Tetracyclo[3,3,1,$0^{2,4}$,$0^{2,8}$]nonane. A Strained Spiro-compound

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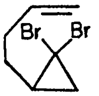
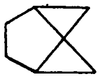
Summary Reaction of the dibromocarbene adduct of 4-vinylcyclohexene with methyl-lithium at −48° to −50° gives the spiro-compound (IV), but by modifying the reaction conditions a ready route to the *exo*-tricyclo-[3,3,1,$0^{2,4}$] ring system is obtained.

SKATTEBØL has reported that reaction of (I) with MeLi gives (II), presumably by intramolecular addition of a carbenoid related to (III) to the double bond.[1] We report a related reaction leading to the tetracyclic spiro-compound (IV).

Treatment of compound (V)†‡ with MeLi§ in ether at 25 — 35°, followed by addition of H_2O, gives, among other products,¶ a colourless oil, $C_9H_{13}I$, b.p. 80—82° at 1 mm Hg, which we have characterised as the iodide (VI; X = H).


(I)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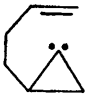
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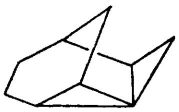
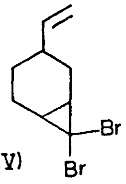
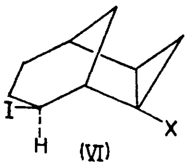
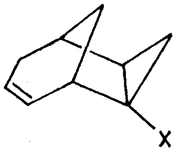
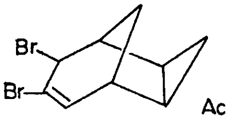
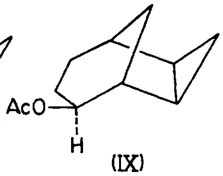

(IV)


(V)


(VI)


(VII)


(VIII)


(IX)

This compound shows no olefinic signals in the n.m.r. spectrum, but signals are seen characteristic of a 1,2-disubstituted cyclopropane and a single proton adjacent to iodine [τ 5·45 (br t, *J ca.* 4 Hz)]; dehydro-iodination with $KOBu^t$–Me_2SO for 30 min at 25° gives a single product (VII; X = H). Compound (VII; X = H)[2] was prepared independently by reduction of (VIII),[3] first with $LiAlH_4$ in ether and then with Na–liq. NH_3. The stereochemistry of the 6-position in (VI; X = H) is in agreement with coupling constants reported in related 9-oxabicyclo[3,3,1]nonanes.[4] Reaction of compound (V) with MeLi at 25—35° followed by treatment with D_2O gave a new compound (VI; X = D), which was dehydro-iodinated to give (VII; X = D).

However, treatment of compound (V) with MeLi at −48° to −50°, followed by aqueous work up does not give (VI), but a new hydrocarbon, C_9H_{12}, appears in its place. This hydrocarbon was characterised as (IV), obtained by intramolecular addition of the carbenoid derived from (VI) across the double bond, and shows no olefinic protons in the n.m.r. spectrum, but does show a single proton triplet (*J* 6 Hz) at τ 9·9.

Compound (IV) reacts with MeLi§ at 25° followed by aqueous work up, or when kept with a suspension of lithium iodide hydrate in ether, to give (VI; X = H); it reacts with AcOH in CCl_4 in 30 s at 25° to give (IX), also obtained from (VI; X = H) and AgOAc–AcOH.

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† Obtained as the major mono-adduct on reaction of 4-vinylcyclohexene with dibromocarbene generated from $KOBu^t$–$CHBr_3$.

‡ Satisfactory microanalyses or exact molecular weights have been obtained for all new compounds.

§ Prepared from Li and MeI in ether.

¶ These will be discussed in detail elsewhere.

[1] L. Skattebøl, *J. Org. Chem.*, 1966, **31**, 2789.
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[3] R. A. Baylouny, K. Hankovsky, D. Kates, and J. P. Sibilia, *Tetrahedron Letters*, 1970, 2093.
[4] C. Ganter, K. Wicker, W. Zwahlen, and K. Schaffner-Sabba, *Helv. Chim. Acta*, 1970, **53**, 1618; C. Ganter, R. O. Duthaler, and W. Zwahlen, *ibid.*, 1971, **54**, 578.