44. Hydride Abstraction from Benzocyclopropene

Preliminary Communication[1]

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(6. X. 72)

Summary. The reaction between benzocyclopropene (**1**) and triphenylmethyl fluoroborate in acetonitrile shows an isotope effect of 6.7 and the isolation of the resulting triphenylmethane and benzaldehyde has been effected. A mechanism for the formation of the latter is proposed, involving an intermediate benzocyclopropenium ion (**2**).

Some 20 years ago *Roberts & Streitwieser* [1] predicted, on the basis of simple *Hückel* calculations, that the benzocyclopropenium ion (**2**) would be a resonance-stabilized species. The delocalization energy of the triplet ground state of **2** was calculated to be 3.65 β. Although this electronic stabilization is even higher than that of the well known, stable tropenium ion (2.98 β) [2], the benzocyclopropenium ion (**2**) has so far neither been isolated nor postulated as a possible reaction intermediate. The calculated resonance energy is of course not the only determining factor for the stability of a particular compound, and in the case of **2** other effects may well override the stabilizing contribution of the π-electrons. Thus benzocyclopropenone, which is also resonance-stabilized, appears to be very unstable and has not yet been isolated [3]. Strain in the σ-skeleton could be so great that benzocyclopropenone and the benzocyclopropenium ion (**2**) could be unstable despite their π-resonance energy. This may explain why *Halton & Milsom* [4] formulated the base-catalyzed hydrolysis of 7,7-dichloro-2,5-diphenyl-benzocyclopropene (**3**)[2] to methyl 2,5-diphenyl-orthobenzoate (**6**) as occurring *via* the ring-opened species **4**, rather than *via* the carbenium ion **5** (Scheme 1). In view of the high stability of benzocyclopropene (**1**) in strong base [5] this mechanism is not very convincing, and an alternative pathway, involving an intermediate substituted benzocyclopropenium ion **5**, is also in agreement with the experimental findings.

Benzocyclopropene (**1**) is an interesting substrate for the study of hydride abstraction by various oxidizing agents. The reaction not only should lead to a resonance-stabilized product, but the substrate itself is aromatic. Although the double bonds of **1** are not entirely inert and react, for example, with iodine [6], they may be expected to show reduced reactivity in comparison with the allylic hydrogen atoms, so that oxidizing agents should attack the allylic position rather than the π-system.

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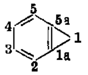
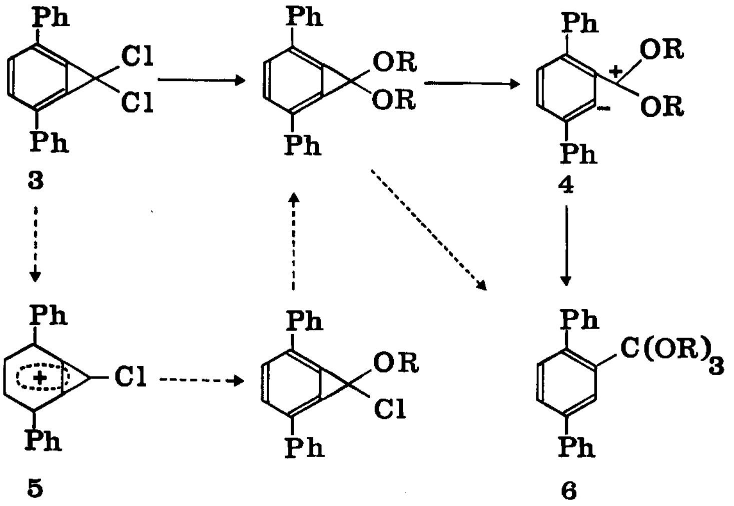
[1] A detailed paper will appear in Helv.

[2] The numbering used in this substituted benzocyclopropene is that derived from perhydrobenzocyclopropene, the terpenoid norcarane. It is not in accordance with that derived by application of IUPAC rules, which would be:



Scheme 1



With many reagents tropilidene undergoes oxidation at the double bonds [7] in such a way that hydride transfer cannot be detected. However hydride transfer from tropilidene, and also from triphenylcyclopropene, occurs under mild conditions using triphenylmethyl fluoroborate [8] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [9]. The gain in resonance energy in passing from tropilidene to tropenium ion is 2.0 β [2]. For estimating the gain in resonance energy for the benzocyclopropene-benzocyclopropenium system, the π-energy of benzene may be assigned to **1**, the perturbation of the aromatic system by the cyclopropene ring (*Mills-Nixon* effect [10]) being neglected; as the same effect occurs in the ion **2**, the error will not be very important. With this assumption the gain in resonance energy in passing from **1** to **2** is 1.65 β. With regard to resonance energy, hydride abstraction from **1** should therefore proceed at a rate comparable to that of tropilidene.

Experimental support for the idea that **2** should be a stable species was obtained from the mass spectrum of benzocyclopropene[3]. This could only be obtained when the inlet system of the spectrometer was cooled down to ca. 60°, otherwise the sample decomposed and other products were formed. In the mass spectrum of benzocyclopropene (**1**) the molecular ion ($m/e = 90$) is also the base peak. The only peak of comparable intensity is at $m/e = 89$ (intensity 86%); another fragment occurs at $m/e = 63$, but the intensity is only 38%. The $M - 1$ peak can only be due to the benzocyclopropenium ion, which shows little tendency for fragmentation. The spectral behaviour of **1** finds its counterpart in the behaviour of tropilidene which gives rise to the tropenium ion in the mass spectrum.

