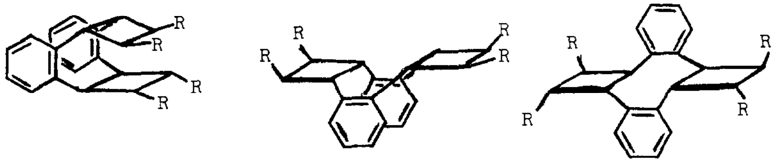
The infrared spectrum of III, a colorless oil, showed conjugated trans double bond (1640 and 975 $cm^{-1}$); the nmr (100MHz) spectrum showed an AB quartet with doublets centered at τ2.21 and 4.04 (2,*J*=16Hz) confirming this, and peaks centered at τ5.75 (q,8,methylenes), 8.67 and 8.69

(t,12,methyls), and 2.9 (m,8,aromatic). The peaks centered at τ5.21 (m,2) and 6.16 (m,2), which complete the spectrum, are typical of a cyclobutane ring system. The mass spectrum of III showed its parent peak at *m/e* 548, indicating a photodimer. From the many possible cinnamic ester type dimers, the structure of III was established by a careful examination of the fine structure (expanded) of the cyclobutane protons, and calculation of the signs of the coupling constants of the 1,3 (diagonal) protons according to the method of Steinmetz (7). A calculated $J$=-0.2Hz requires that the 1,3 protons are *trans*. Furthermore, III was readily saponified (equivalent found: 145, theory: 137) and the resulting acid converted to the anhydride (infrared spectrum: 1860, 1810, and 1790 $cm^{-1}$) with acetic anhydride. It is well known that *trans* cyclobutane decarboxylic acids cannot form anhydrides (8), so the *cis* arrangement of the carbethoxy groups, and the structure of III, is established.

Compound IV, obtainable in quantities of the order of 0.5%, is a colorless solid, m.p. (from hexane) 77°. The ultraviolet spectrum (hexane) showed a broad band at 289 mμ (ε 18,400) with shoulders at 282 mμ (ε 17,900) and 310 mμ (ε 8,650), compared to 1,2-dihydronaphthalene ($\lambda_{max}$258(ε 9,950)). A bathochromic shift of 31 mμ and the increase in extinction coefficient are in excellent agreement with the predicted value for the addition of the ester group as in diethyl 1,2-dihydro-2,3-naphthalenedicarboxylate (IV). The nmr spectrum (60MHz) showed peaks at τ2.39 (s,1,olefinic), 2.81 (s,4,aromatic), 5.72 and 5.97 (q,4,methylenes), and 8.96 (t,6,methyls). An examination of the 3 proton 12 line ABX system, which completes the spectrum with peaks at τ6.05, 6.12, 6.18, 6.24, 6.46, 6.52, 6.73, 6.78, 6.79, 6.89, 7.03, and 7.15, gave (10) coupling constant values $J_{AB}$=16.1, $J_{AX}$=4.2, and $J_{BX}$=7.5Hz. Chemical confirmation for the structure of IV involved saponification to the diacid which melted at 190°, solidified immediately and remelted at 215° (probably anhydride formation). Reduction with sodium amalgam gave the known 1,2,3,4-tetrahydro-2,3-dicarboxylic acid (11), m.p. 199° (lit. (11) m.p. 199°); remelted, after cooling, at 185° (anhydride, lit. (11) m.p. 184°).

Compound V was detected (by tlc) in all the photolyses of I, in quantities of the order of 0.1%. The most notable spectroscopic characteristic of this solid, m.p. (from hexane) 173°, was the complete absence of any olefinic unsaturation. The mass spectrum of V showed its parent peak at *m/e* 548, suggesting a photodimer in which the four double bonds had formed two cyclobutane rings. Calculation of the signs (7) of the coupling constants of the cyclobutane 1,3 protons, from the nmr (100MHz) spectrum, required a *trans* arrangement ($J$=-2.8Hz), as before. Also, the fact that the aromatic multiplet, centered at τ2.58, was symmetrical suggests a symmetric arrangement of the cyclobutane systems. However, the data available from the limited amount of material do not allow a differentiation between the three possibilities shown in Fig. 2. Other materials detectable in trace amounts by thin-layer chromatography have not been identified.

