

THE PHOTOREDUCTION OF CONJUGATED DIACETYLENES
TO VINYLACETYLENES

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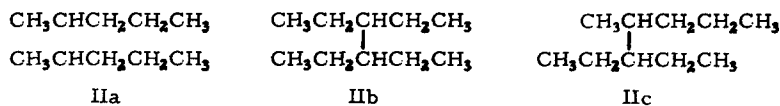
The solution photochemistry of conjugated diacetylenes has not been studied until now. Recently Pontrelli (1) showed that on vapor phase irradiation of 1,3-butadiyne with 2537 Å light the only gaseous products observed were acetylene and a little 1,3,5-hexatriyne. His results indicated the existence of an electronically excited bent 1,3-butadiyne when it absorbed 2537 Å light.

We now find that conjugated diacetylenes on irradiation in hydrogen-donor solvents act as hydrogen acceptors. Thus, irradiation of 0.1 g 5,7-dodecadiyne (I) [$\lambda_{\max}^{\text{EtOH}}$ 215, 227, 240, 255 $m\mu$ (ϵ 290, 385, 370 220); ν_{\max}^{neat} 2262, 2169 cm^{-1}] in 120 ml pentane with a 2537 Å low pressure mercury quartz immersion lamp (Hanau NK 6/20) for 4 hrs yielded a reaction mixture which by vpc analysis consisted of a mixture of branched decanes (II) (13%), cis-5-dodecen-7-yne (cis-III) (44%), trans-5-dodecen-7-yne (trans-III) (26%) and two addition products $\text{C}_{17}\text{H}_{30}$ of a molecule of pentane to one of the triple bonds of I [IV (10%) and V (7%)]. Vpc analysis (using an internal standard) showed that the above products accounted for ca. 35% of the reaction mixture; another 55% was a viscous brown oil. Irradiation of 3,5-octadiyne in pentane yielded analogous results.

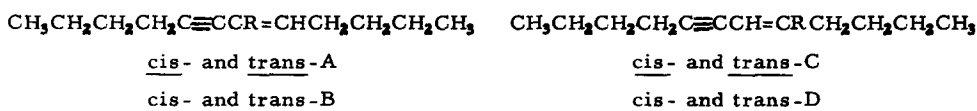
For preparative purposes 1 g batches of I in 185 ml pentane were irradiated with a 450-w Hanovia high pressure mercury lamp fitted into a quartz immersion probe for 7.5 hrs, distilled in high vacuo and the distillate (ca. 45% yield) separated by preparative vpc. cis- and trans-III were identified by their spectral properties as well as by vpc comparison with authentic samples. The latter were prepared by the Weedon modification of the Straus reaction (2) from 1-hexyne. From the reaction mixture cis- and trans-III were separated by preparative vpc: cis-III [bp 114-115° (25 mm); n_D^{26} 1.4616; $\lambda_{\max}^{\text{EtOH}}$ 227, 235sh $m\mu$ (ϵ 15, 250, 12, 400); ν_{\max}^{neat} 2217, 1618, 739 cm^{-1}]; trans-III (containing 4.5% cis-III) [bp 123-124° (25 mm); n_D^{26} 1.4669; $\lambda_{\max}^{\text{EtOH}}$ 228, 235sh $m\mu$ (ϵ 15, 400, 13, 300); ν_{\max}^{neat} 2217, 966 cm^{-1}].

The physical properties of II (molecular ion 142; no absorption in the UV; only saturated

methyl and methylene protons in the nmr) and its vpc analysis indicated it to be a mixture of branched decanes, possibly IIa-c, which were formed on dimerization of 2- and 3-pentyl radicals.



The spectral properties of oils IV [molecular ion 234; $\lambda_{\text{max}}^{\text{EtOH}}$ 228 m μ (ϵ 7, 800); $\nu_{\text{max}}^{\text{CHCl}_3}$ 2217 cm.⁻¹; $\delta_{\text{ppm}}^{\text{CDCl}_3}$ ratio of saturated methyl and methylene protons/allylic and propargylic protons ca. 22.5:5, and very low smeared-out olefinic band at ca. 5.1-6.0] and V [molecular ion 234; $\lambda_{\text{max}}^{\text{EtOH}}$ 228 m μ (ϵ 8, 500); $\nu_{\text{max}}^{\text{CHCl}_3}$ 2198 cm.⁻¹; $\delta_{\text{ppm}}^{\text{CDCl}_3}$ ratio of saturated methyl and methylene protons/allylic and propargylic protons ca. 24.5:5, and very low smeared-out olefinic band at ca. 5.2-6.1, ca. 1H] and their vpc analysis showed them to be mixtures of substituted vinylacetylenes which were formed on addition of pentane to one of the triple bonds of I. Formulas A-D may account for the structures of



(R=CH₃CHCH₂CH₂CH₃ for A and C and CH₃CH₂CHCH₂CH₃ for B and D)

hydrogen (molecular ion 238) whereas on full hydrogenation (10% Pd/C in acetic acid/perchloric acid) the peak at 238 as well as a molecular ion at 240 were absent, the latter because of the high branching in the fully saturated product (3).

Direct irradiation of I in other hydrogen-donor solvents (cyclohexane, methylene chloride, methanol, isopropanol) also yielded cis- and trans-III and smaller amounts of higher boiling products (possibly also addition products of I and solvent) as well as dimers of solvent radicals. Thus, in cyclohexane and in methylene chloride dicyclohexyl and 1,1,2,2-tetrachloroethane respectively, were formed. However in all these solvents the major products were brown oily polymers, which in methanol* and isopropanol amounted to about 80% of the photolysis mixture. On the other hand we find that disappearance of I is much slower when irradiated in a relatively poor hydrogen-donor solvent such as t-butanol, only traces of the isomers of III being formed and I is almost completely converted to a brown oily polymer.

