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THE SYNTHESIS AND PHOTOCHEMISTRY OF BICYCLO[4.2.0]OCTA-2,4,7-TRIENES

Ronald N. Warrener[a], *Ian W. McCay*[a], *Richard Y.S. Tan*[a] *and Richard A. Russell*[b]

a. Department of Chemistry, S.G.S., Australian National University, Canberra, A.C.T. 2601.
b. Department of Chemistry, Faculty of Military Studies, University of New South Wales,
Duntroon, A.C.T. 2600, Australia.

ABSTRACT. *Two new crystalline bicyclo[4.2.0]octa-2,4,7-trienes have been prepared by photodecarbonylation of the appropriate tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-ones and their structures confirmed by ^{13}C-n.m.r. The title compounds all undergo thermal ring opening to cyclooctatetraenes, but photolysis is substituent dependent.*

The thermal lability of bicyclo[4.2.0]octa-2,4,7-trienes towards ring-opening to form the more stable valence-isomeric cyclooctatetraene has been a limiting factor in their synthesis. In fact Paquette and his co-workers have exploited this feature in the preparation of cyclooctatetraenes since the intermediate bicyclooctatrienes formed by Ramberg-Bäcklund reaction of bicyclic α-halosulphones immediately undergo ring-opening under the reaction conditions.[1] Specific methods for the formation of bicyclo[4.2.0]octa-2,4,7-trienes are available and these include low-temperature dehalogenation of dihalobicyclo[4.2.0]octa-2,4,7-dienes[2] or controlled liberation from metal carbonyl complexes.[3] We[4,5] and others[6,7] have described photochemical routes to bicyclo[4.2.0]octa-2,4,7-trienes, and the present paper elaborates further on this topic.

In our initial communication on this subject we reported that the tricyclic ketone (1a) yielded the oily 2,5-dimethyl-3,4-diphenylbicyclo[4.2.0]octa-2,4,7-triene (2a) upon irradiatio in acetone solution.[4,8] The difficulty with this reaction as a synthetic procedure was the photolability of the desired product (2a) under the reaction conditions. Thus irradiation had to be stopped after about 50% conversion for a reasonably pure product to be obtained; prolonged irradiation yielded a complex mixture of products (discussed later) due to secondary photolysis of the bicyclo[4.2.0]octa-2,4,7-triene (2a) competing with the decarbonylation step by which it was produced. This bicyclo[4.2.0]octa-2,4,7-triene (2a) was thermally stable at room temperature and required prolonged heating (24 hrs, refluxing chloroform) to effect thermal ring-opening to the cyclooctatetraene (3a) which reequilibrates, even at room temperature, with a new bicyclo[4.2.0]octa-2,4,7-triene (4a).

Since we wanted to study the chemistry of the bicyclo[4.2.0]octa-2,4,7-triene system we sought a more stable derivative. In this respect the tetraphenyl derivative (2b) was dichotomous: thermal stability was reduced, but photostability increased. Irradiation of the corresponding ketone (1b)[9] yielded 2,3,4,5-tetraphenylbicyclo[4.2.0]octa-2,4,7-triene in moderate yield together with two other products (see below). The reduced thermal stability of the product resulted in conversion to the ring-opened cyclooctatetraene (3b) at a little above room temperature. However, by working at sub-ambient temperature throughout the photolysis and subsequent chromatographic separation the tetraphenylbicyclo[4.2.0]octa-2,4,7-triene could be isolated and recrystallised at low temperature, m.p.105-105.5°C. The ^1H-n.m.r. spectrum of this compound is shown in Fig. 1.

The low temperature photochemical apparatus used for this work is shown in Diagram 1.

Replacing only one of the methyl groups of (2a) with a phenyl group retained the thermal stability of the bicyclo[4.2.0]octa-2,4,7-triene and also increased its photostability. Thus irradiation (acetone, 0°C) of the bridged ketone (1c)[9] could be taken to 75% completion and chromatographic isolation of the resultant bicyclo[4.2.0]octa-2,4,7-triene (2c) achieved in yields in excess of 80% (based on converted ketone). Conventional crystallisation techniques yielded the bicyclo[4.2.0]octa-2,4,7-triene (2c), m.p.109-110°C (^1H-n.m.r. spectrum - Fig. 2).

