Tetrahedron Letters No.14, pp. 891-894, 1971. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL CYCLOADDITION OF CYCLOOCTYNE TO BENZENE

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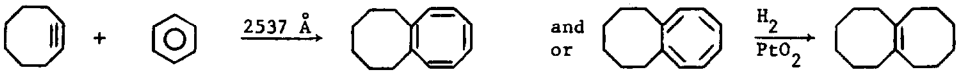
(Received in USA 13 January 1971; received in UK for publication 12 March 1971)

The photochemical cycloaddition of acetylene to benzene and its simple derivatives leading ultimately to cyclooctatetraenes has enjoyed rather limited applicability. Previously, successful examples were confined to electron deficient acetylenes or activated aromatic systems.[1] Very recently, Bryce-Smith and co-workers[2] have reported the inefficient production of cyclooctatetraene ($\Phi < 0.001$) upon irradiation of benzene and acetylene, and have claimed the formation of n-butylcyclooctatetraene in unspecified yield from the irradiation of 1-hexyne and benzene.

In order to evaluate the effect of high ground state energy and fixed cisoid geometry of cyclic acetylenes on photochemical reactivity, as well as the synthetic possibility of producing a potentially useful fused ring derivative containing the cyclooctatetraene moiety, the photochemical reaction of cyclooctyne, 1, and benzene was investigated.

The irradiation at 2537 Å of a degassed solution of cyclooctyne (0.039 M) in benzene solution for 42.5 hours produced cleanly, and in high yield, a single 1:1 adduct of cyclooctyne and the solvent.[3] Sampling of the photolysate at frequent intervals showed that the rapid initial build up of adduct was followed by a gradual slowdown in the reaction as the ratio of adduct/cyclooctyne approached a limiting value of ca., 1.9. At this point, increased irradiation time or transfer of the solution to a fresh tube had little effect on this ratio. After 42.5 hours (66% conversion) the yield of the adduct was 56%. A solution of cyclooctyne in benzene was completely stable under the reaction conditions in the dark.

The structural assignment of the product, 2, rests firmly on spectral, analytical, and catalytic hydrogenation data. The NMR spectrum of 2 consisted of absorptions at τ ($CDCl_3$) 3.16 (multiplet, 6H); 7.90 (broad multiplet, 4H, allylic protons); and 8.4 (broad singlet, 8H, nonallylic cylooctyl ring protons). The infrared spectrum (neat) exhibited strong bands at 2800, 1470, and 690 cm^{-1} with a weak absorption at 1635 cm^{-1} (carbon-carbon double bond). The 70 eV mass spectrum showed a parent ion at m/e 186 and strong fragmentation peaks at 158, 143, 129 (base peak), 117, 115, and 91. The ultraviolet spectrum (C_6H_{12}) of the pale yellow adduct was particularly informative. It showed strong end absorption at $\lambda > 220$ nm, with a pronounced shoulder at 283 nm ($\varepsilon = 312$). This spectrum is consistent with that reported for cyclooctatetraene and a number of simple substituted derivatives.[4] Consideration of this spectral data lends support to the assignment of adduct as 2.[5]



1 2 3

Further confirmation of this structure was provided by catalytic reduction. The hydrogenation (1 atm) of 2 in hexane over Adam's catalyst resulted in the rapid uptake of 95% of three equivalents of hydrogen.[6] The structure of the hydrogenated product, which could be separated from some minor contaminants by preparative glpc, was supported by spectral data and comparison with an authentic sample recently prepared by an unambiguous route.[7] The NMR spectrum of 3 showed absorbances at τ (CCl_4) 7.95 (multiplet, 8H, allylic protons) and 8.57 (broad singlet, 16H, cyclooctyl ring protons). The 70 eV mass spectrum showed a parent ion at m/e 192 and major fragmentation peaks at 96, 95, 82, 81, 79, and 67 (base peak).

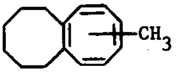
That the adduct was not produced as a consequence of subsequent thermal rearrangement upon glpc purification was verified by NMR examination of the crude photolysate which clearly showed the characteristic resonances of 1 and 2.

The question of the eventual cessation in the conversion of starting material to product once the ratio of 2/1 reached ca., 1.9 was considered in the following manner. The possibility of dominant light absorption by 2 was eliminated by calculations based on the extinction coefficient of 2 ($\varepsilon^{2537} = 554$) which indicated that the benzene was still absorbing ca., 98% of the incident light. The question of a possible photostationary equilibrium involving 1 and 2 was resolved by the irradiation of pure 2 in benzene solution. After 70 hours of irradiation the ratio of 2/1 was 19/1. Hence, although some cyclooctyne is produced, even after 70 hours, it comprises only 5-7% of the mixture and not the 35% observed in the original photolysate.