Fig. 2



R = COOEt

DISCUSSION

The well known photoinduced cis-trans isomerization to II was the predominating process in all the photolyses of I. Of particular interest is that only one of two identical trans double bonds was isomerized. The generation of II from I was rapid until a certain cis/trans ratio was achieved (Table 1), generally after 1-1½ hr (except in the experiment using benzophenone as sensitizer - 30 min). Further irradiation consumed II and increased the quantity of polymer; and the concentration of I (0.5% soln) did not change significantly until enough II had been consumed to effect a cis/trans ratio of 2 (i.e. 66.7% cis), whereupon the concentration of both I and II decreased.

TABLE 1

| Solvent | Moles/l. | Lamp(Å) | Cis/Trans |
|---|---|---|---|
| $CH_3CN$ | 0.182 | 3500 | 2.0 |
| $CH_3CN$ | 0.0182 | 3500 | 7.0 |
| $CH_3CN$ | 0.0182 | 2537 | 7.9 |
| $CH_3OH$ | 0.0182 | 3500 | 3.1 |
| hexane | 0.0182 | 3500 | 3.8 |
| $CH_3CN$ | 0.0182* | 3500 | 2.5 |

*1% Benzophenone added

This behaviour is consistent with the establishment of a photostationary state like that which has been studied extensively for the photochemical isomerization of cis- and trans-cinnamic acids (12). Control experiments with mixtures containing 50% and 97% of the cis-trans-isomer (II) gave the same cis/trans ratios as were obtained from the pure trans-trans-isomer (I), confirming this hypothesis. Furthermore, the data in Table I are consistent with the reports that in unsensitized photoisomerizations decreasing cis-isomer concentrations are observed with increasing wavelength (13) and with higher concentrations (12,14).

No dimer product III (or V) could be detected by tlc analysis of the experiment which began with 97% II. Furthermore, no dimer product could be detected in the experiment using benzophenone as sensitizer. If efficient sensitization of the acceptor by benzophenone ($E_T$ = 69 kcal) can be assumed, these observations suggest that dimerization occurs via the singlet excited state of the trans-trans-isomer (I) exclusively (triplet involvement in the isomerization would be expected). Dimers must arise from excited trans-trans molecules prior to stationary state adjustment, since no dimer was detected in the photolysis beginning with 97% of the cis-trans isomer (II), but was detected in all experiments beginning with pure trans-trans-isomer (I).

Formation of dimer III (or V) must be via the "allowed" ${}_{\pi}2_s + {}_{\pi}2_s$ (15) cycloaddition of an excited (singlet) trans-trans-molecule (I) on one in the ground state, by analogy with other bimolecular dimerizations.

No intramolecular isomerization product related to the benzobicyclo[3.1.0]hexene or indane systems, by analogy to the o-divinylbenzenes (3), was found. Formation of IV may require a diradical intermediate with subsequent hydrogen atom migration (1,2); however, an electrocyclic mechanism might be involved in the formation of such an intermediate. On the basis of calculations and the use of state correlation diagrams, it can be shown[3] that if o-divinylbenzene were to undergo an "electrocyclic" reaction (rather than the $2_s + 2_s + 2_a$ cycloaddition (15) proposed for the formation of a bicyclo[3.1.0]hexene system (1,2)) only the conrotatory mode could proceed from the first excited state. It should be noted that calculations done on I (including the carbethoxy substituents as part of the conjugated system) showed the same orbital symmetry relationships as for unsubstituted o-divinylbenzene.[3] The product, a substituted benzobicyclo-[2.2.0]hexene, would be unstable, firstly, for the more obvious reason that the cyclobutanes would be tran-fused, and secondly, because one of the two new σ-orbitals would be antibonding,[3] which describes the tetrahydronaphthalene 1,4-diradical. The decomposition of benzobicyclo-

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3. E.C.W. Scheuneman and W.G. Laidlaw, University of Calgary, private communication. We thank the authors for making this information available prior to publication.

[2.2.0]hexene to 1,2-dihydronaphthalene has been reported (16).

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