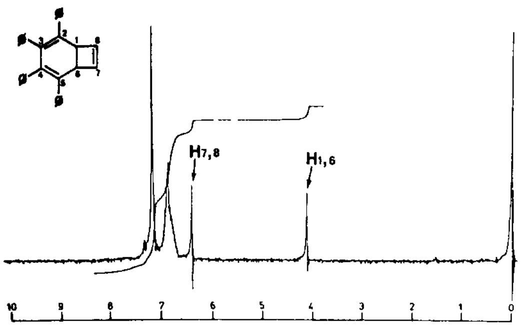


Fig. 1. ^1H-n.m.r. (100 MHz) of (2b) in $CDCl_3$ at 0°C.

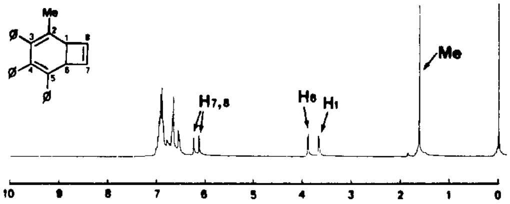


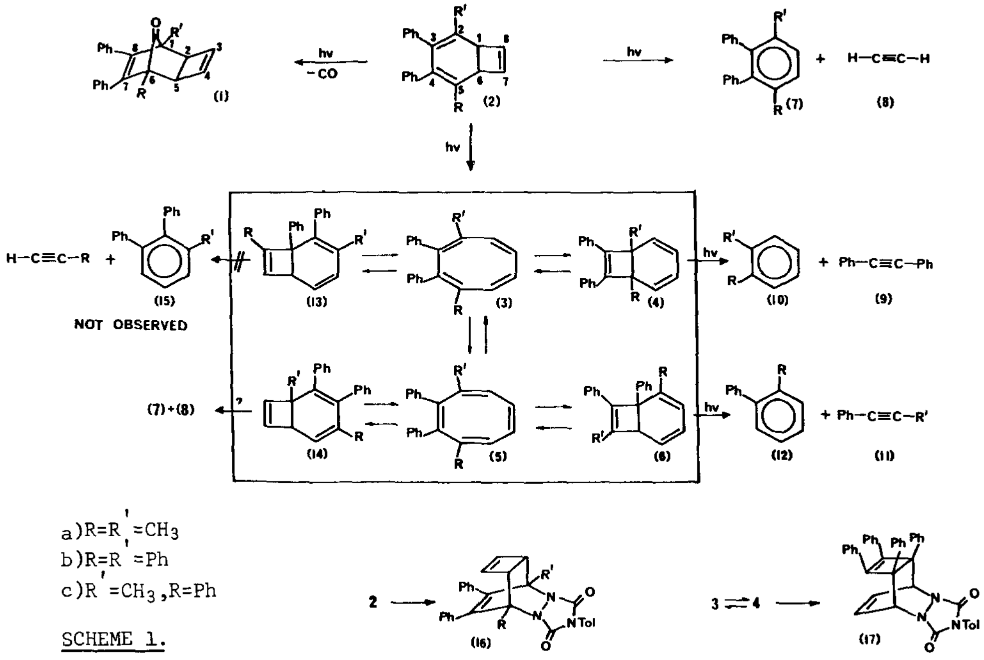
Fig. 2. ^1H-n.m.r. (270 MHz) of (2c) in $CDCl_3$

The structures of these bicyclo[4.2.0]octa-2,4,7-trienes were established by spectrometric measurements and chemical reactivity. The ^{13}C-n.m.r. spectra which are summarised in the Table fully support the bicyclo[4.2.0]octa-2,4,7-triene structure and rule out valence-isomeric forms. Each bicyclo[4.2.0]octa-2,4,7-triene was further characterised as its adduct (16) with *N*-p-tolyl-triazolinedione, and in each case reaction occurred spontaneously at room temperature. [Adduct from (2b) m.p.220°C; (2c) m.p.216°C].

Table 1. ^{13}C-N.M.R. DATA† FOR RING CARBONS OF (2b) AND (2c) AT 67.89MHz.

	C_1	C_6	C_2, C_3, C_4 and C_5	C_7	C_8	Me
2b	47.8	47.8	135.6, 134.0	139.9	139.9	-
2c	47.3	47.9	131.3, 132.3, 133.2, 134.2	139.6	138.9	19.4

† *Chemical shifts in* $CDCl_3$ *relative TMS (2b) at 258°K; (2c) at ambient.*



a)R=R'=CH_3
b)R=R'=Ph
c)R'=CH_3,R=Ph

SCHEME 1.

