Incubation of ε-(N^4-formyl benzylpenicilloyl amido)-caproic acid with L-*cystine.* The disodium salts of ε-benzylpenicilloyl amidocaproic acid (50 mg) and of the formylated derivative (68 mg) in 1 ml 0.1 M phosphate buffer pH 7.6 each, were stirred at 37° with 75 mg L-cystine each. After 40 h. the suspensions were centrifuged and aliquots of the supernatants (A and B respectively) were used for PC. with phenol/water (100 g/39 ml). A and B (0.2 ml each) were mixed with 0.05 ml 5N HCl, kept 15 min. at ambient temp. and neutralized with 0.05 ml 5N NaOH. These solutions (A′ and B′) were also chromatographed together with PSSC and a B-supernatant (B″) obtained from an unincubated suspension. Fig. 3 shows that B contains no new compound (not present in B″) and B′ contains no PSSC as does A′. In order to establish that the HCl treatment would indeed liberate PSSC from the formyl derivative, 10 mg diformyl-D-penicillamine disulfide [11] were dissolved in 0.5 ml 1N HCl and neutralized after a few min. with 0.5 ml 1N NaOH. 20 μl aliquots as well as D-penicillamine disulfide as a reference were chromatographed with phenol/water on descending paper strips. Densitometry of the ninhydrin (0.3% in acetone) treated strips showed that D-penicillamine disulfide (Rf 0.37) had formed in at least 60% yield.

This work has been supported in part by the *Swiss National Foundation for Scientific Research* and the *Emil Barell Foundation* of *F. Hoffmann-La Roche Ltd.*, Basel.

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125. The Dehydrogenation of 1,4-Cyclohexadienes with 2,3-Dichloro-5,6-dicyanobenzoquinone and Triphenylmethylfluoroborate

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(21. II. 73)

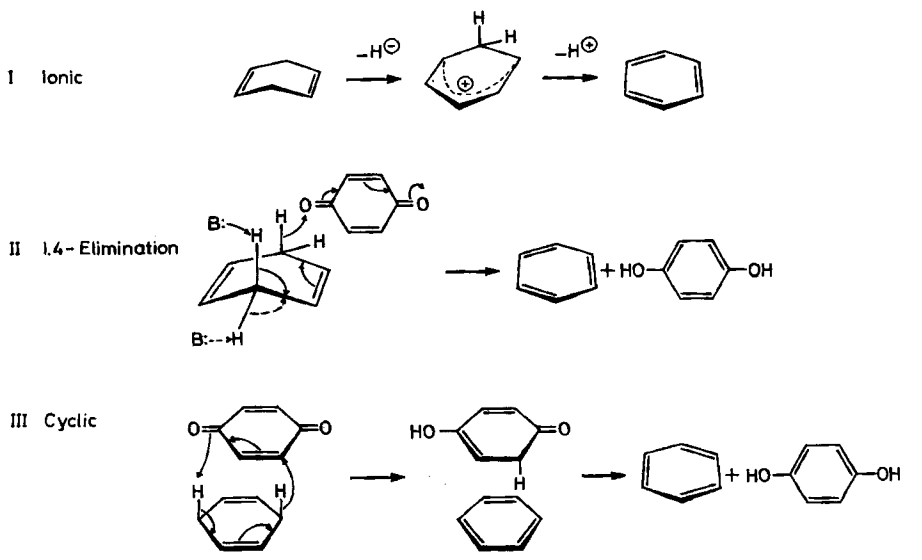
Summary. The dehydrogenation of 1,4-cyclohexadiene (**1**) *cis*-3,6-dimethyl-1,4-cyclohexadiene (**2**) and *trans*-3,6-dimethyl-1,4-cyclohexadiene (**3**) with triphenylmethylfluoroborate in acetonitrile or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) proceeds in the same reactivity sequence **2** > **1** > **3**. The mechanism of the dehydrogenation of 1,4-cyclohexadienes with tri-

phenylmethylfluoroborate and DDQ is discussed in the light of these results and in view of the kinetic isotope effects.

