

A STABLE TETRACHLOROBICYCLO[4,2,0]OCTA-2,4,7-TRIENE
AND ITS BOND-FIXED CYCLOOCTATETRAENE VALENCE TAUTOMERS

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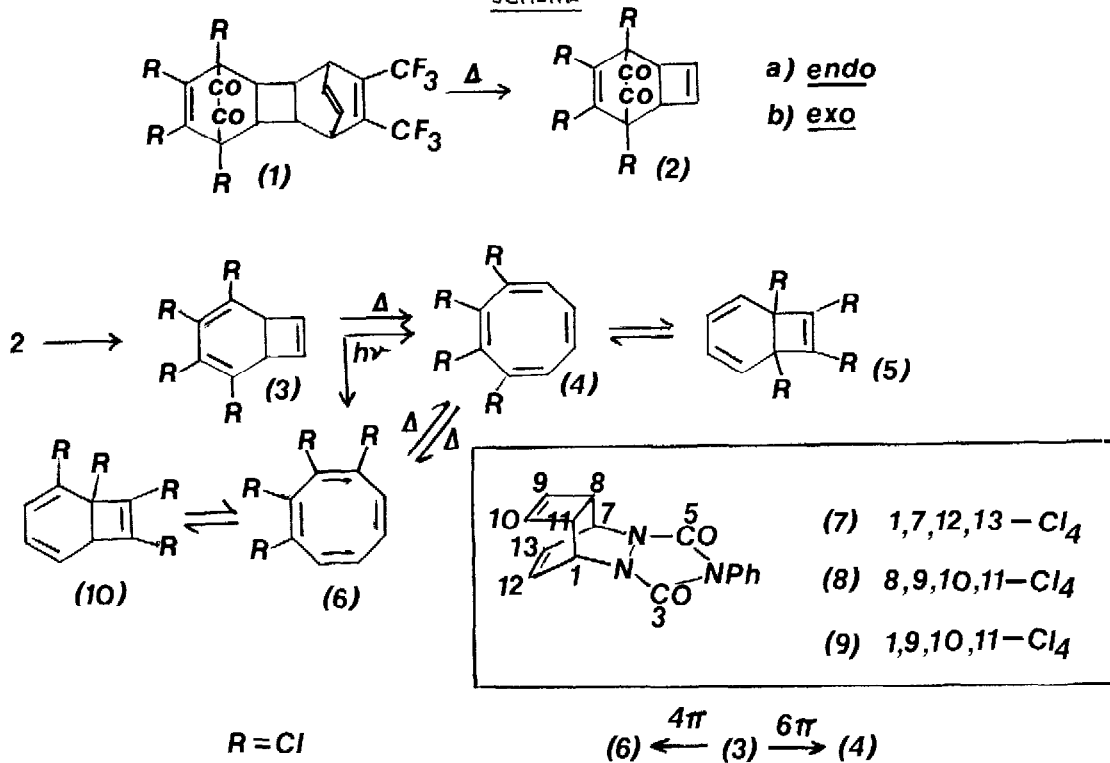
Some years ago we reported that photochemical decarbonylation of tricyclo[4,2,1,0^{2,5}]nona-3,7-dien-9-ones offered a versatile route to the thermally labile bicyclo[4,2,0]octa-2,4,7-triene (BiCOT) system.¹ Although there are numerous elegant routes available for cyclooctatetraene syntheses, synthetic routes to the BiCOT system are few.² In this communication we report a new, photochemically induced, bisdecarbonylation method which is exemplified by the synthesis of the BiCOT 2,3,4,5-tetrachlorobicyclo[4,2,0]octa-2,4,7-triene (3) a stable crystalline compound. In addition we present our data concerning the controlled thermal ring-opening of BiCOT (3) to the crystalline bond-fixed tetrachloroCOT (4), and the mild thermal isomerisation of COT (4) to the bond-shifted isomeric COT (5).

Reaction of o-chloroanil with 7,8-bis(trifluoromethyl)tricyclo[4,2,2,0^{2,5}]deca-3,7,9-triene formed a mixture (4:3) of the endo-adduct (1a) and the exo-adduct (1b).[†] This mixture was subjected to thermal (210°) retro-diene cleavage to yield a similar mixture of the stereoisomeric diketones (2), which was suitable for photodecarbonylation. Brief irradiation in chloroform solution³ effected the smooth bisdecarbonylation to 2,3,4,5-tetrachlorobicyclo[4,2,0]octa-2,4,7-triene (3) [m.p. 38-9°; pmr δ 3.94 (s, bridgehead); 6.26 (s, vinylic); $\bar{\nu}$ 239.9070, calc. for C₈H₄Cl₄ 239.9067]. Rapid reaction occurred between BiCOT (3) and N-phenyl triazolinedione, below room temperature, to form the adduct (7), m.p. ca. 175° dec., which retained C_s-symmetry as judged from the pmr spectrum.

[†] The stereochemistry of these adducts was determined by conversion to their quinoxaline derivatives, through reaction with o-phenylene diamine and analysis of the shielding effect of the quinoxaline ring on the chemical shift of the cyclobutenyl protons (see ref. 3).