PHOTOCHEMISTRY OF THE BICYCLO[4.2.0]OCTA-2,4,7-TRIENES (2a) AND (2b)

Continued irradiation of the ketone (1a) or the bicyclo[4.2.0]octa-2,4,7-triene (2a) yielded a mixture which was separated by v.p.c.[10] The resulting products (7a), (9), (10a), (11a) and (12a) were identified by mass spectrometry and by comparison with authentic samples. No evidence could be found for the terphenyl (15). The formation of this series of aromatic and acetylenic compounds could be rationalised by the equilibria and reactions shown in Scheme 1. However, the means of interconversion of the products shown inside the boxed area must remain speculative and most likely represents a combination of thermal[4] and photochemical processes.

Irradiation of the tetraphenylbicyclo[4.2.0]octa-2,4,7-triene (2b) yielded the tetraphenylcyclooctatetraene (3b) together with a minor unidentified product and considerable polymeric material. The cyclooctatetraene was characterised by its ^{13}C-n.m.r. and ^{1}H-n.m.r. spectra (Fig. 3). Reaction with *N*-p-tolyl-triazolinedione occurred slowly and yielded the adduct (17), (m.p.220°, ^{1}H-n.m.r., Fig. 4), which shows that the cyclooctatetraene is in thermal equilibrium with the valence-isomer (4b) and not (13b). Crystallisation of this equilibrium mixture gives the crystalline cyclooctatetraene (3b) and thereby contrasts with the related equilibrium in the dimethyl diphenyl series where the crystalline material has the bicyclic form (4a). The nature of the crystalline form was established by low temperature spectroscopy immediately following dissolution.

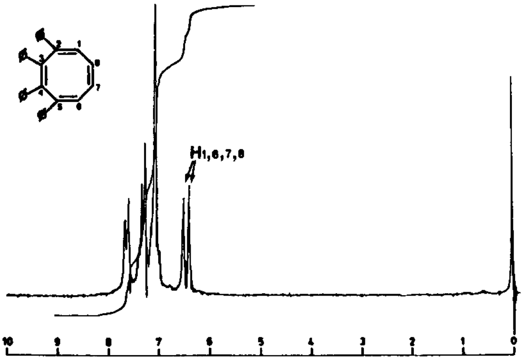


Fig. 3. ^{1}H-n.m.r.(100 MHz) of (3b) in $CDCl_3$

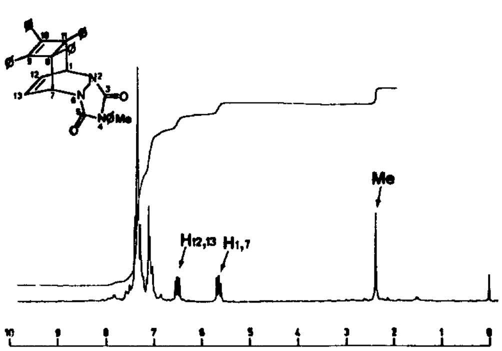
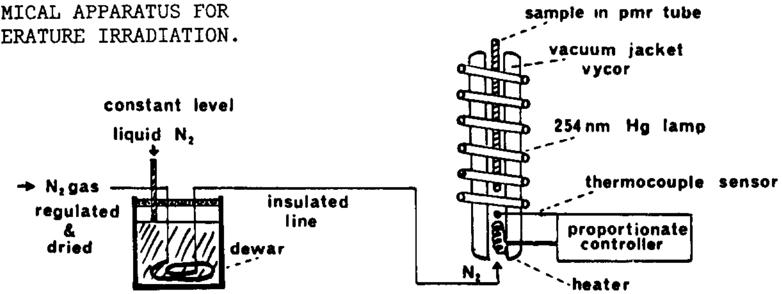


Fig. 4. ^{1}H-n.m.r. (80 MHz) of (17) in $CDCl_3$

DIAGRAM 1.

PHOTOCHEMICAL APPARATUS FOR
LOW TEMPERATURE IRRADIATION.



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10. V.p.c. used a stationary phase of 10% SE.30 or SE.52 coated onto an Embacel support.

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