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ADDITION OF DIBROMOCARBENE TO TRICYCLO [3.2.1.$0^{2,4}$] OCT-6-ENES. THE TRICYCLO [3.3.1.$0^{2,4}$] NON-6-ENE RING SYSTEM.

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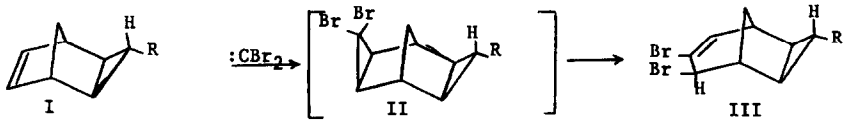
The addition of dihalocarbenes to norbornene and its derivatives produces an intermediate which undergoes a cyclopropyl-allyl rearrangement.[2] The gem-dihalocyclopropane, isolated in some cases,[2b,c] ionizes presumably to a tight ion pair which collapses to the allylic structure. Since the ring expansion involves a concerted disrotatory process [2c,3] and the allylic cation intermediate must maintain an all cis geometry the transition state is restricted to the ionization of the syn halogen (toward the bridge).

In search for a convenient synthesis of substituted barbaralanes, 3-substituted 7,8-dibromotricyclo [3.2.1.$0^{2,4}$] non-6-enes were prepared from appropriately substituted tricyclo [3.2.1.$0^{2,4}$] octenes. This method represents a direct entry into the tricyclo [3.2.1.$0^{2,4}$] non-6-ene ring system.

The reaction of tricyclo [3.2.1.$0^{2,4}$] octene (Ia) [4] with dibromocarbene, generated from bromoform and potassium t-butoxide in pentane at 0°, afforded a dibromide adduct [5] in 35% yield. The adduct, mp = 65° molecular weight 278, gave an instantaneous precipitate with silver nitrate, attributable to an allylic halide. Spectroscopic data permitted its structural assignment as IIIa: ir, ν = 3030, 3012, 1605 (vinyl bromide), 1027 and 1020 cm^{-1} (cyclopropyl) plus many absorptions in the fingerprint region; nmr (see Table I). A coupling constant of 2.0 Hz for H_c corresponds to an endo hydrogen (exo bromide) in the -CHBr- group [2a,b,6]. The gem-dibromo cyclopropane intermediate (IIa) thereby had an exo configuration in agreement with a well established exo attack on norbornenes. [7]



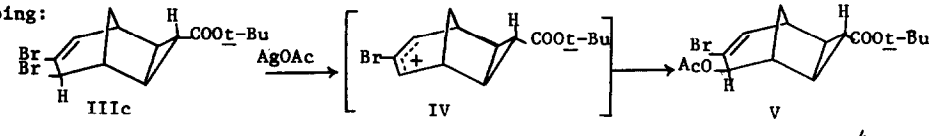
a) R=H b) R=$COOCH_3$ c) R=COOt-Bu

When an exo, endo (cyclopropyl) mixture of Ia was used, the corresponding exo-exo (IIIa) and exo-endo (IIIa′) dibromides were formed, differing only in the configuration of the cyclopropane ring. Vinyl and allyl protons in IIIa′ were shifted upfield presumably due to the shielding effect of the cyclopropyl ring in the endo position[8]. The allyl bromide in IIIa′ similarly occupied the exo position.

The interaction of Ib (2:1 ratio of exo-endo isomers [8]) with dibromocarbene, generated as above except that potassium methoxide was used as base, yielded a dibromide in 1.5% yield having similar spectroscopic properties as IIIa. After standing in the cold for several days, a solid material, m.p. 131-2° molecular weight 336, assigned the structure IIIb, separated: ir, ν = 1705 (ester carbonyl), 1606 cm^{-1} (vinyl bromide); nmr (see Table I). IIIb also gave an instantaneous precipitate with silver nitrate. The coupling constant of 2.0 Hz for H_c indicates an exo bromide.

