Tetrahedron Letters No.8, pp. 663-666, 1969. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMISTRY OF BI-2,4,6-CYCLOHEPTATRIEN-1-YL

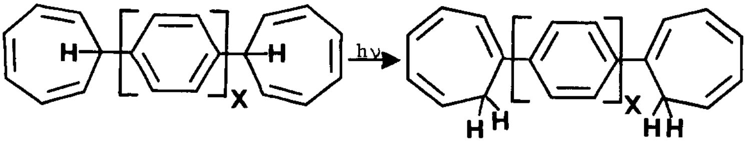
Richard S. Givens
Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

(Received in USA 9 October 1968; received in UK for publication 16 January 1969)

We presently report some quantitative results on the photochemistry of bi-2,4,6-cycloheptatrien-1-yl (ditropyl). I. The isomerization does not proceed to an excited state of the product. II. We have established the 1,7 sigmatropic hydrogen migration for this system as a singlet reaction.

Two reports[1,2] have appeared on the photochemistry of systems containing two cycloheptatriene rings fused at the saturated carbon (I and II). Both report that the only isomerization product isolated was the result of two 1,7 hydrogen shifts (III and IV, respectively). If these are the primary products of the photochemical reaction, then an intriguing question arises concerning the rearrangement pathway. In order to undergo two 1,7 shifts from the same initially excited molecule, the first 1,7 hydrogen migration must proceed along a pathway to an electronically excited product. Before demotion occurs to the electronic ground state a second 1,7 migration in the other tropilidene ring must ensue, leading to the double migration product (III or IV). This would be a double reaction per quantum process. Such rearrangements proceeding through the excited state of the product are rare. On the other hand, if demotion to a thermally excited ground state occurred at some stage prior to the second migration, one would expect the symmetry allowed 1,5 migration[3] product instead of the observed 1,7 migration.

I, X = 0
II, X = 1

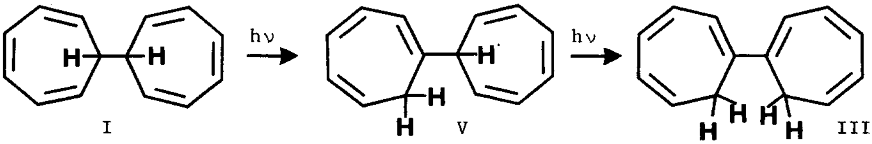


III, X = 0
IV, X = 1

Irradiation of solutions of ditropyl[4] with a 450-watt Hanovia lamp in a variety of solvents (benzene, hexane, ether, t-butyl alcohol and ethanol) led to two detectable products. Examination of the mixture at low conversion revealed the presence of only one product which upon further irradiation built up to a maximum, finally giving way to the second product. Upon extended irradiation, only the second product and some polymer could be detected.

By working up the reaction mixture at an intermediate stage, the two products could be isolated in good yield. This required removal of the solvent, chromatography of the crude mixture on alumina (Woelm, activity I) with hexane to separate the remaining ditropyl from the two products. The two could then be separated by an additional chromatography on 3% silver nitrate on silica gel. Eluting with 5% ether in hexane, the first product from the column was obtained as a yellow oil with nmr absorption at (CCl_4) τ 3.6-4.0, m, 8 H; 4.45-4.9, d of d, 2 H; 7.45, d, (J = 7cps) 4 H: ir absorption at (CCl_4) 3050, 1440, 1370, 1290 and 705 cm^{-1}: uv absorption at λ_{max}^{EtOH} 340 (ϵ 10^4) and 262 mμ (ϵ 4.0 x 10^3): and a molecular ion peak at m/e 182. This data is consistent only with 1-(1,3,5-cycloheptatrienyl)-1,3,5-cycloheptatriene (III). The nmr and ir spectra of this compound are identical to those of the second product detected in the irradiation. Further evidence for the structure was provided by the hydrogenation of III which took up 6 mole-equivalents and yielded bicycloheptyl as the only detectable product.

The second compound, eluted with 10% ether in hexane, showed nmr absorption at τ 3.3-3.6 m, 4 H; 3.7-3.9, m, 4 H; 4.5-5.0, m, 3 H; 7.4-7.7, a doublet (J = 7cps) superimposed on a multiplet, 3 H: ir absorption at 3025, 1625 w, 1475, 1370 w and 700 cm^{-1}: uv absorption at λ_{max}^{EtOH} 262 mμ (ϵ 6.2 x 10^3): and a molecular ion peak at m/e 182. Hydrogenation on Pd/C required 6 mole-equivalents and yielded bicycloheptyl. These results are consistent with 1-(2,4,6-cycloheptatrienyl)-1,3,5-cycloheptatriene (V), the intermediate in the double 1,7 hydrogen migration to compound III.



I V III

Thus the evidence is against the excited state of V as being the initial product[5] (*i.e.*, $I \xrightarrow{h\nu} I^*$, $I^* \longrightarrow V^* \longrightarrow III$).

