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# PHOTOCHEMISTRY OF TRICYCLO $[4.2.2.0^{2,5}]$ DECA-3,7-DIEN-9-ONE: A SOURCE OF MANY INTERESTING POLYCYCLES

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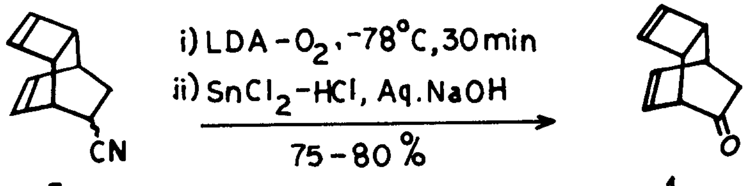
New syntheses of tricyclo $[4.2.2.0^{2,5}]$ deca-3,7-dien-9-one are described. Direct and sensitised photolysis of this ring system provides facile entry to several novel polycyclics.

The mechanistic and synthetic aspects of the photochemistry of β,γ-unsaturated ketones has attracted considerable attention in the past decade[1]. The β,γ-unsaturated ketones incorporate two isolated chromophores (alkene and carbonyl) in the same molecule and therefore undergo two unique photochemical reactions: the 1,3-shift and the 1,2-shift (oxa-di-π-methane rearrangement). The tricyclo $[4.2.2.0^{2,5}]$ deca-3,7-dien-9-one 1 is an interesting β,γ-unsaturated ketone, bearing an additional double bond and cyclobutane ring, and we expected it to provide a photochemical entry into several small ring polycyclic compounds. In this communication, we describe simple and efficient synthesis as well as photochemistry of parent ring system 1 and its bromo-substituted derivative 2[2]. The presence of this bromo substituent in 2 provides an additional handle for some further interesting transformations.

The parent tricyclo $[4.2.2.0^{2,5}]$ deca-3,7-dien-9-one 1 was conveniently synthesised, in one pot reaction, from readily available[2] cyclo-octatetraene (COT)-acrylonitrile adduct 3 employing the oxidative decyanation procedure of Watt[3]. In another approach, reaction of dibromo-COT 4 with α-chloroacrylonitrile (3 moles) in a sealed tube (105°, 8hr) and filtration through a column (silica gel) furnished the solid adduct 5, mp.180-1°, as an epimeric mixture (60-65% yield)[4]. Hydrolysis of 5, in aq.KOH-DMSO furnished the crystalline ketone 2, mp.82-4°, ir(KBr): 1730cm$^{-1}$(carbonyl); $^1$H nmr(CDCl$_3$): δ5.9-6.5(3H, m,olefinic), 2.7-3.3(4H,m,ring CH); 1.8-2.15(2H,dq,$-CH_2-\overset{|}{C}=O$); $^{13}$C nmr(CDCl$_3$-



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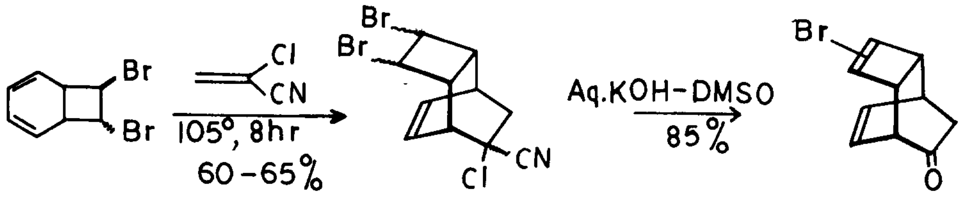
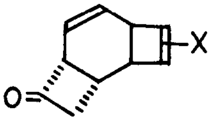


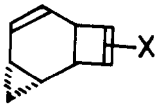
4 5 2

$CFCl_3$): δ139.4, 134.07, 127.0, 119.0, 53.55, 50.04, 46.69, 37.36, 35.67; in 85% yield.