When Ib was treated with bromoform in pentane in the presence of potassium t-butoxide, only a transesterified product was isolated. The t-butyl ester (m.p. = 84-5°), thus obtained, was readily purified by recrystallization from heptane to a 96:4, exo: endo ratio (Ic). Reaction of dibromocarbene with Ic produced an adduct [9] (IIIc), m.p: = 138-9° molecular weight = 378 [363 (M^+-15), 322 (M^+-56)], which had spectral properties similar to those for the methyl ester: ir, ν = 3020, 1720 (ester carbonyl), 1605 cm^{-1} (vinyl bromide); nmr (see Table I).

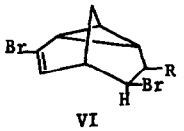
Upon reaction with silver acetate IIIc gave an acetate (V) in about 10% yield: m.p. = 107-110°; ir, ν = 1745, 1720, 1595 cm^{-1} (vinyl bromide); nmr (see Table I). V did not give a precipitate with silver nitrate. A coupling constant of 2.0 Hz for H_c is indicative of an exo acetate grouping:



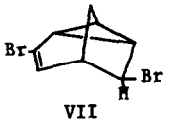
IIIc IV V

Interestingly, H_a and H_c of IIIa, IIIb, IIIc and V display long-range coupling (^4J = 1.0 and ~0.5 c.p.s., respectively) in addition to the relatively large coupling with their nearest bridgehead neighbor. These are believed to be due to bridge protons [2d]; no change in the display of H_a and H_c were observed when bridgehead protons (H_c and H_d) were irradiated.

At the outset of this work, we had anticipated a transannular effect involving a cyclopropyl bond leading to a tricyclene-like structure such as VI, analogous to a similar transformation found previously to give VII[2a].



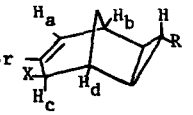
VI



VII

None were found, however, notwithstanding the intermediacy of cationic species, such as those involved in the above cyclopropyl-allyl rearrangements and in IV, well suited to shifts of this kind.

TABLE I

Nuclear Magnetic Resonances* of: 

Compound	H_a	H_b	H_c	H_d	Others
IIIa, R=H, X=Br	6.50 d ($J_{H_aH_b}$=7.0 ^4J=1.0)	2.46 q	4.54 d ($J_{H_cH_d}$=2.0)	2.82 q	0.43-0.82 (m, 2H, cyclopropyl) 1.0-2.0 (m, 4H)
IIIa', R=H, X=Br (cyclopropyl endo)	6.08d ($J_{H_aH_b}$=7.0 ^4J=1.0)		4.2 d ($J_{H_cH_d}$=2.0)		
IIIb R=COOMe, X=Br	6.56 d ($J_{H_aH_b}$=7.0 ^4J=1.0)	2.62 q	4.65 d ($J_{H_cH_d}$=2.0)	2.97 q	1.15-1.42 (m, 2H) 1.71 (q, 1H) 1.97 (quintet, 1H) 2.13 (q, 1H), 3.65 (s, methoxy)
IIIc R=COO<u>t</u>-Bu X = Br	6.50 d ($J_{H_aH_b}$=7.0 ^4J=1.0)	2.58 q	4.58 d ($J_{H_cH_d}$=2.0)	2.92 q	1.4 (s, <u>t</u>-butoxy) 1.53-1.7 (m, 2H) 1.75 (t, 1H) 1.82-2.08 (m, 2H)
IV R=COO<u>t</u>-Bu X=OAc	6.67 d ($J_{H_aH_b}$=6.5)		5.2 d ($J_{H_cH_d}$=2.0)		1.17-1.41 (m, 1H) 1.41 (s, <u>t</u>-butoxy) 1.62-1.7 (m, 4H) 2.10 (s, methoxy) 2.44-2.7 (m, 2H)

*Absorptions are tabulated downfield (ppm) from tetramethylsilane as internal standard and carbon tetrachloride as solvent, using 60 MHz and 100 MHz spectrometers: m = multiplet, q = quartet, d = doublet, s = singlet. Assignments were made with double resonance experiments.

Acknowledgements

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References

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(9) A tetrabromide, molecular weight 550, was also isolated.