

coefficient of 0.928. In our opinion it cannot be decided if $(H_0)_I$ or δ_H is a more appropriate parameter for the rate of this reaction.

Based on the tentative explanations suggested above for the increasing influence of formaldehyde on the acidity in systems of small water content, we think that it might be feasible to assume that cationic proton donors other than H_3O^+ may be effective for the acid catalyzed hydrolysis of cellulose. However, we have to emphasize again, that the intrinsic difficulties in the mechanistic analysis of reactions in moderately to strong acidic media do not allow any definitive conclusions at this time.

We thank the International Institute for Cotton for financial support of this work.

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78. Synthesis of 2,5-Diphenylbenzocyclopropene and 7,7-Dideuteriobenzocyclopropene¹⁾

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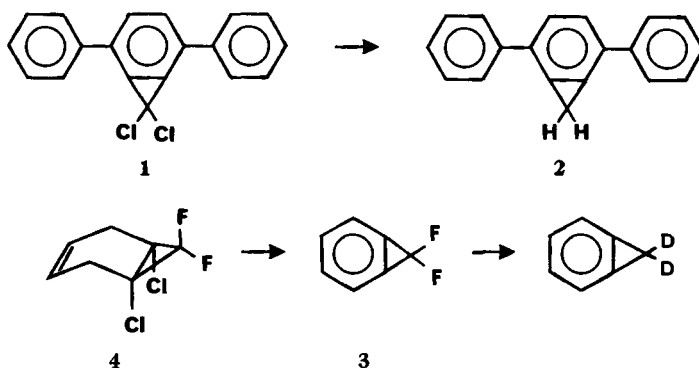
Summary. Die Reduktion von 7,7-Dichloro-2,5-diphenylbenzocyclopropen¹⁾ (**1**) mit Aluminiumhydrid liefert in 50% Ausbeute 2,5-Diphenylbenzocyclopropen (**2**). Aluminiumdeuterid wandelt 7,7-Difluorobenzocyclopropen (**3**) in 7,7-Dideuteriobenzocyclopropen um.

In connection with mechanistic studies [1] [2] a sample of 7,7-dideuteriobenzocyclopropene¹⁾ was needed. Although the original benzocyclopropene synthesis of Vogel [4] offers a straightforward way to the deuterated compound, an alternative approach was sought which would allow introduction of the deuterium atoms in the very last step of the sequence. The readily accessible 7,7-dichloro-2,5-diphenyl-

¹⁾ The numbering used here and in the literature [3] for the benzocyclopropene skeleton does not agree with the IUPAC rules [1]. The correct numbering would be 1,1-dideuteriobenzocyclopropene and 1,1-dichloro-2,5-diphenylbenzocyclopropene for **1**, respectively.

benzocyclopropene (**1**) [5] offered an attractive model to study reductive replacement of the halogens by deuterium.

The dichloro compound **1** was treated with tributyl tin hydride or lithium aluminium hydride (LAH) under various conditions. None of the desired 2,5-diphenylbenzocyclopropene (**2**) was formed. Either the starting material or unidentified decomposition products were recovered. The failure of the reagents was surprising in view of the successful application of tributyl tin hydride in the reduction of tetrachlorocyclopropene [6] and of LAH in the reduction of triphenylcyclopropenyl

