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# THE FIRST STABLE MEMBER OF THE 8-OXATRICYCLO[4.3.0.0.$^{7,9}$]NONA-2,4-DIENE RING-SYSTEM

Ronald N. Warrener*, Richard A. Russell† and Richard Y.S. Tan

*Department of Chemistry, S.G.S., Australian National University, Canberra, A.C.T. 2600, Australia*

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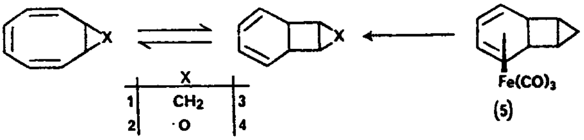
Homologues and heterologues of cyclooctatetraene (COT) are available by replacement of the π-bonds by the appropriate 3-membered ring. Bicyclo[6.1.0]nona-2,4,6-triene (1) (homo-COT), like COT itself is known to be in equilibrium with its 6π valence isomeric form, although the proportion of isomer (3) [(1):(3) = 4500:1][1] is too low to be detected by normal spectroscopic means. Similarly COT epoxide (2) is considered to participate in a related equilibrium (2 ⇄ 4), since reaction with dienophiles yields adducts [e.g. of type (9)] which are logically derived from the valence-isomeric form (4). The 1,2,7,8 tetramethyl derivative of (2) behaves in a similar manner.[2]

Synthetic entry into the valence isomeric series (3, 4) (homo-biCOTs) has been limited to the methylene series, where two methods have been reported to date. Thus Mackenzie and his co-workers have developed an indirect approach[3], while the Brookhart group have prepared the parent system by regeneration from the metal carbonyl complex (5) at low temperature[1,4].



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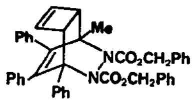
† Visiting Fellow from Faculty of Military Studies, University of N.S.W., Duntroon, A.C.T., 2600, Australia.

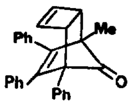
We have previously demonstrated that a photodecarbonylation route can be successfully applied to the synthesis of bicyclo[4.2.0]octa-2,4,7-trienes (biCOTs),[6] and now show that this approach can be extended to the homo-biCOT series. Thus we approached the synthesis of homo-biCOT (16) by irradiation of the pentacyclic ketone (15), again taking advantage of substituent stabilisation to facilitate isolation. A complimentary thermal route involving orbital-assisted nitrogen elimination in the final step, has led to the preparation, isolation and characterisation of the first example of the 8-oxahomo-biCOT ring system (4).

In practice the success of this latter approach [to (4)] hinged about the choice of protecting groups on the hydrazo-bridge. The carbobenzyloxy group was chosen since it could be removed under mild non-hydrolytic conditions ($H_2$/Pd on C) without risk of harming the epoxide ring.

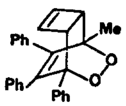
Thus epoxidation of the adduct (6), formed from the reaction of dibenzyl azodicarboxylate and 2-methyl-3,4,5-triphenylbicyclo[4.2.0]octa-2,4,7-triene[7], was achieved by heating with m-chloroperbenzoic acid (m-CPBA) in chloroform solution. Site selective epoxidation occurred at the $\Delta^{3,4}$-cyclobutenyl $\pi$-system to yield (9), which contrasts with the similarly substituted ketone (7) where reaction was observed to occur initially at the $\Delta^{7,8}$-stilbene site.[7,8] We have attributed this difference to an inductive effect induced on the stilbene $\pi$-system by the electronegative nitrogen atoms of the hydrazo-bridge. This explanation is preferred to one based on steric shielding of the stilbene face by the nitrogen substituents (these are expected to adopt a transoid configuration),[7] since $\Delta^{3,4}$ selectivity is observed in the cyclic peroxide (8),[9] where such steric considerations are inappropriate, but strong inductive effects are still present.



