SUBSTITUENT EFFECTS ON THE BICYCLO[4.2.0]OCTA-2,4,7-TRIENE

INTO CYCLOOCTATETRAENE INTERCONVERSION.

PROOF OF A TRUE EQUILIBRIUM AT ROOM TEMPERATURE.

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In spite of numerous synthetic (1) and photochemical (2) studies on cyclo-octatetraene (COT) (or substituted derivatives thereof), all evidence to date suggests that simple bicyclo[4.2.0]octa-2,4,7-trienes (biCOT) have only transient existence at room temperature, and are rapidly converted into the monocyclic form. Prior to the present study (3) the only stable isomers of the biCOT ring system which have been reported are the perchloro derivative (4) and annelated derivatives (5). The COT/biCOT interconversion has not lacked champions (1,2) and although the interconversion is thermally allowed by orbital symmetry considerations (6), evidence for the existence of a true equilibrium, although plausible, remains deductive rather than definitive.

SCHEME 1

(I)   (II)   (III)   (IV)
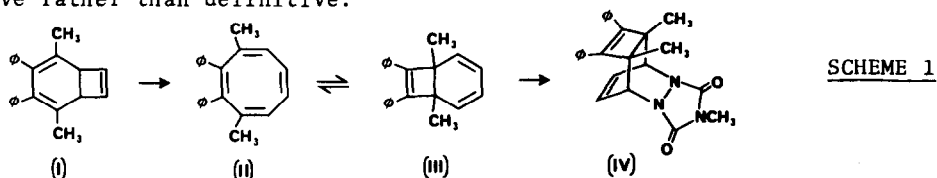
Thermal studies on the "stable" biCOT isomer (I) (3) have now provided definitive evidence bearing on this subject. Thus heating a solution of (I) in deuterochloroform solution at about 65° showed the loss of the p.m.r. signals due to (I) ($t\frac{1}{2}$ = ca. 90 min.) and formation of a new set of signals (mixture A; p.m.r. fig. 1). This process was thermally irreversible. Evidence that mixture A was an equilibrium mixture of (II) and (III) (Scheme I) was deduced as follows.

Evaporation of mixture A gave solid material. Recrystallisation from n-hexane yielded pure biCOT isomer (III), m.p. 105°. Dissolution of this product

in deuterochloroform at -40°, and inspection of the p.m.r. spectrum at -30° indic-
ated that only one set of signals, those assigned to biCOT (III) (fig.1) were
present. Slow conversion to COT (II) was evident at -30°, and this conversion
was rapid at 0°. This confirmed that the biCOT to COT interconversion was rapid
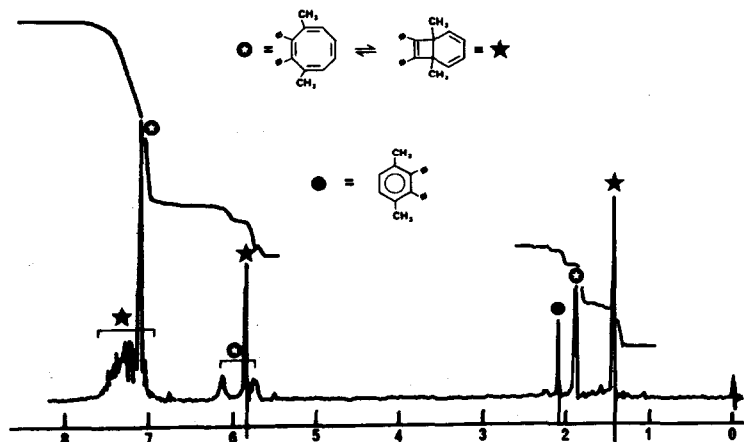and that the *bicyclic form was the more stable in the crystalline state.*

FIGURE 1
p.m.r. of *mixture A*
in CDCl$_3$

A deuterochloroform solution of *mixture A* was rapidly cooled to -60°. The
p.m.r. spectrum indicated roughly equal proportions of (II) and (III). This was
treated at *ca.* -40° with excess 4-methyl-1,2,4-triazoline-3,5-dione and inspection
of the p.m.r. spectrum showed that all signals due to the biCOT (III) had been
removed, but that those due to the COT (II) remained. Additional signals due to
excess triazoline-3,5-dione (N-CH$_3$ δ = 3.25) and the adduct (IV): δ 7.33 (s, 10H,
phenyl); δ 6.23 (t, 2H, vinyl); δ 4.89 (t, 2H, bridgehead adjacent to nitrogen);
δ 3.05 (s, 3H, N-CH$_3$); δ 1.58 (s, 6H, C-CH$_3$) were also present. This mixture
was stable at -30°. Above this temperature (rapidly at 0°) signals due to COT
(II) decreased and those of the adduct increased. This experiment confirms that
COT to biCOT interconversion is also rapid (but slow on p.m.r. time scale) and
that the activation energy is slightly higher than the reverse transformation.
The adduct was isolated by TLC and crystallised from ethanol, m.p. 220°. Maleic
anhydride also rapidly formed a similar adduct at room temperature, m.p. 203°.

