Stereospecific Reduction and Methylation of Two 1-Iodo-*trans*-cycloalkenes

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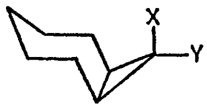
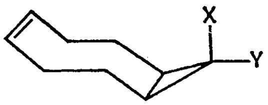
Summary Two 1-iodo-*trans*-cycloalkenes, obtained by ring expansion of suitable *gem*-di-iodocyclopropanes with silver perchlorate in methanol, can be converted into the *trans*-cyclo-alkene, 1-deuterio-*trans*-cyclo-alkene, and the 1-methyl-*trans*-cycloalkene.

THERE have been a number of recent reports concerning the ring expansion of *exo*-8-bromobicyclo[5,1,0]octanes to 3-methoxy-*trans*-cyclo-octenes and of 8,8-dibromobicyclo-[5,1,0]octanes to 2-bromo-3-methoxy-*trans*-cyclo-octenes using $AgClO_4$ in MeOH; thus the parent systems (I; X = H, Y = Br) and (I; X = Y = Br) give (IIa) and (IIb) respectively.[1a] These reactions may also be applied to the preparation of *trans*-cyclononenes;[1a,2] in this way (III; X = Y = Br) gives (IVb).[2]

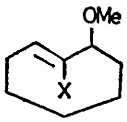
Reaction of cycloheptene with $KOBu^t$ and iodoform[3]



(I)

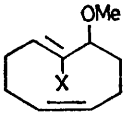


(III)

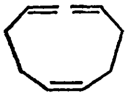


a; X = H d; X = D
b; X = Br e; X = Me
c; X = I

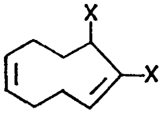
(II)



(IV)



(V)



(VI)

gave 8,8-di-iodobicyclo[5,1,0]octane (I; X = Y = I)† (58%) as a brown oil, stable for several weeks at 25°. Treatment of (I; X = Y = I) with $AgClO_4$ in MeOH at 25° gave the *trans*-cyclo-octene derivative (IIc) (90%); the n.m.r. spectrum of (IIc) was similar to that of (IIb), and contained a double doublet at τ 3·95 (J = 10 and 5·5 Hz). Treatment of (IIc) with MeLi‡ in ether for 15 s at 25—35° followed by quenching with H_2O gave (IIa) (60%), identical by n.m.r. and i.r. spectroscopy with an authentic sample.§ If the reaction was repeated, but quenched with D_2O, the product was (IId), but if the products were stirred with an excess of MeI before adding water, (IIe) was the major product.

Reaction of *cis,cis*-cyclo-octa-1,5-diene with iodoform and $KOBu^t$[3] gave (III; X = Y = I) (63%);¶ treatment of (III; X = Y = I) with $AgClO_4$ in MeOH gave (IVc) (89%). Reaction of (IVc) with MeLi in ether at 25° followed by H_2O quenching gave (V) as the major product, together with (IVa) and (IVe). However, reaction of (IVc) with $LiCuMe_2$ (from Cu_2I_2 and MeLi[6]) for 35 min followed by quenching with H_2O gave (IVa) (60%) relatively cleanly; the geometry of the 2,3-bond was confirmed as *trans* on examination of the n.m.r. spectrum, which showed a 16 Hz coupling between the two protons.** By working up the above reaction with D_2O instead of H_2O the deuteriated olefin (IVd) could be readily obtained (66%). It was also possible to obtain the methylated compound (IVe) (80%) as the major product by reaction of (IVc) with MeLi at 0° followed by treatment with excess of MeI.

The reactions described above provide a useful extension to the known syntheses of *trans*-cyclo-olefins, particularly when the *exo*-bromobicyclo[*n*,1,0]alkane necessary for stereospecific ring opening to the *trans*-cyclo-olefin is not readily available, as is the case for (III; X = H, Y = Br).[7]

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† Satisfactory microanalyses or high resolution molecular weights have been obtained for all new compounds.

‡ For lithiation of other 1-halogenocycloalkenes see ref. 4. MeLi obtained from Alfa Inorganics.

§ We thank Professor C. B. Reese for providing the spectra of authentic (IIb).

¶ This was stable for long periods at 0°, but decomposed when kept at 25° in daylight for several weeks; a crystalline di-iodide, m.p. 58—59°, was isolated from the products, and characterised as (VI; X = I) by comparison of its spectra with those of (VI; X = Br).[2,5]

** The four olefinic protons appeared as a complex signal in the n.m.r. spectrum of (IVa), but were differentially shifted in the presence of $[Pr(fod)_3]$.

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