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) abstracts an hydride ion from tropilidene and triphenylcyclopropene to yield the corresponding tropenium and triphenylcyclopropenium ions [1] [2]. A stepwise ionic mechanism, involving hydride abstraction followed by loss of a proton, takes place in vicinal dehydrogenations as exemplified by 1,3-cyclohexadiene [3] and acenaphthene [4]. For the dehydrogenation of 1,4-cyclohexadienes *Braude, Jackman & Linstead* [5] proposed an analogous 2-step mechanism in which hydride transfer from C(3) and subsequent loss of a proton from C(6) occurs (Scheme I). The same authors considered mechanisms consisting of concerted loss of 2 hydrogens from 1,4-cyclohexadienes to yield aromatic benzene derivatives in a single-step process, but rejected all of them for various reasons [6]. However, this mechanism was invoked again when it was found that the dehydrogenation rate of 1,4-cyclohexadiene (**1**) was very close to that of tropilidene (**7**), but several orders of magnitude faster than that of other 1,4-dienes incapable of yielding an aromatic product in a one-step process. The higher reactivity by a factor of 20 of *cis*-3,6-dimethyl-1,4-cyclohexadiene (**2**) over the *trans*-isomer **3** (Table) suggested a preference for the cyclic mechanism where two *cis*-hydrogens are transferred in a concerted process to the oxygen and C(3) of the quinone [2] [7]. For reasons of conservation of orbital symmetry, the hydrogen transfer may not take place at both oxygen atoms of the quinone (anti-aromatic transition state). Scheme I summarizes possible mechanisms proposed for dehydrogenation of 1,4-cyclohexadienes.

The results quoted could also be interpreted in another way. The preference for *cis*-elimination of 1,4-cyclohexadienes may not be due to a symmetry allowed transition state but rather to steric hindrance to the approach of the quinone by the methyl

Scheme I

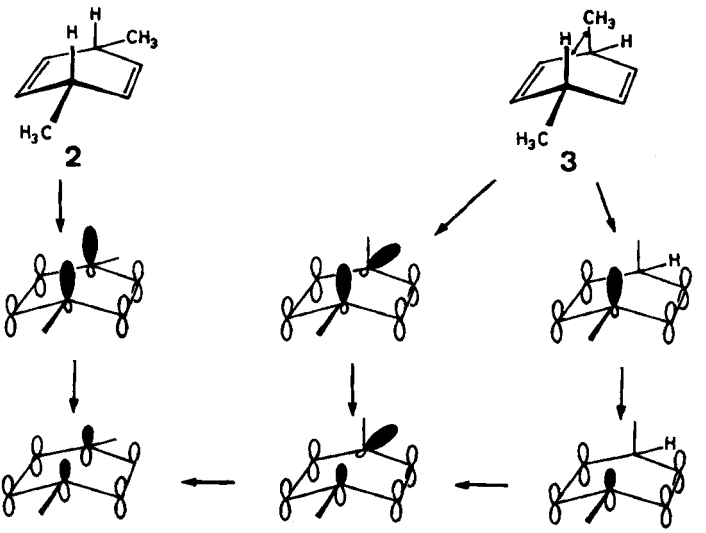


groups in **3**. The rate enhancement of **2** over 1,4-cyclohexadiene (**1**) could be ascribed to higher stabilisation of the tertiary carbenium ion as compared to the corresponding secondary carbenium ion. As only one face of the ring is hindered, steric effects should be of minor importance in **2**. Both sides of the *trans*-isomer **3** are hindered and thus its lower reactivity. However, on these grounds the *trans*-isomer **3** should be of the same reactivity as 3,3-dimethyl-1,4-cyclohexadiene (**4**), while in reality it is 30 times more reactive than **4**. The factor of 10^2 to 10^3 in rates between 1,4-cyclohexadienes and common 1,4-dienes such as 1,4-pentadiene **5** and **4** rules out the ionic mechanism for the dehydrogenation of 1,4-cyclohexadiene (**1**) and *cis*-3,6-dimethyl-1,4-cyclohexadiene (**2**) with DDQ.