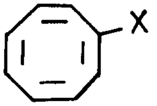
Irradiation of 1% dry benzene solution ($N_2$-purged) of 2 in a quartz vessel with a medium pressure Hanovia 450 W lamp for 15 min furnished a mixture of three products and some starting material[5]. The crude reaction product, which contained some polymeric impurities, was separated ($SiO_2$ gel and alumina chromatography) into three components. The major, polar component (~40% isolated yield) is formulated as 6a, mp.40-6°, $C_{10}H_9BrO$, ir(neat): 1790(carbonyl), 1670, 1590cm$^{-1}$(olefinic); $^1H$ nmr($CDCl_3$): δ6.27(1H,s,cyclobutene), 5.5-6.0(2H,m, olefinic), 3.55(2H,m,ring CH), 2.8-3.3(4H,m,ring CH); $^{13}C$ nmr($CDCl_3$): δ205.01 (carbonyl), 137.97, 126.04, 122.23, 121.06 (all olefinic C's); on the basis of its spectral characteristics. The non-polar part of the photolysate (30%) consisted of a 2:3 mixture of 7a and 8a+9. The structure of vinyl cyclopropane 7a was established on the basis of its $^1H$ nmr($CDCl_3$): δ0.05-0.25(1H,m), 0.8-1.3 (3H,m), 6.3(1H,s,cyclobutene), 5.35(1H,dd,$J_1$=9Hz,$J_2$=4Hz), 5.9-6.25(1H,br d,J= 9Hz), 3.15(1H,t,J=4Hz), 3.35(1H,d,J=4Hz) and $^{13}C$ nmr spectrum which showed three diagnostic cyclopropane carbon signals at δ12.86, 14.88 and 19.88. The mixture of bromo-COT 8a and trans-β-bromostyrene 9 could not be separated but their presence was conclusively established[6] through comparison of UV and $^1H$ nmr spectra with authentic specimen. Trans-β-bromostyrene 9 is probably an artefact formed *via* very facile[7] rearrangement of bromo-COT. It was further shown that 6a initially formed from 2 on further irradiation gave rise to 7a and 8a.



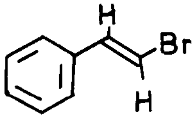
6a X = Br
6b X = H



7a X = Br
7b X = H



8a X = Br
8b X = H



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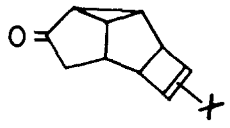
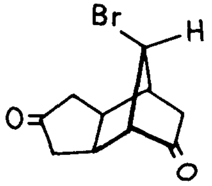
Irradiation of 1 under condition identical to that for 2 for 10 min led to the isolation of cyclobutanone 6b [ir(neat): 1785cm$^{-1}$; $^1H$ nmr($CDCl_3$): δ6.2 (2H,d), 6.0(1H,m), 5.5(1H,dd), 2.7-3.7(6H,m); $^{13}C$ nmr($CDCl_3$): δ206.24, 140.02, 139.20, 129.34, 119.0, 58.24, 50.19, 42.85, 39.80 and 24.60] in 20% yield and COT 8b in 40% yield[5]. GLC analysis of the crude photolysate indicated the presence of another component (~10%), probably 7b, but it could not be obtained pure to enable unambiguous characterisation.

Sensitised photolysis of 2 in acetone (1% soln, $N_2$-purged, quartz immersion well), with a 450 W Hanovia lamp for 50 min resulted in the formation of a major volatile product (80% by GLC) along with some polymeric material[5]. Chromatography ($SiO_2$ gel) led to the isolation (44% yield) of a crystalline product which was formulated as the oxa-di-π-methane rearrangement product 10a on the basis of its spectral characteristics: ir(neat): 1730(carbonyl), 1585cm$^{-1}$ (cyclobutene); $^1$H nmr($CDCl_3$): $\delta$6.07(1H,s,olefinic), 3.44(1H,br s, allylic H), 2.35-3.0(4H,m,ring CH), 1.65-2.25(3H,m,ring CH); $^{13}$C nmr($CDCl_3$): $\delta$213.62(s), 137.77(d), 121.9(s), 54.64(d), 56.47(d), 50.56(t), 36.32(d), 35.15 (d,2C) and 32.23(d). Treatment of 10a with conc. $H_2SO_4$ led to a deep seated



10a X = Br

10b X = H



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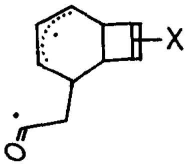