No reaction could be observed between **1** and DDQ in benzene, but, triphenylmethyl fluoroborate in acetonitrile reacted with benzocyclopropene (**1**) in a UV.-cell at 25.0° with a rate constant of 7.8 ± 0.7 mol^{-1} min^{-1}. The runs were difficult to reproduce and sometimes showed deviations from first-order kinetics, the value given

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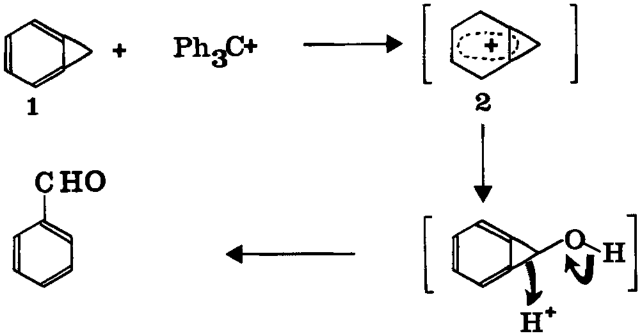
[3] I wish to thank Dr. *B. Wilhalm, Firmenich S.A.*, Genève, for this spectrum.

being an average of 5 determinations. After the reaction the contents of the cell were colourless, but darkened slowly owing to decomposition. Unter the same conditions tropilidene showed five times the reactivity of benzocyclopropene. The kinetic isotope effect for the reaction of **1** was determined with a sample containing one H- and one D-atom in the allylic position [11] and the rate constant found to be 4.45 mol^{-1} min^{-1}. After correction for the hydrogen content in the allylic position of the sample, the isotope effect k_H/k_D is 7.0, in good agreement with the value for hydride abstraction from tropilidene [12].

Since the kinetic results were considered to be somewhat unreliable, they were confirmed by determining the amount of deuterium incorporated in triphenylmethane, the main reaction product that could be isolated. In a typical experiment 120 mg of 2-deuterio-benzocyclopropene was mixed with an equimolar amount of triphenylmethylfluoroborate in dry acetonitrile just above its freezing point, then allowed to warm up to room temperature with stirring; after 2 additional hours of stirring it was quenched with water. Working up yielded 115 mg of triphenylmethane and 53 mg of triphenylmethanol. Mass spectral analysis showed the presence of undeuteriated and deuteriated triphenylmethane in the ratio of 100:13.7, which corresponds to an isotope effect of 7.3. The average result from 3 determinations using substrate and oxidant in 3 different proportions, was 6.5. The agreement with the kinetic result is within the expected limits.

The isotope effect and the isolation of triphenylmethane both suggest that the first reaction product is benzocyclopropenium ion (**2**). Two additional products could be isolated from the reaction mixture in 5–10% yield. The first has the molecular ion in the mass spectrum at $m/e = 109$, and is believed to have been formed by reaction of the solvent with **2**, but its structure has not yet been established. The second product is benzaldehyde, identified by its characteristic odour and by co-injection into the gas chromatograph. A possible mechanism for the formation of benzaldehyde involving benzocyclopropenium ion as an intermediate is proposed in Scheme 2. Experiments for detection of benzocyclopropenium ion directly in the NMR. tube have so far not been successful.

Scheme 2



Although direct evidence is still missing, these results indicate that the benzocyclopropenium ion may be formed by hydride abstraction from benzocyclopropene.

Further experiments will be directed towards spectroscopic detection and, if possible, isolation of this ion.

I wish to thank Prof. *A. Buchs*, University of Geneva, for the mass spectra, Dr. *U. Burger*, of our Department, for the NMR. measurements and Mr. *J. Pfyffer* for excellent technical assistance.

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45. Alkyl Transition Metal Compounds IX[1])

Synthesis and Structure of $[(Me_3SiCH_2)_2Cr(bipy)_2]$ I

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(14. XII. 72)

Summary. Bis(trimethylsilylmethyl)-bis-(2,2′-bipyridyl)chromium(III) iodide has been synthesized and its structure determined; the Cr-C(sp^3) bond length is 2.107(9) Å.

The factors influencing the stability of σ-bonded alkyl or aryl transition metal compounds are a source of constant interest [2]–[4]. Thus it is found that many aryl metal compounds are more stable thermally than their alkyl analogues [4]–[7], and this observation is difficult to rationalize in terms of simple bond homolytic processes. It is often presumed that one of the factors contributing to this variation in thermal stability involves fundamental differences in the nature of the metal to carbon bonding in the two types of compounds. This in so far as the aryl group, in contrast to the alkyl group, may donate or accept electrons from the metal center. We have now extended our synthesis of octahedral bis-arylchromium(III) compounds of the type $[R_2Cr(bipy)_2]I$, (bipy = 2,2′-bipyridyl) [8]–[9] to the preparation of the bis-alkyl-

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[1]) Part VIII, see [1].