Still another interpretation of the data is based on the argument that the relative reactivities of the *cis*- and *trans*-isomer **2** and **3** are not only in agreement with the cyclic mechanism III, but also with mechanism II, in which a proton is transferred to the solvent. Although this mechanism has been rejected, because the reaction rate was found to show little dependency upon changing the basicity of the solvent [6], it should be noted that solvent change also influences the oxidation potential of the quinone [8], which is directly related to the reaction rate [6]. For example dehydrogenations of ketones in the steroid field are catalysed by *p*-toluenesulfonic acid [9] and the dehydrogenation rate of 1,4-dihydronaphthalene increases upon addition of acidic catalysts to the solvent [6]. Thus the expected rate enhancement by general base catalysis upon solvent change may be counter-balanced by another effect, for example a lower oxidation of the quinone.

It is readily seen from models that in mechanism II the *cis*-isomer **2** should also be more reactive than the *trans*-isomer **3**. On steric grounds alone, **3** appears to be of higher energy than **2** because it suffers axial methyl-hydrogen interactions [10] (Scheme II). This interaction is absent in the *cis*-isomer **2**, both methyl groups occupying equatorial positions in the most stable conformation. The higher amount

Scheme II



of strain in **3** over **2** may be counterbalanced by a stereoelectronic effect in the transition state for mechanisms II and III. Loss of an axial hydrogen leads to a p-orbital that may be stabilised by the π-orbitals of the diene. In the *cis*-isomer **2**, both hydrogens are axial and both orbitals are stabilised in this manner. The aromatic stabilisation of the product, benzene, can already be reflected in the transition state. This is not the case for **3**, where one of the developing orbitals lies in the node of the π-system. The carbon skeleton has to be distorted in order to allow this orbital to interact with the others. For this reason simultaneous loss of two hydrogens is an energetically favoured process with the *cis*-isomer only. The elimination mechanism II as well as the cyclic mechanism III could equally well take advantage of this favourable steric arrangement. On the other hand, with the *trans*-isomer **3** loss of 2 hydrogens at the same time brings no particular advantage over the two-step hydride mechanism I. Although the relative reactivities of **2** and **3** towards DDQ suggest two different mechanisms to be operative, that is *cis*-elimination in **2** and a stepwise mechanism in **3**, they cannot provide an argument favouring the cyclic mechanism III over *cis*-elimination (mechanism II).

Additional evidence for simultaneous transfer of two hydrogens in **1** and **2** was expected to be provided by the isotope effect in the dehydrogenation with DDQ. Perdeuterio-1,4-cyclohexadiene (**1**-d_8) was synthesised by *Birch*-reduction of perdeuterated benzene in liquid deuterated ammonia [11] and its reaction rate with DDQ was measured in both benzene and dioxane. The measured isotope effect was 9.24 in benzene and 9.30 in dioxane. After correction for contamination with undeuterated material (see exp. Part) these values are increased to 10.0. Hexadeuterio-1,4-cyclohexadiene (**1**-d_6), containing one hydrogen and one deuterium each in the methylene group without specified configuration had an isotope effect of 1.70. The isotope effect observed with **1**-d_8 is considerably higher than values reported in the literature for hydride abstraction by DDQ. Thus DDQ shows an isotope effect of 4.0 with tropilidene, 6.9 with triphenylcyclopropene [2] and 3.49 with acenaphthene [4]. In both tropilidene and acenaphthene the observed values may be partially due to a secondary effect arising from a hybridisation change at the reacting carbon atom which is still substituted by one deuterium. The secondary effect is also present in deuterio-1,4-cyclohexadiene (**1**-d_8). However, the observed value of 10.0 appears to be too high to be attributed to the sum of normal primary and secondary effects; it appears to be more reasonable to invoke cleavage of 2 C–H bonds in the rate limiting step. On the other hand the isotope effect of 1.70 for hexadeuterio-1,4-cyclohexadiene (**1**-d_6) is also compatible with the stepwise hydride mechanism I. The argument, based on the isotope effect with **1**-d_8 in favour of simultaneous transfer of two hydrogens is somewhat weakened by the observation of primary isotope effects of the order of 10 in the oxidation of anisyl alcohol with DDQ in dioxane [12], although values reported for steroidal allylic alcohols are in the range of **5** [13].