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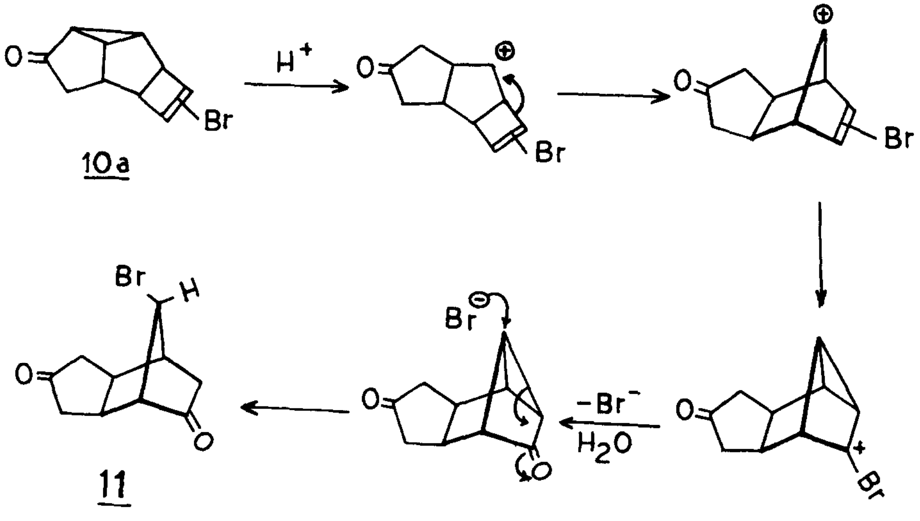
rearrangement and diketone 11 was isolated. Structure of 11, (M$^+$ 244), mp.155-56° was derived from its spectral data: ir($CHCl_3$): 1755 and 1735cm$^{-1}$ (carbonyl); $^1$H nmr($CDCl_3$): $\delta$ 4.15(1H,s,$\underline{H}$-$\overset{|}{C}$-Br), 2.4-2.9(8H,m), 2.1-2.2(2H,m); $^{13}$C nmr($CDCl_3$): $\delta$218.7(s), 208.59(s), 60.82(d), 49.43(d), 48.43(d), 47.38(d), 43.27(t), 43.03 (d), 42.56(t) and 38.28(d). A plausible mechanism for the genesis of 11 from 2 is depicted in Scheme 1.

SCHEME 1



Sensitised photolysis of 1 in 1% acetone for 7 min indicated formation of the oxa-di-π-methane rearrangement product 10b in 66% yield (GLC) besides unreacted starting material[5]. The structure of 10b follows from its ir spectrum(neat): 1730cm$^{-1}$; $^1$H nmr(CDCl$_3$): δ6.2(1H,d,J=2Hz), 6.1(1H,d st,J=2Hz), 3.45(1H,br s), 2.4-3.0(3H,m), 1.7-2.3(4H,m) and $^{13}$C nmr(CDCl$_3$): δ214.52, 140.13, 138.61, 58.76, 50.9, 49.78, 37.39, 36.63, 35.93 and 32.76.

Formation of 1,2-shift (oxa-di-π-methane) and 1,3-shift products from 1 and 2 on sensitised and direct photolysis, respectively, is mechanistically unexceptional[1]. Hydrocarbon products 7 and 8 can be accounted for *via* a diradical intermediate 12 which can either loose ketene or CO. Lastly, tricyclic compounds 6 and 7, obtained in this study, are endowed with requisite functionality to serve as direct precursors of annulated benzocyclopropenes and benzocyclobutenes of current interest[8].

References and Notes:

1. (a) S.S. Hixson, P.S. Mariano and H.E. Zimmerman, Chem. Rev., 73, 531 (1973); (b) K.N. Houk, ibid, 76, 1 (1976); (c) W.G. Dauben, G. Lodder and J. Ipaktschi, Fortschr, Chem. Forsch., 54, 73 (1975) and references cited therein.
2. For a synthesis of 1, see P.K. Freeman and D.M. Balls, J. Org. Chem., 33, 2211 (1968). However, the synthesis of 1 described here provides a superior preparative entry to this useful tricyclic ketone.
3. S.J. Selikson and D.S. Watt, J. Org. Chem., 40, 267 (1975).
4. It has been reported[2] that COT does not add to α-chloroacrylonitrile. Repitition of this addition in a sealed tube and hydrolysis of the adduct furnished the ketone 1 in less than 5% yield. However, in view of the generally observed fact that dibromo-COT is more reactive than COT, we successfully reacted the former with the ketene equivalent α-chloroacrylonitrile. In an attempt to prepare 1, adduct 5 was subjected to debromination with Zn-DMF as well as sodium-phenanthrenide. Unfortunately, dechlorination also occured and an epimeric mixture of COT-acrylonitrile adducts[2] was obtained.
5. The product distribution, yields and complexity of the reaction products showed marked dependence on the photolysis time. In general, with increased time more of saturated, ketene loss and polymeric products were formed.
6. The mixture of 8a and 9 exhibited $^1$H nmr signals at δ7.26 (s,ar) and 6.95, 6.8(AB q, J=14Hz, olefinic) due to *trans*-β-bromostyrene and at δ5.5-6.1(m,olefinic) due to bromo-COT. The relative ratio of 8a : 9 varied from sample to sample depending upon the extent of isomerisation of 8a to 9.
7. A.C. Cope and M. Burg, J. Amer. Chem. Soc., 74, 168 (1952); R. Huisgen and W.F. Konz, ibid., 92, 4102 (1970).
8. W.E. Billups, Acc. Chem. Res., 11, 245 (1978); R.P. Thummel and W. Nutakul, J. Org. Chem., 42, 300 (1977) and references cited therein.

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