Mechanistic Studies

Information was desired concerning the multiplicity of the excited state leading to the 1,7 hydrogen migration. Since the triplet energy of the cycloheptatriene ring system is unknown, the quencher chosen was di-t-butylnitroxide, a paramagnetic triplet quencher.[6,7] In a similar manner triplet sensitizers were selected on the basis of their high triplet energies (acetophenone, 74 kcal/mole and benzophenone, 68 kcal/mole[8]) in order to attempt efficient triplet energy transfer. The results of several runs are listed in the table.

Additive[a]	Concentration (M)	Ditropyl Concentration (M)	ϕ Ditropyl Disappearance
None[b]		2×10^{-2}	0.14
Di-t-butyl nitroxide[b]	0.08	2×10^{-2}	0.14
Benzophenone[b]	1.0	2×10^{-2}	0.0
Benzophenone[c]	0.1	2×10^{-2}	0.0
Acetophenone[c]	0.004	2×10^{-3}	0.0

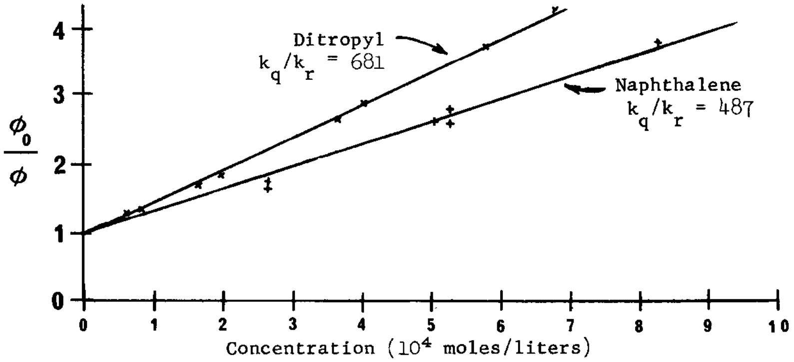
a. All Runs were in benzene using pyrex sample compartments. The samples were degassed with nitrogen and irradiated in a "merry-go-round" apparatus.

b. Light Source: RPR-3000, Southern New England Ultraviolet Company.

c. Light Source: RPR-3500.

That the triplet energy of benzophenone was transferred to ditropyl was shown to be the case by separate experiments using ditropyl as a quencher in the photoreduction of benzophenone by benzohydrol in benzene.[9] Excellent agreement with the Stern-Volmer relationship was obtained and demonstrated a diffusion controlled quenching efficiency greater than that of naphthalene.[10]

The Stern-Volmer Plot of the Quenching
Of Benzophenone Photoreduction by Energy Transfer to Ditropyl



These results establish the nature of the excited state leading to hydrogen migration as being the singlet. The triplet of ditropyl does not undergo any reaction leading to detectable products and must return to ground state through some energy dissipating process. Since the triplet and the singlet both undergo very inefficient chemical transformation ($\phi_S = 0.14$ and $\phi_T = 0.0$) the mechanism for energy dissipation remains uncertain. There is evidence that excited ditropyl undergoes a homolytic cleavage to two tropenyl radicals[11] but the nature and extent of this photochemical process is unknown. Work is in progress concerning this and alternate pathways for the decay of the excited ditropyl to the ground state.

Acknowledgments

We gratefully acknowledge a Frederick Gardner Cottrell Grant from the Research Corporation and a Type G Grant from the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References

1. R. W. Murray and M. L. Kaplan, J. Amer. Chem. Soc., 88, 3527 (1966).

2. E. E. van Tamelen, T. M. Cole, R. Greeley and H. Schumacher, ibid., 90, 1372 (1968).

3. a. W. Volland and G. Vincow, ibid., 90, 4537 (1968).
   b. G. Vincow, M. L. Morrell, W. Volland, H. J. Dauben, Jr., and F. R. Hunter, ibid., 87, 3527 (1965).

4. W. von E. Doering and L. H. Knox, ibid., 79, 352 (1957).

5. Our reinvestigation of the photochemical conversion of the tropylium bromide in ethanol to the conjugated product III (reported in ref. 2) revealed that at low conversion, the mono-1,7-hydrogen migrated species (V) was the initial product.

6. H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley and M. Semmelhack, ibid., 88, 1965 (1966).

7. Attempted quenching of the photochemical 1,7 hydrogen migration using oxygen in benzene (G. W. Bordon, O. L. Chapman, R. Swindell, and T. Tezuka, ibid., 89, 2979 (1967)) proved unsuccessful. This could be due to the singlet being the multiplicity leading to migration or the rate of the migration being too fast for oxygen quenching to compete. The maximum concentration of oxygen in benzene is only 10^{-3} M.

8. W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, ibid., 86, 4537 (1964).

9. In cases where the triplet energy of the acceptor molecule is unknown, it is important to establish that energy has been transferred by some other method. A convenient method in our study was the use of ditropyl as a quencher for another reaction, the photoreduction of benzophenone by benzpinacol in benzene. Previous studies on cycloheptatrienyl systems have not established the triplet energy transfer step.

10. W. M. Moore and M. Ketchum, ibid., 84, 1368 (1962).

11. G. Vincow, M. L. Morrell, F. R. Hunter, H. J. Dauben, Jr., J. Chem. Phys., 48, 2876 (1968).