In view of the possibility of the cyclic mechanism III for dehydrogenation of 1,4-cyclohexadiene (**1**) with DDQ it is interesting to compare the DDQ-rates and isotope effects with the rates for a typical hydride abstracting reagent such as triphenylmethylfluoroborate. This reagent abstracts hydride from compounds such as tropilidene (**7**) [14] and triphenylcyclopropene (**6**) [15] to yield the corresponding carbenium ion. Anthracene is formed in quantitative yield by its reaction with

9,10-dihydroanthracene [16], while 1,4-cyclohexadiene is dehydrogenated to benzene in 80% yield (see Exp. Part). It was not attempted to isolate products from the reaction of triphenylmethylfluoroborate with substituted 1,4-cyclohexadienes **2** and **3**, which, by analogy, are assumed to yield *p*-xylene. Although the mechanism of hydride transfer with triphenylmethylfluoroborate is complex [17], attack takes place at the methylene group in tropilidene as evidenced by the isotope effect of *ca.* 7 [18] [19].

The kinetics of the reaction between triphenylmethylfluoroborate and organic substrates was investigated, using 1,4-cyclohexadiene (**1**) as model, under pseudo-first order conditions with excess substrate. Reaction rates were determined in dry acetonitrile at 25.0°. The disappearance of the yellow colour of the reagent was measured spectrophotometrically at *ca.* 450 nm. The determination of the rate constants in this system presented some difficulties. Reproductibility was poor, and the plots sometimes showed deviations from pseudo-first order kinetics. Upon introduction of the substrate into the UV.-cell containing the reagent there was an almost instantaneous drop of absorbance. This is ascribed to the reaction of trace amounts of impurities with the triphenylmethylfluoroborate. Furthermore, rate constants determined with triphenylmethylfluoroborate from two different batches were consistently different by a factor of *ca.* 3. Therefore, the rate constants are all reported relative to the standard 1,4-cyclohexadiene (**1**).

The rate constant k_1 showed first-order dependence from the substrate concentration in the range of 1.1 to $6.3 \cdot 10^{-2}$ M. The data are represented in Fig. 1 which also illustrates the considerable scatter in the measured rate constants.

The relative reactivities of the other substrates with triphenylmethylfluoroborate and with DDQ are summarized in the Table. The experimental uncertainties indicated refer to the reproducibility; the accuracy of the measurements with triphenylmethylfluoroborate is in the order of 10%. With substrates where only few runs were measured it is even less. However, except for the isotope effects even an error of 50% would have no influence on the conclusions drawn on the basis of these data.

The isotope effects observed with perdeuterio-1,4-cyclohexadiene (**1**-d_8) and hexadeuterio-1,4-cyclohexadiene (**1**-d_6) of 4.2 and 2.8 respectively indicate that C–H bonds are broken in the rate determining step of the reaction. The agreement with the corresponding values of the DDQ reaction (10.0 and 1.7) is poor. It is believed that in view of the scatter in the data no other conclusions can be safely drawn from the isotope effects. The presence of a kinetic isotope effect with **1** rules out the possibility of rate determining complex formation between substrate and reagent, which would also be in agreement with the concentration dependence of k_1. If complexation takes place the complex may be present only in low (steady-state) concentration. A higher complex concentration would require deviations from linearity in the plot of k_1 against substrate concentration (Fig. 1). In the extreme case, where the reagent is completely complexed, k_1 would become constant with increasing substrate concentration.