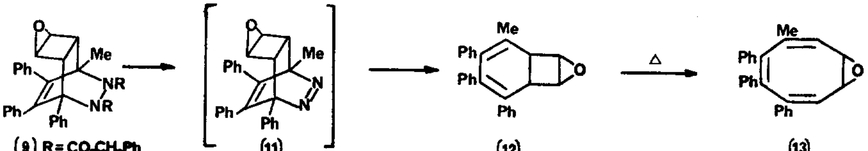
(6)



(7)



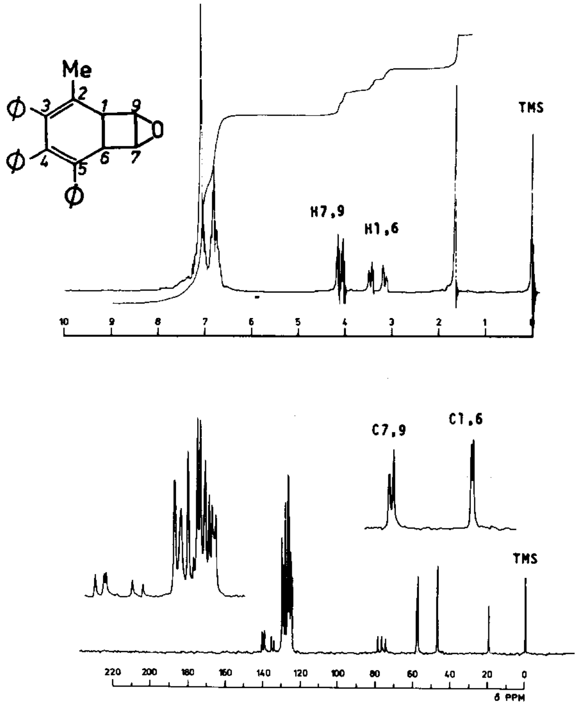
(8)



(9) R=$CO_2CH_2Ph$
(10) R=H
(11)
(12)
(13)

The benzyl groups were removed by hydrogenolysis and the intermediate hydrazo compound (10) not isolated, but treated directly with mercuric oxide at r.t. The resultant product which was isolated by chromatography (p.l.c. on silica, 1:1 light petrol:$CH_2Cl_2$), m.p. 127-8°C was shown to be the tricyclic product (12). Nitrogen elimination must have occurred spontaneously from the first formed azo compound (11), but there is ample precedent for facile ejection of the nitrogen molecule from related systems.[10]

The structure of the 8-oxahomo-biCOT (12) followed from its u.v. spectrum ($\lambda_{max}$, 95% ethanol, 248, 304, 312 nm) which supported the conjugated diene chromophore and its $^1H$-n.m.r. spectrum (Fig. 1a) where cyclobutyl protons are clearly evident. The $^{13}C$-n.m.r. spectrum (Fig. 1b), where only five $sp^3$-type C-resonances were present, ruled out valence isomeric structures such as the (13) (3 × $sp^3$). In addition the presence of the oxirane ring supported by the typical C-resonances at δ57.8, 58.3 ($^{13}C$-H J = 200, 199 Hz). Chemical support for the diene grouping was obtained by the spontaneous reaction of (12) with *N*-p-tolyl-triazolinedione at r.t. (adduct m.p. 216-218°C).

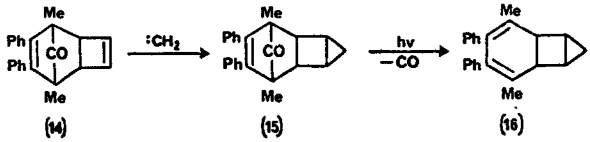


-*FIG. 1*-

*Spectra of 8-oxatricyclo*$[4.3.0.0^{7,9}]$ *nona-2,4-diene (12).*

*a) 100 MHz p.m.r. spectrum in* $CDCl_3$.

*b)* $^{13}C$-$[^1H]$*-n.m.r. spectrum in* $CDCl_3$ *at 15.04 MHz.*



The preparation of the related homo-biCOT (16) was achieved *via* the sequence (14 → 16). Cyclopropanation of the ketone (14) with Simmons-Smith reagent resulted in a site selective reaction at the cyclobutenyl π-bond to yield the bicyclopentane derivative (15), m.p. 160°C. Irradiation of (15) (acetone, $N_2$, 254 nm, 0°C) yielded the oily homo-biCOT (16), which was characterised as its *N*-p-tolyl-triazolinedione adduct, m.p. 222-223°C. The compound was identical with material produced *via* another route.[7]

The formation of this 8-oxahomo-biCOT has culminated a number of years work in this area, where more direct methods have insisted on following other callings. One of these, involving the epoxidation of biCOTs, is discussed in the accompanying communication,[9] and while unrewarding in the synthesis of 8-oxahomo-biCOTs has opened up an interesting area of chemistry in its own right.

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