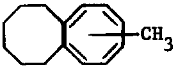
These data imply that the adduct itself or some undetected side product may be quenching further photochemical conversion of the starting material.[8] Consistently, the irradiation of cyclooctyne and benzene in the presence of varying concentrations of purified cyclooctatetraene results in the formation of only minor quantitites of 2. At the same time no new products could be detected nor was the added cyclooctatetraene consumed.

Attempts to sensitize the reaction produced an interesting result. When cyclooctyne in benzene solution was irradiated at $\lambda > 3000$ Å using either naphthalene or acetophenone as the sensitizer, virtually none of the desired adduct 2 could be detected by glpc. The latter sensitizer led to the rapid consumption of starting material but none of the desired cycloadduct. However, if acetone was used as a dilute solution in benzene (0.5-2M) the adduct 2 was produced in an overall yield comparable to the direct irradiation. The formation of adduct in the acetone irradiations was strongly quenched by the addition of *trans*-piperylene. This successful sensitization is particularly interesting in light of the report[1d] that the addition of benzophenone actually inhibits the photochemical cycloaddition of dimethyl acetylenedicarboxylate to benzene. These facts, considered with the improbable endothermic transfer of triplet energy from acetone to benzene, lead to the interesting possibility that the acetylene triplet may be the reactive species in the cycloaddition.

Preliminary attempts to extend this reaction to other benzene derivatives have met with mixed success. The irradiation of cyclooctyne in toluene (2537 Å) produces the expected cyclooctatetraene derivative, 4, in 25-30% yield. The overall structure of 4 is secured by its spectral data.[5] The nmr spectrum of 4 shows absorbances at τ (CCl_4) 4.41 (m, 5H) and 7.48-8.97 (m, 15 H, dominated by a broad allylic methyl singlet at 8.33 and a broad singlet at 8.5 due to cyclooctyl ring protons). The uv spectrum (C_6H_{12}) of 4 exhibited strong end absorption at $\lambda >$ 220 nm with a shoulder at 280 nm ($\varepsilon = 330$). The partial (70 eV) mass spectrum showed a parent mass at m/e 200 and strong fragment peaks at 157, 143 (base), 131, 129, and 91. Perhaps unexpectedly, however, the substitution of *o*-xylene as the solvent in the irradiation leads to the formation of a complex mixture of high boiling products in very low yield.



and
or
4



Further comprehensive synthetic and mechanistic investigation of the photochemistry of medium-sized cycloalkynes is proceeding.

REFERENCES

1. (a) E. Grovenstein, Jr., and D. Rao, Tetrahedron Lett., 148 (1961);
   (b) E. Grovenstein, Jr., T. C. Cambell, and T. Shibata, J. Org. Chem. 34, 2418 (1969);
   (c) D. Bryce-Smith and J. E. Lodge, Proc. Chem. Soc., 333 (1961);
   (d) D. Bryce-Smith and J. E. Lodge, J. Chem. Soc., 695 (1963);
   (e) G. Buchi, J. G. Atkinson, D. E. Ayer, and E. W. Roff, J. Am. Chem. Soc. 85, 2257 (1963);
   (f) R. S. H. Liu and C. G. Krespan, J. Org. Chem. 34, 1271 (1969).
2. D. Bryce-Smith, A. Gilbert, and J. Grzonka, Chem. Comm. 498 (1970).
3. Satisfactory elemental analyses were received for all unknown compounds.
4. A. A. Cope and H. C. Campbell, J. Am. Chem. Soc. 74, 179 (1952).
5. These spectral data alone do not rigorously establish the double bond positions within the unsaturated ring nor rule out a mobile equilibrium between the double bond isomers. Additional work in this area is proceeding.
6. The failure of 2 to rapidly absorb four moles of hydrogen under these conditions is expected based on the steric hindrance of the hexahydroderivative and finds precedence in the literature.[1]
7. K. Lin, D. Patterson, and P. Eaton, unpublished results; this material was prepared by a method analogous to that described by K. Lin, Thesis, University of Chicago, 1966.
8. The ability of cyclooctatetraene itself to quench triplets has been reported previously.[9]
9. (a) G. S.Hammond, N. J. Turro, and P. A. Leermakers, J. Phys. Chem. 66, 1144 (1962);
   (b) I. Hartmann, W. Hartmann, and G. O. Schenck, Chem. Ber. 100, 3146 (1967).