Comparison of the rate constants of the triphenylmethylfluoroborate reaction with those of the dehydrogenation with DDQ is represented on a logarithmic scale in Fig. 2. The rate constants of both reactions are spread over a range of *ca.* 10000. The sequences run entirely parallel with one minor exception (triphenylcyclo-

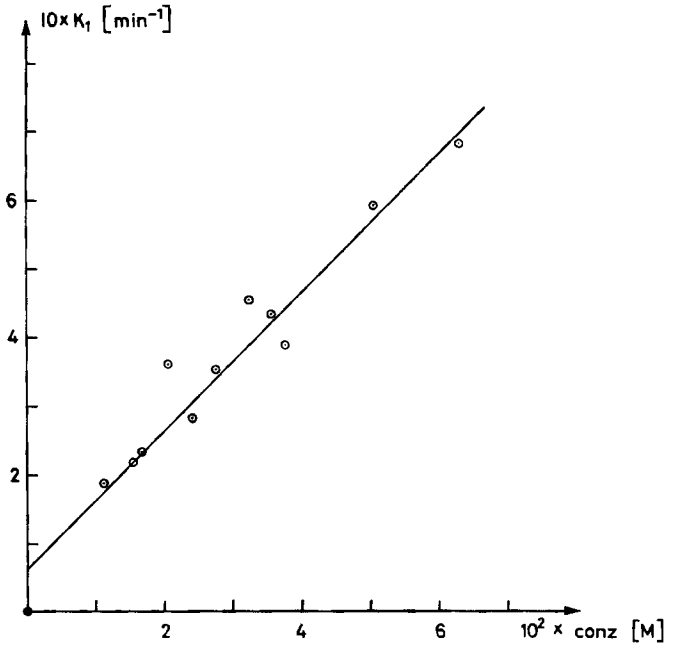


Fig. 1. *First-order dependence of the rate constant k_1 from substrate concentration for triphenylmethylfluoroborate and 1,4-cyclohexadiene* (**1**) *in acetonitrile* (T = 25.0°)

Relative reaction rates with triphenylmethylfluoroborate in acetonitrile and with DDQ

Substrate	No.	$Ph_3C^{\oplus}BF_4^{\ominus}$		DDQ (AcOH)[a]	DDQ (Benzene)	
		runs	k_{rel}	k_{rel}	runs	k_{rel}
1,4-Cyclohexadiene	**1**	10	100 ± 10	100	4	100 ± 0.5
1,4-Cyclohexadiene-d_6	**1**-d_6	7	35.4 ± 2	–	2	58.7 ± 1.5
1,4-Cyclohexadiene-d_8	**1**-d_8	2	23.8 ± 0.1	–	4	10 ± 0.05
cis-3,6-Dimethyl-1,4-cyclohexadiene	**2**	2	255 ± 15	143	–	148[a]
trans-3,6-Dimethyl-1,4-cyclohexadiene	**3**	5	20.7 ± 0.2	6.78	–	7.15[a]
3,3-Dimethyl-1,4-cyclohexadiene	**4**	2	2.27 ± 0.5	0.223	–	–
1,4-Pentadiene	**5**	2	0.13 ± 0.01	0.045	–	–
1,2,3-Triphenyl-cyclopropene	**6**	4	708 ± 90	108.5	–	–
Cycloheptatriene	**7**	9	1240 ± 100	372	–	311[a]

[a] Ref. [7].

propene (**6**) should be somewhat more reactive towards DDQ to be in the right sequence). The slope of the straight line of best fit is 0.916, the intercept 0.697 and the correlation coefficient 0.977. The correlation strongly suggests that both reactions should proceed by the same mechanisms. It is particularly interesting to note that the