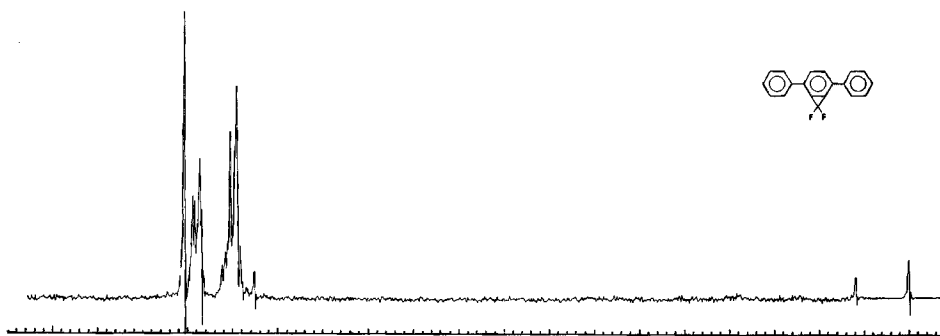
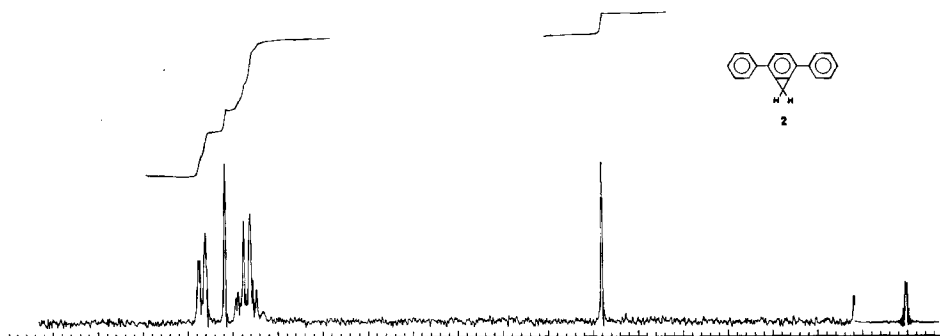
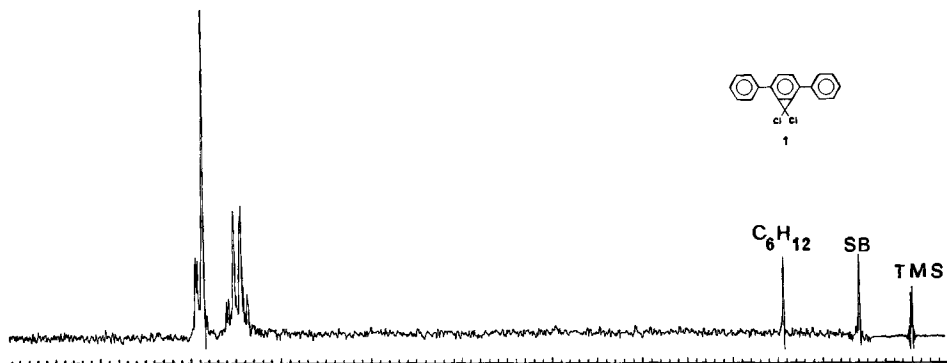


bromide [7] as well as of geminal cyclopropyl dihalides in general [8]. It may be due to the instability of the benzocyclopropenyl radical [6] or anion [8] intermediates which must be formed during the reaction.

Recently it was observed that **1** exchanges the chloride substituents with silver fluoride with preservation of the benzocyclopropene skeleton, presumably *via* an S_N1 process [9], assisted by the silver ion in the role of a *Lewis* acid [10]. Consequently aluminium hydride, which also has *Lewis* acid properties, was applied to the reduction of 7,7-dichloro-2,5-diphenylbenzocyclopropene (**1**) to **2**.

Reaction of **1** at -60° with an excess of aluminium hydride prepared *in situ* [11] gave 2,5-diphenylbenzocyclopropene (**2**) in *ca.* 50% yield. Compound **2** has m.p. 144–146. The IR. absorption band typical for benzocyclopropenes [3] appears at 1678 cm^{-1} . The mass spectrum shows the molecular ion at m/e 242 (base peak) and a major fragment at 241 ($-\text{H}$). The NMR. spectrum of **2** (Fig.) is very similar to those of **1** and of 7,7-difluoro-2,5-diphenylbenzocyclopropene. The allylic protons appear at δ 3.39 ppm with $1/6$ th the intensity of the aromatic protons. The pattern of the aromatic protons is very similar in all compounds with the exception of the singlet of the protons of the central ring. Its position shows a marked dependence on the electronegativity of the allylic substituents. The spectrum of the reduction product of **1** with aluminium deuteride was identical with that of **2** except for the allylic protons which were absent. The mass spectrum of the deuterated compound had the molecular ion at m/e 244.