* A similar result was obtained in Professor W. G. Dauben's laboratory on irradiation of I in methanol, to whom acknowledgement is made for this information and for his interest in this work.

Evans (4) located the triplet energy of I at 79.5 kcal which is close to that of isolated double bonds (≈ 80 kcal). This is supported by our finding that benzene (E_T 85 kcal) (5), toluene (E_T 83 kcal) (5) and *p*-xylene sensitize the diyne photoreduction in hydrogen-donor solvents, whereas triphenylene (E_T 65 kcal) does not. Furthermore, in the presence of sensitizers of intermediate triplet energies, such as acetophenone (E_T 74 kcal) and acetone ($E_T > 75$ or > 70 kcal) (6) disappearance of I was very slow but none the less *cis*- and *trans*-III were formed among other products. Thus, whereas disappearance of I (0.1 g in 120 ml pentane) on direct irradiation with a 2537 Å lamp was complete after 4 hrs, in the presence of the above aromatic hydrocarbon sensitizers (0.1 g, 115 ml pentane, 5 ml sensitizer; about 98% of the light absorbed by the sensitizer at 254 m μ) I was wholly consumed after 1.75 hrs in benzene, after 1 hr in toluene and after 1.5 hrs in *p*-xylene. Product distribution, e. g. in benzene, was as follows: II 9%, *cis*-III 27%, *trans*-III 26%, IV 22% and V 16%, but as in the direct irradiation the above products accounted for ca. 20% of the photolysis mixture, the remainder being a brown oil.

The photostationary ratio *cis*-III/*trans*-III was found on irradiation of either isomer in pentane with 2537 Å light to be ≈ 1.7 and on sensitized irradiation (5% benzene in pentane) to be ≈ 1.0 . It has already been shown that conjugated vinylacetylenic systems on irradiation undergo only *cis-trans* isomerization (7).

The above results identify electronically excited conjugated diynes as hydrogen acceptors and the reaction is reminiscent of the photoreduction of saturated aliphatic and aromatic ketones (8, 9), thioketones (10), ketoimides (11) and nitrobenzene (12). The photoreduction sensitized by aromatic hydrocarbons (13) may proceed by way of the triplet state of the diyne (formed by triplet energy transfer from triplet sensitizer) which first abstracts a hydrogen atom from the solvent to give an alkynylvinyl radical and the latter then accepts a second hydrogen atom from the solvent to give an enyne, or reacts with a solvent radical to give substituted vinylacetylenes. The observation that this sensitized photoreduction proceeds faster than photoreduction by direct irradiation and only with sensitizers of triplet energy larger than that of the diyne (but not at all with triphenylene) lends support to such a mechanism. Furthermore, the slow photoreduction with sensitizers of somewhat lower triplet energy than that of the diyne (acetone, acetophenone) may also be significant to the above arguments (14). Transfer of singlet energy from the aromatic hydrocarbon sensitizer to the diyne is unlikely since this requires large overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor (15) and this condition is practically not fulfilled for benzene (16) and evidently less so for toluene and *p*-xylene.

As the photoreduction by direct irradiation proceeds it is to some extent slowed down by light absorption by the produced vinylacetylenes (at λ 254 m μ , ϵ 50). Another contribution to this slow-down may be quenching of diyne triplets by the vinylacetylenes formed, although the route of the photoreduction by direct irradiation is yet unknown. This, as well as the photochemistry of other acetylenic systems is now under investigation.

References

1. G. C. Pontrelli, J. Chem. Phys., 43, 2571 (1965).
2. M. Akhtar and B. C. L. Weedon, Proceed. Chem. Soc., 303 (1958); R. F. Garweed, E. Oskay and B. C. L. Weedon, Chem. Ind. (London), 1684 (1962).
3. R. I. Reed, Applications of Mass Spectrometry to Organic Chemistry, p. 44. Academic Press, London and New York (1966).
4. D. F. Evans, J. Chem. Soc., 1735 (1960).
5. R. B. Cundall, Progress in Reaction Kinetics, Vol. 2, p. 165. Pergamon Press (1964).
6. (a) R. C. Helgeson and D. J. Cram, J. Am. Chem. Soc., 88, 509 (1966); (b) G. S. Hammond, N. J. Turro and P. A. Leermakers, J. Phys. Chem., 66, 1144 (1962).
7. J. B. Jones, J. Chem. Soc., 5759 (1963).
8. J. Saltiel, Survey of Progress in Chemistry, Vol. 2, p. 239. A. F. Scott, Ed., Academic Press, New York and London (1964).
9. N. C. Yang, 13th Council of Chemistry, International Institute of Chemistry (Solvay), Interscience Press, New York, N. Y., in press.
10. G. Oster, L. Citarel and M. Goodman, J. Am. Chem. Soc., 84, 703 (1962).
11. M. Fischer, Tetrahedron Letters, 43, 5273 (1966).
12. R. Hurley and A. C. Testa, J. Am. Chem. Soc., 88, 4330 (1966).
13. For triplet energy transfer from aromatic hydrocarbons to isolated double bonds which have triplet energies close to those of conjugated diynes see P. J. Kropp, J. Am. Chem. Soc., 88, 4091 (1966); J. A. Marshall and R. D. Carroll, ibid., 88, 4092 (1966).
14. For analogous inefficient triplet energy transfer in cis-trans isomerization of 2-pentene see reference (6b).
15. T. Forster, Discussions Faraday Soc., 27, 1 (1959).
16. C. A. Parker, Anal. Chem., 34, 502 (1962); J. G. Calvert and J. N. Pitts, Jr., Photochemistry, p. 282. John Wiley and Sons, Inc., New York, London and Sydney (1966).