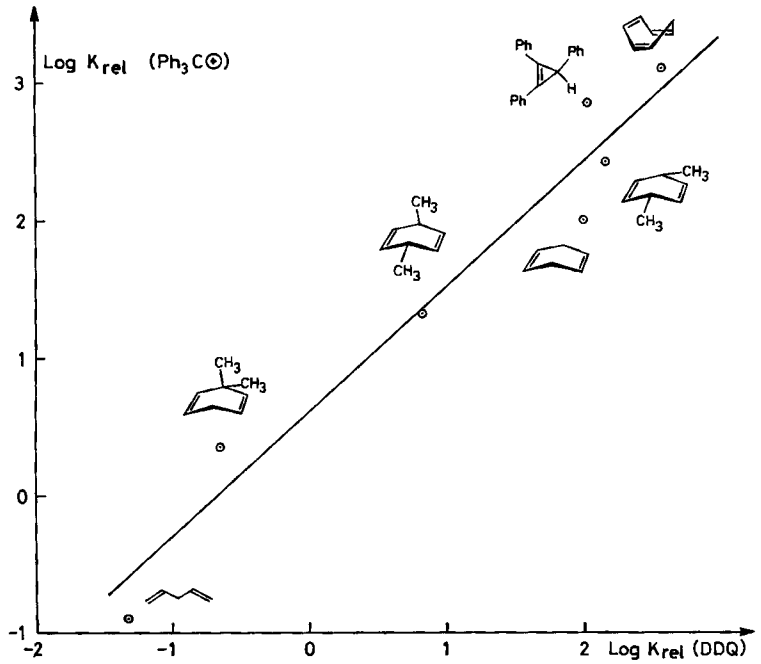


Fig. 2. *Log of relative rate constants for dehydrogenation with triphenylmethylfluoroborate and DDQ.* Reference compound in both reactions is 1,4-cyclohexadiene (**1**) with $k_{rel} = 100$.

relative reactivities of *cis*-3,6-dimethyl-1,4-cyclohexadiene (**2**), *trans*-3,6-dimethyl-1,4-cyclohexadiene (**3**) and 1,4-cyclohexadiene (**1**) are the same in both reactions. The hydride mechanism I has already been rejected for the reaction between DDQ and **1** and **2**. The same arguments may be used to rule it out for the reaction of these substrates with triphenylmethylfluoroborate. The cyclic mechanism III cannot take place with triphenylmethylfluoroborate, and therefore there appears to be no need to invoke a cyclic mechanism for the reaction of **1** and **2** with DDQ. As has been mentioned earlier, the reason for the high reactivity of **1** and **2** towards triphenylmethylfluoroborate and DDQ lies in the stabilisation of the developing coaxial *p*-orbitals by the adjacent π-bonds. Both hydrogens are transferred in the rate determining step; one will reduce the oxidating agent, the other may be lost as proton and combine with the solvent or the counterion.

The reactivity of the *trans*-isomer **3** fits well into this picture if the normal hydride transfer mechanism I is assumed. Only one hydrogen is axial and this can give rise to a stabilised *p*-orbital on the corresponding carbon atom. **3** is more reactive than 3,3-dimethyl-1,4-cyclohexadiene (**4**) because the carbenium ion formed upon hydride abstraction is tertiary in the former while only secondary in the latter. Participation

of the equatorial hydrogen in **3** might contribute somewhat to its reactivity; but this would require deformation of the carbon skeleton, and therefore increase the energy of the transition state relative to that of the *cis*-isomer (**2**).

Admittedly the kinetic results do not rule out the possibility of rate determining complexation in the case of **3** and **4** with DDQ and triphenylmethylfluoroborate. However, complexation is in general a very fast process. It appears to be more likely that steric hindrance to complex formation would result in a lower steady-state concentration of the complex than in a change of the rate determining step. Isotope effects determined in the reaction of DDQ with 1,4-cyclohexadiene (**1**), triphenylcyclopropene (**6**) [2] and tropilidene (**7**) [18] rule out in these cases the interference of charge transfer complexes in significant amounts. DDQ does form such complexes; but even with excellent π-donors such as hexamethylbenzene it is questionable whether they are on the reaction coordinate of dehydrogenation [20]. Complexation between poor donors such as 1,4-dienes and DDQ should be of even minor importance. No reference is made in the literature concerning charge transfer complexes between triphenylmethylfluoroborate and organic substrates. If they are formed they should lead to addition [21] or polymerisation products [22] rather than to dehydrogenation.

Financial support by the *Fonds National Suisse de la Recherche Scientifique* (Project No. 2.657.72) is gratefully acknowledged. I also thank Miss *Ch. Linder* and *Mr. J. Pfyffer* for excellent experimental work.