For the preparation of 7,7-dideuteriobenzocyclopropene the difluoro derivative **3** was used as precursor. **3** was readily obtained by bisdehydrochlorination of 1,6-dichloro-7,7-difluorobicyclo[4.1.0]hept-3-ene (**4**) [12] with potassium *t*-butoxide in



NMR. spectra of **1**, **2** (in CCl_4) and 7,7-difluoro-2,2-diphenylbenzocyclopropene (in CDCl_3)

45% yield [13]. Reaction of **3** with aluminium deuteride as described above yielded 7,7-dideuteriobenzocyclopropene in 20% yield. The product was identified by comparison of the VPC. retention time with that of undeuterated benzocyclopropene prepared according to *Billups* [14], by analysis of the NMR. spectrum, and on the basis of its characteristic penetrating odour.

I am indebted to the *Swiss National Science Foundation* for financial support (No. 2.657.72) and to the *Société Académique de Genève (Fonds Frédéric Firmenich)* for financial help towards the purchase of a VPC. I thank Dr. *U. Burger* for the NMR. spectra, Mrs. *F. Klöti* for the mass spectra and Mr. *J. Pfyffer* for excellent work at the bench.

Experimental Part

IR. spectra were recorded with chloroform solutions on a *Perkin-Elmer 257* spectrometer. NMR. spectra were determined at 100 MHz on a *Varian XL-100* instrument with deuteriochloroform as solvent. Chemical shifts are expressed as ppm with reference to tetramethylsilane taken as zero.

2,5-Diphenylbenzocyclopropene (2). To a suspension of 400 mg lithium aluminium hydride (LAH, 10.5 mmol) in ether was added 600 mg freshly sublimed aluminium chloride (4.5 mmol) at -30° . The mixture was kept at 0° for 1 h, then it was cooled to -60 to -70° . 1.0 g *7,7-dichloro-2,5-diphenylbenzocyclopropene (1)* [5] (3.2 mmol) in ether was added dropwise. After 3 h the solution was allowed to warm up to room temperature. It was decomposed with 100 ml saturated sodium hydrogencarbonate. The layers were separated and the ether was washed twice with water. After drying (magnesium sulfate) the ether was evaporated and the residue recrystallized from cyclohexane. Yield 40–60% of **2**, m. p. 144–146°. The spectral properties of the product are discussed earlier in the paper.

7,7-Difluorobenzocyclopropene (3). To a suspension of 5.4 g potassium *t*-butoxide (48 mmol) in 150 ml dry tetrahydrofurane at -50 to -60° was added 4.4 g (22.4 mmol) 1,6-dichloro-7,7-difluorobicyclo[4.1.0]hept-3-ene (**4**) [12] dropwise. After 1 h the cooling bath was removed and the mixture was allowed to warm up to room temperature. THF was distilled off, and the residue was dissolved in ether. After distillation 1.3 g (45%) of 7,7-difluorobenzocyclopropene (**3**) was obtained. The ^1H - and ^{19}F -NMR. spectra agree with those reported in the literature [13].

7,7-Dideuteriobenzocyclopropene. Aluminium deuteride in ether was prepared from 200 mg (4.8 mmol) LAD and 300 mg (2.2 mmol) aluminium chloride in 50 ml of dry ether as described above. To this solution was added at -50° 450 mg (3.6 mmol) of **3** in ether. The characteristic stretch of benzocyclopropene appeared immediately. The reaction mixture was allowed to warm up to room temperature, and it was decomposed with aqueous sodium carbonate solution. After usual work up the ether was distilled. Distillation of the reaction product at *ca.* 60 mm afforded 7,7-dideuteriobenzocyclopropene in 20% yield. The compound had the same VPC. retention time (column SE 30 at 50° , injector at 70°) as benzocyclopropene prepared by the method of *Billups* [14]. In the NMR. (CDCl_2) the signal for the aromatic protons appeared at 7.15 ppm. The peak corresponding to the allylic protons was absent. No starting material (**3**) could be detected.

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