Although BiCOT (3) is quite stable at ambient temperatures, it underwent a smooth electrocyclic ring-opening to 1,2,3,8-tetrachlorocyclooctatetraene (4), m.p. 55-57°, at 60° ($t_{1/2} = 15$ min). The pmr spectrum of COT (4) displayed two symmetrical multiplets (δ 6.32, 6.14 in CDCl_3) corresponding to the vinylic protons, thereby confirming the C_5 symmetry of the molecule. The conversion (3) \rightarrow (4) is essentially quantitative (by pmr): thus COT (4) is thermodynamically more stable than BiCOT (3) by at least 4 Kcal mol⁻¹. COT (4) is also in equilibrium with the other C_5 symmetric BiCOT (5). This was verified by the very slow formation of the *N*-phenyl triazolinedione adduct (8), from (4) in the presence of the dienophile. The adduct (m.p. 270° dec.) has C_5 -symmetry [pmr: δ 5.25 (dd, H1,7-allylic and adjacent to nitrogen); 6.57 (dd, H12,13-vinylic); 7.50 (s, phenyl)]. BiCOT (5) is present in minute quantities at equilibrium (not detectable by pmr), and therefore it could not be isolated. Upon more vigorous heating (150°) COT (4) was converted into an equilibrium mixture of (4) and its bond shifted isomer (6). Although attempts to isolate pure (6) failed, it was characterised by its pmr

SCHEME



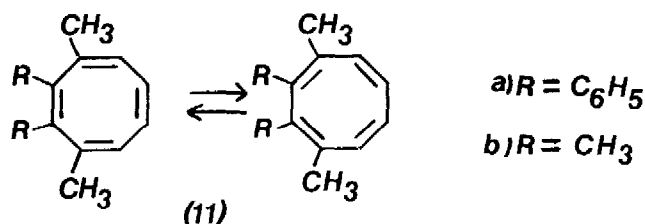
spectrum (sharp singlet δ 6.23; C_5 symmetry) and the N-phenyl triazolinedione derivative (9) (m.p. ca. 225° dec.). The adduct, which formed only slowly, gave a pmr spectrum which clearly indicated lack of any symmetry [pmr: δ 3.86 (1H, m, cyclobutyl); 5.30 (1H, m, bridgehead); 6.55 (2H, m, vinylic); 7.52 (5H, s, phenyl)]. Thus COT (6) must be in equilibrium with BiCOT (10) [from which adduct (9) is formed]. Again the equilibrium greatly favours the monocyclic COT form. The detection of (4) and (6) is another example of the existence of stable bond-switched isomers in cyclooctatetraenes which do not interconvert at normal working temperatures, of which only a few examples have been reported to date.^{1,6}

The photochemical behaviour of BiCOT (3) was next studied. Irradiation of (3) for 3 hr gave unchanged starting material (80%) and a mixture of the COTs (4) and (6) in equal amounts. Fragmentation to acetylene and tetrachlorobenzene was not observed.[‡] Irradiation of COT (4) for 4 hr led to a photostationary state consisting of (4) and (6) in the respective proportions 2:3. Unfortunately the composition of the COTs (4) and (6) in the photochemical reaction of (3) do not necessarily reflect the relative ease of ring-opening of (3) via the photochemical 6π and 4π electrocyclic pathways (Scheme) for the following reasons: (a) the occurrence of the secondary photochemical interconversion (4) \rightleftharpoons (6); (b) some of the COT (4) may have arisen from a vibrationally excited electronic ground state of (3); (c) the presence of halogens render the multiplicity of the reacting excited state of (3) uncertain (i.e. the heavy atoms may induce intersystem crossing to the 1T state⁷).

Finally, we comment on the relative ease of the interconversion between the bond-shift COTs having four adjacent substituents. The dimethyldiphenyl system (11a) interconverts readily at ca. 135°,¹ yet the tetramethyl system (11b) is slow, even at 350°. These results are consistent with the buttressing hypothesis.² The phenyl groups may rotate out of the plane of the (planar) bond delocalised transition state, thereby relieving the steric congestion; such manoeuvres are not possible with the tetramethyl system. Interconversion in the tetrachloro system, (4) \rightleftharpoons (6) is again significantly lower (150°) than

[‡] This contrasts with the dimethyldiphenyl COTs where the various BiCOT forms gave rise to aromatic and acetylene products.⁵

the tetramethyl system. This effect is consistent with observation that vicinal chlorine-chlorine interaction is much lower than the corresponding methyl-methyl interaction as observed in the relative thermodynamic stability of the isomers in 1,2-dichloroethene [(E)-isomer more stable] compared with those of the but-2-enes [(Z)-isomer more stable].



REFERENCES

1. I. W. McCay and R. N. Warrener, Tetrahedron Lett., 1970, 4779; I. W. McCay and R. N. Warrener, ibid, 1970, 4783.
2. Review: L. A. Paquette, Tetrahedron, 1975, 31, 2855.
3. E. E. Nunn, W. S. Wilson, and R. N. Warrener, Tetrahedron Lett., 1975, 175.
4. General photochemical conditions employed were: 0° , N_2 atmosphere, pyrex filter, American Hanovia 450 watt Hg-lamp.
5. I. W. McCay and R. N. Warrener, unpublished data.
6. L. A. Paquette, J. M. Photis and G. D. Ewing, J. Amer. Chem. Soc., 1975, 97, 3538.
7. N. J. Turro "Molecular Photochemistry" W. A. Benjamin, N.Y., 1965, p.57.