The p.m.r. of *mixture A* indicated that the equilibrium between (II) and
(III) was only slightly changed in position over the temperature range 0° to +100°
Marked changes in the shape of the spectra were observed towards the upper temper-

mixture A ⇌ (V) ⇌ (VI) → (VII)   SCHEME 2
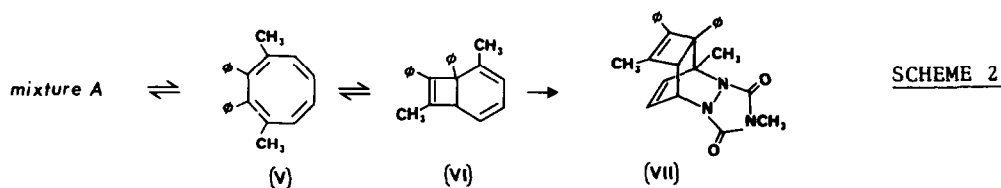
ature limit, but these were completely reversible.

At 120°, and above, gradual conversion to a new mixture (*mixture B*, fig. 2) occurred, which did not change on continued heating (equilibrium conditions attained). Reaction of *mixture B* with 4-methyl-1,2,4-triazoline-3,5-dione at room temperature effected complete conversion into two adducts: the symmetrical adduct (IV) and the unsymmetrical adduct (VII), m.p. 236° [separated by TLC on silica gel/chloroform; p.m.r. $CDCl_3$; δ 7.55 - 7.15 (m, 10H, phenyl); δ 6.46 - 6.03 (m, 2H, vinyl) δ 5.33 - 5.1 (m, 1H, methine adjacent to *N*); δ 3.27 (br d, 1H, cyclobutenyl); δ 3.02 (s, 3H, *N*-methyl); δ 1.79, 1.70 (s, d, 3H, 3H, *C*-methyl)]. Here again we propose an equilibrium, this time between a new biCOT : COT pair [(V) and (VI)] as indicated in Scheme 2, to account for the selective formation of (VII). Adduct (IV), of course, is derived from (III) [and (II)] still components in the *mixture B*
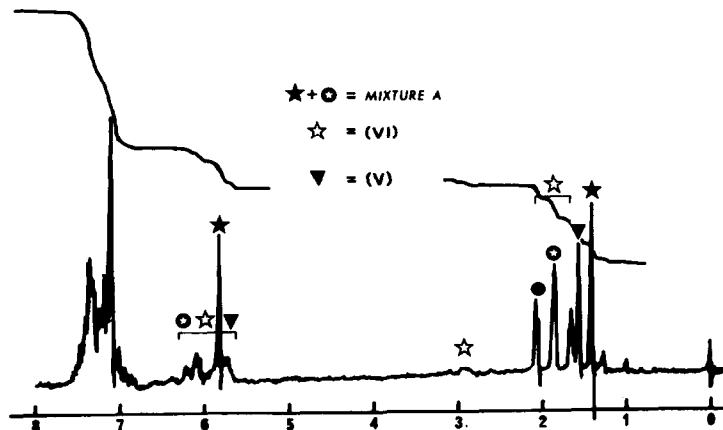

★+○ = MIXTURE A
☆ = (VI)
▼ = (V)

FIGURE 2
p.m.r. of *mixture B*
in $CDCl_3$

Inspection of the p.m.r. of *mixture B* reveals that peaks, in particular the high field methyl resonances (δ 1.0, 1.25), are present which cannot be assigned to components of the equilibrium as outlined in Scheme 2. These may be due to semibullvalenes, which are known to be formed thermally from cyclooctatetraenes (7), but no evidence bearing on these minor components is available at this time.

The selectivity in formation of the biCOT isomers seems to be governed by the
desire for maximum substitution of the cyclobutene double bond and is reminiscent
of the substituent effect on the equilibrium position in the 7,8-dihydro series
(8). The known preference for the substituent to be located on the cyclobutene
bond in adducts of mono-substituted COTs would suggest a similar preference, but
this must be interpreted with caution in view of the recent results obtained by
Huisgen (1c). The conversion of the bond fixed COT isomer (II) into the isomeric
COT (V) has ample precedent both thermally and photochemically (2c), but the
activation energy for this process is much higher than previously appreciated.
This may reflect the reluctance of the four vicinal substituents, in the present
case, to assume a coplanar orientation as required in the transition state for
such an interconversion.

Kinetics for the conversion (I) to (II), and the equilibrium parameters
(II) to (III) and (V) to (VI) are presently being determined and will be presented
in the full paper.

<div align="center">REFERENCES</div>

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