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THE UNUSUAL BEHAVIOUR OF ENDO-DICYCLOPENTADIENE TOWARD DICHLOROCARBENE.

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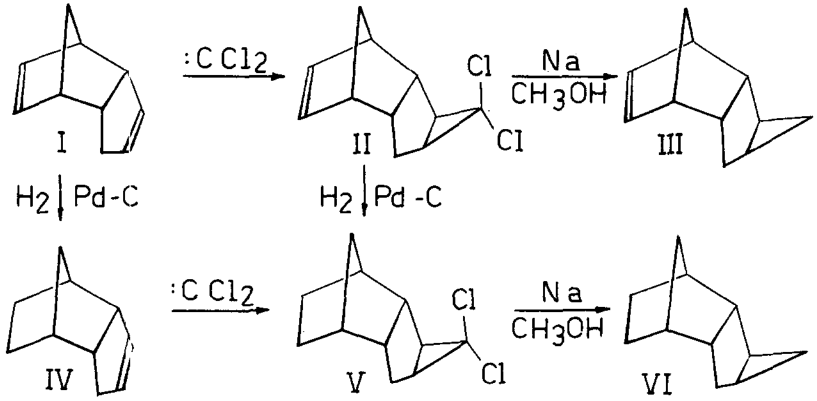
Molecules with a rigid skeleton are often helpful for studying reaction mechanisms. Recently (I) our attention was drawn by the poor reactivity of norbornene toward dichlorocarbene. This observation led us to examine the behaviour of endo-dicyclopentadiene toward carbenes. This diolefin is known (2) to undergo easily addition reactions at the site of the strained (3) bicyclic system under conditions which let the other double bond unaffected. Recently, however, Simmons, Blanchard and Smith (4) have described the methylene transfer from an excess of bis (iodomethyl) zinc. zinc iodide complex to endo-dicyclopentadiene. They obtained a mixture of the two isomeric monoadducts besides a high yield of diadduct.

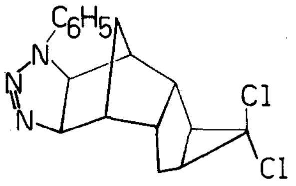
We wish to present a unique example of preferential addition of a reagent to the cyclopentene ring of endo-dicyclopentadiene. (I).

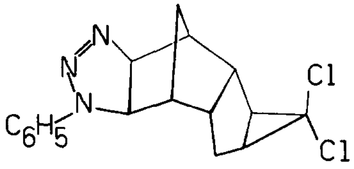
Dichlorocarbene was formed at O° by the reaction of methyl trichloroacetate with sodium methoxide (5). In the presence of a ten-fold excess of (I) in pentane, a product $C_{11}H_{12}Cl_2$ (6), b.p. 78-81°/0.6 mm. $n_D^{25} = 1.5382$, was formed in 55 % yield. Vapor phase chromatography and spectral data indicated the presence of one major component ($>$ 96 %) slightly contaminated by an isomeric material.

The main product was shown to be 4, 4' dichloro-quadricyclo $[6.2.1.0^{2,7}.0^{3,5}]$undec-9-ene (II). Thus it showed infra-red absorption at 1577 cm^{-1}, a characteristic band of the strained double bond of the bicyclo [2.2.1] hept-2-ene system. The presence of a cyclopropane ring was suggested by the presence of a band at 1017 cm^{-1}; Though not particularly significant the proton magnetic resonance spectrum (7) was in agreement with the proposed structure: it showed three bands centered respectively



at τ= 3.88 (relative area : 1.94), τ ca. 7, 3 (broad, relative area: 4.05) and τ ca. 8.38 (broad, relative area: 6.02). The position and the pattern of the signal at τ = 3.88 were indicative of two olefinic protons of the norbornene type. This was confirmed by the rapid reaction of (II) with phenyl azide to yield a crystalline adduct $C_{17}H_{17}Cl_2N_3$, m.p. 145-147° (dec). after two recrystallisations from ethyl acetate, spectral data in agreement with structures (VII a) and (VII b) (8).


VII a


VII b

Treatment of (II) by sodium in moist methanol (9) yielded an olefin (86 %) $C_{11}H_{14}$ whose properties were identical with those of compound (III) prepared by Simmons and al. (4).

Final proof for structure (II) was obtained by reducing it catalytically (Pd-C) in ethanol. The hydrogenation product (V) was identical to the adduct of CCl_2 and dihydrodicylopentadiene (IV) $C_{11}H_{14}Cl_2$, b. p. 86-88°/0. 5 mm, n_D^{25} = 1, 5341, no more unsaturation. Dehalogenation of (V) by sodium in moist methanol (9) yielded a new hydrocarbon, $C_{11}H_{16}$ b. p. 79-80°/11 mm, n_D^{25} = 1, 5031, infra-red and n. m. r. spectra in agreement with structure (VI).

Inspection of scale models of (I) showed that the endo face of the cyclopentene double bond in strongly screened by the olefinic hydrogens of the bicyclic system. The attack of a reagent from the endo side should be even more difficult in the case of dihydrodicyclopentadiene (V) due to the new endo hydrogens at C_8 and C_9. The fact that we observed identical configuration in both additions to (I) and (IV) indicated that the cyclopropane ring must have the exo configuration.

The description of the transition states for free carbene additions (10) assumes that the carbene is reacting in the singlet state and is forming the new carbon-carbon bonds almost simultaneously. In contrast with many other addition reactions (2), here there is not much energy to be gained from the relief of angle strain in forming the new cyclopropane ring. In the case of the addition of CCl_2 to the bicyclic double bond of (I) this rather small activating effect would be largely overcome by a raising of the energy barrier between reagents and product due to large non bonded interactions between the approaching CCl_2 and the syn hydrogen of the methylene bridge. These interactions are absent in the transition state leading to (II).

Such an explanation is as yet tentative and awaits new experimental data in order to obtain a more precise idea on the geometric requirements of such transition states. Such studies are in progress and will be reported soon.

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6. Elemental analysis within ± 0.3 % of the theoretical values have been obtained for all new compounds.

7. It is a pleasure to acknowledge the assistance of Dr. G. Slinckx in obtaining and interpreting the n. m. r. spectra (Varian A 60). They will be discussed in the full publication.

8. As already pointed out in ref. 4, a cyclopropane ring does apparently not introduce sufficient assymetry in the molecule to allow separation of (VII a) and (VII b).

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