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A PHOTOCHEMICAL ROUTE TO SPIRO[2.8]UNDECA-2,4,6,8-TETRAENE (2-SPIROCYCLOPROPYLISOINDENE)[1]

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Molecules which contain the o-xylylene moiety have proved to be a challenge to the synthetic chemist, not so much because they are difficult to form, but rather that they have proved to be so very reactive. Thus o-xylylene chemistry abounds with dimeric and polymeric products[2], and chemists have been forced often to accept indirect evidence for the existence of the monomeric form. A standard method has been to trap the transient monomeric species in some form of derivative, such as a $[_{\pi}4_s + {}_{\pi}2_s]$cycloadduct[2] or some organometallic complex[3].

The organic chemist has endeavoured, with a large measure of success, to stabilise the target molecule by some chemical manoeuver. Perisubstitution has been particularly successful[4], and this, combined with electronic stabilisation has, for example, yielded the only monomeric isobenzofulvene[5]. While o-xylylene itself has capitulated to matrix isolation[6], a clever incorporation of this moiety into a carbocyclic framework has resulted in a molecule existing well above room temperature[7].

Our own approach, directed at the synthesis of parent members of each series, has been twofold. First, we have endeavoured to utilise low-activation electrocyclic processes to generate thermally the monomeric species; isobenzofuran[8], isoindoles[9], but not isobenzofulvenes[2], have responded to this approach. The second has been a photochemical one. We have sought thermally stable precursors as synthons for use in a subsequent low-temperature photochemical step. In particular we have exploited the photobisdecarbonylation reaction as an entry into the isoin-

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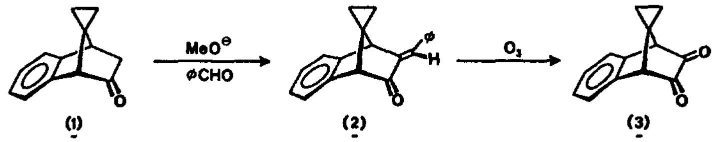
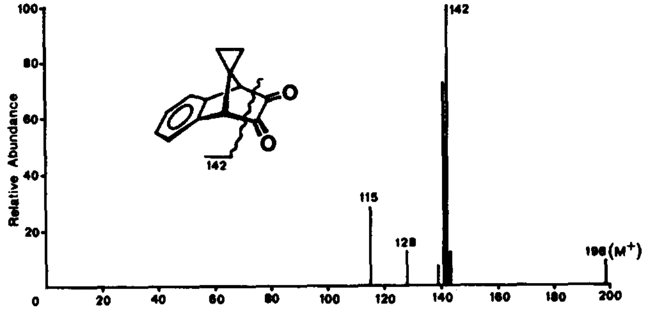
dene area, as already described[1]. The present report deals with an approach to the spiro[2.8] undeca-2,4,6,8-tetraene (4) a 2-spirocyclopropyl derivative of isoindene. This was selected in order to evaluate the stabilising effect of the spirocyclopropyl group on isoindene[10].

Scheme 1



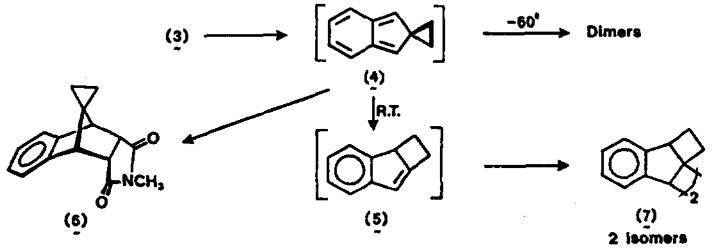
The α-diketone (3) was chosen as the photochemical substrate for generation of the 2-spirocyclopropylisoindene. This α-diketone was synthetised, after some digressions, from the known ketone (1)[13] as outlined above in scheme 1, and obtained as deep orange-coloured crystals m.p.91-92° [λ_{max}245, 285, 447 (inf), 455 (inf), 464 (inf), 473, 486, 490 (inf), 510 nm; G 2680, 2900, 310, 390, 460, 490, 470, 370, 270. P.m.r. ($CDCl_3$; δppm) 0.84 (s, 4H, cyclopropyl; 3.38 (s, 2H, bridgehead); 7.40 (s, 4H, Ar-H)]. The mass spectrum,shown below, indicated a major loss of C_2O_2 to yield a base peak at *m/e* 142 which corresponds to 2-spirocyclopropylisoindene (or an isomer) and augered well for the present approach.

Figure 1



Ultra-violet irradiation of the α-diketone (3) at either long or short wavelength in acetone solution ($0^{o}C$) in the presence of *N*-methylmaleimide gave exclusively the *endo*-adduct (6) m.p. 169-70° (65% yield isolated). The structure of the adduct followed from its pmr spectrum [C_s-symmetry, cyclopropyls (δ0.64) AABB' pattern for bridgeheads, typical of *endo*-adducts].

Scheme 2



Similar irradiations, in the absence of trapping agent, at room temperature, gave rise to two hydrocarbons (ratio 1:1; 60%). Separation (t.l.c.) yielded two isomers, $C_{22}H_{20}$ (*m/e* 284). The pmr spectrum of each isomer showed 5 groups of protons, none at high field, indicating no cyclopropyl resonances. In practice these were entirely consistent with cyclobutyl dimers of 3,4: benzobicyclo[3.2.0]hepta-1,3-diene (5) where [2+2] addition had occurred about the Δ^{12} bond. Low temperature (-60^{o}) irradiation, on the other hand, while still yielding a hydrocarbon fraction (*m/e* 284), this time showed cyclopropyl resonances in the pmr spectrum. These products, presumed to arise from 2-spirocyclopropylisoindene, have not yet been fully characterised.

The significant features of this study are: i) while the 2-spirocyclopropylisoindene can be trapped in adduct form, no spectral evidence could be obtained for its existence at, or below room temperature. ii) rearrangement of (4) occurs[14] at around R.T. to yield 3,4:benzobicyclo [3.2.0]hepta-1,3-diene (5) which forms cyclobutane type dimers either photochemically[15] or thermally[16]. iii) at lower temperatures this isomerisation is suppressed, and dimers involving 2-spirocyclopropylisoindene (4) are produced. iv) no evidence for rearranged α-diketones of the type described recently by Scharf and coworkers[19], or Norrish type 1 cleavage products similar to those obtained in the isoindene work described earlier[1] was observed.

Isomerisation of the isoindene (4) to the indene (5) is similar to other 1,2-alkyl shifts characteristic of 1,1-disubstituted isoindenes.[20] An interesting feature, which was reported[17] by Breslow, and more recently by Moss,[21] relates to the stabilities of the non-benzoannelated derivatives corresponding to (4) and (5). In that case bicyclo[3.2.0]hepta-1,3-diene had only transient existence, spontaneously isomerising to the spiro[2.4]hepta-2,4-diene. It is not difficult to explain the thermodynamic reversal in the present case, since the aromatic ring present in (5) would more than offset other strain considerations.

The propensity for both the 2-spirocyclopropylisoindene and the 3,4:benzobicyclo[3.2.0]hept-1,3-diene to form dimeric products indicate that we need to explore new low-temperature (photochemical) routes to these products: such experiments are under active investigation.

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