Experimental Part

Products. 1,4-Cyclohexadiene (**1**) (*Fluka*, purum) and tropilidene (**7**) (*Fluka*, tech.) were purified by preparative VPC. Triphenylcyclopropene (**6**) was prepared by reduction of triphenylcyclopropenium bromide with $LiAlH_4$ [22]. The methyl-substituted cyclohexadienes **2**, **3** and **4** were prepared according to the procedure of *Frey* [23] and *Rocek* [7]. The compounds were purified by preparative VPC. NMR. analyses of the purified samples demonstrated the absence of detectable amounts of impurities. 1,4-Pentadiene (*EGA-Chemie*) was used without purification. Hexadeuterio-1,4-cyclohexadiene (**1**-d_6) and octadeuterio-1,4-cyclohexadiene (**1**-d_8) were synthesised by *Birch* reduction [24] of deuterated benzene (*Fluka*, > 99% D) with sodium in liquid ammonia and deuterated ammonia [11] respectively. The reaction in undeuterated solvent yields a product consisting of 50% *cis*- and 50% *trans*-isomers with respect to hydrogen and deuterium in the allylic positions [10]. Analysis of the perdeuterated sample by mass spectrometry (*Atlas CH-4*) revealed an isotopic purity of 97.8%. The isotopic contamination was distributed over the allylic and olefinic positions in a ratio of 1.00:0.40. This corresponds to an isotopic purity of 98.4 in the allylic position.

The procedure of *Dauben* [25] was used for the preparation of triphenylmethylfluoroborate. The product was not recrystallized and contained traces of propionic anhydride [25]. DDQ (*Fluka*, purum) was used without purification.

Kinetic measurements. – a) *Triphenylmethylfluoroborate.* Stock solutions were prepared by dissolving *ca.* 30 mg of triphenylmethylfluoroborate in 10.0 ml of acetonitrile (*Merck*, 'zur Synthese', distilled from phosphorous pentoxide). 100 μl of this solution were added to 3.00 ml of solvent (acetonitrile) in an UV.-cell. The concentration of reagent at the beginning of the runs was *ca.* 3×10^{-4} M. The cell was thermostated to 25.0° in the cell compartment of a *Perkin-Elmer* 402 UV.-spectrophotometer. Substrate was introduced by means of a syringe so that its concentration in the cell was *ca.* 2×10^{-2} M. The amount of substrate was determined by differential weighing of the syringe before and after the injection. The disappearance of the yellow colour was recorded at *ca.* 450 nm and the rate constants determined graphically.

b) *DDQ.* The procedure described for benzene [7] and acetic acid [2] was adapted to dioxane as reaction medium. Dioxane was distilled from lithium aluminium hydride and used within one week after purification. The rate constants determined in benzene are (in mol^{-1} min^{-1}) 1.71 for

1,4-cyclohexadiene (**1**), 1.00 for hexadeuterio-1,4-cyclohexadiene (**1**-d_6) and 0.185 for perdeuterio-1,4-cyclohexadiene (**1**-d_8). The values for dioxane are 0.958 for **1** and 0.103 for **1**-d_8.

Reaction of triphenylmethylfluoroborate with 1,4-cyclohexadiene (1). - To a solution of 1.70 g of triphenylmethylfluoroborate (5.15 mmol) in 15 ml of dry acetonitrile was added dropwise 200 mg of 1,4-cyclohexadiene (2.50 mmol) in 5 ml of acetonitrile.

After the addition (15 min.) the reaction mixture was stirred for 2 additional h. at room temperature. The excess triphenylmethylfluoroborate was decomposed by addition of 2 g sodium hydrogencarbonate. A known quantity of toluene was added as standard followed by 50 ml of water. The solution was extracted with ether. After washing with water and drying with magnesium sulfate the organic layer was concentrated under a 30 cm *Vigreux* column. VPC. analysis of the residue using the added toluene as reference revealed the presence of benzene in 80% yield. After evaporation of the solution the solid residue was subjected to column chromatography on silica gel, using chloroform as solvent. Triphenylmethane (530 mg, 217 mmol) and triphenylmethanol (581 mg, 2.24 mmol) were recovered in 87 and 85% yield respectively.

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