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Abstract

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FACILE HETEROLYTIC CLEAVAGE OF THE CARBON-CARBON BOND IN CYCLOHEPTATRIENE DERIVATIVES

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The aromaticity of the tropylium system determines its high stability, in comparison with other carbonium ions, and the increased ease of its formation. Thus, in contrast to the ordinary C—O bond in simple ethers, which is cleaved only under severe conditions, in ditropyl ether the C—O bond is broken even under the action of weak acids, with formation of the tropylium cation ([1]). Heterolytic cleavage of the C—H bond in cycloheptatriene occurs comparatively readily; in this process a hydride ion is split off and the tropylium cation is formed ([2]).

Of special interest is the question of the possibility of heterolytic cleavage of carbon-carbon bonds in cycloheptatriene derivatives. Until now only one reaction of this kind has been known: cleavage of the cycloheptatrienyl-carbon bond in those cases where a carbonium center is situated in the β-position to the cycloheptatrienyl residue (fragmentation reaction):

$$[\text{cycloheptatrienyl-C-C}^{+}\text{ fragment}] \longrightarrow [\text{tropylium cation}] + [\text{alkene fragment}]$$

As Conrow ([3]) and we ([4]) have shown, this reaction proceeds under the action of strong acids on β-hydroxy and β-carbonyl compounds, or of $AgNO_3$ on β-bromo derivatives of 7-substituted cycloheptatrienes. However, we recently found that the reaction of heterolytic cleavage of the C—C bond in cycloheptatriene derivatives has a considerably more general character. It turned out that unusually facile cleavage of the cycloheptatrienyl-carbon bond

Table 1

Cleavage of cycloheptatrienylmalonic acid

Reagent	Experimental conditions	Tropylium content, %	Reagent	Experimental conditions	Tropylium content, %
Bromine	chloroform, 20°	83	PCl_5	benzene, 20°, 15 min	77
HCl gas	benzene, 20°	66	$(CH_3CO)_2O$	20°*	28
HBr gas	benzene, 20°	80	$(C_6H_5)_3C^+BF_4^-$	benzene, boiling, 20 min	26
H_2SO_4	20°*	99	tert.-C_4H_9Br	boiling, 20 min	18
CH_3COOH	20°*	13	$ZnCl_2$	benzene, 3 h, 20°	19
H_3PO_4	20°*	42	$FeCl_3$	benzene, 3 h, 20°	24

* Precipitation of tropylium chloroplatinate was carried out immediately after addition of the reagent.

is a characteristic property of cycloheptatriene derivatives with electron-acceptor substituents in the side chain. Thus, cycloheptatrienylmalonic acid, cycloheptatrienylacetylacetone, cycloheptatrienylacetaldehyde, and cycloheptatrienylacetoacetic ester are cleaved under the action of the most diverse electrophilic reagents with

with formation of the tropylium ion (see Table 1). For example, cycloheptatrienylmalonic acid is rapidly cleaved at room temperature under the action of protonic acids (HCl, HBr, H_2SO_4, H_3PO_4, CH_3COOH). The corresponding tropylium salt and malonic acid are formed:

$$(\text{cycloheptatrienyl})\text{CH}(\text{COOH})_2 + \text{H}^+\text{X}^- \rightarrow [\text{C}_7\text{H}_7]^+\text{X}^- + \text{CH}_2(\text{COOH})_2$$

An analogous reaction takes place under the action of Lewis acids ($ZnCl_2$, $FeCl_3$, PCl_5), bromine, acetic anhydride, and sources of carbonium ions—triphenylmethyl bromide and tertiary alkyl halides, for example:

$$(\text{cycloheptatrienyl})\text{CH}(\text{COOH})_2 + \text{Br} : \text{Br} \rightarrow [\text{C}_7\text{H}_7]^+\text{Br}^- + \text{BrCH}(\text{COOH})_2$$

Compounds such as cycloheptatrienylacetylacetone and cycloheptatrienylacetoacetic ester react with electrophilic reagents with still greater ease. Even

upon treatment with an alcoholic solution of chloroplatinic acid, a precipitate of tropylium chloroplatinate is immediately formed (cycloheptatrienylmalonic acid under these conditions is not cleaved so rapidly). Evidently, the cleavage reaction of cycloheptatrienyl derivatives by acids is a process reverse to the tropylation reaction (replacement of hydrogen by the cycloheptatrienyl residue) ([5]):

$$\text{(cycloheptatrienyl)-C(H)(-)} \; + \; \text{H}^+\text{X}^- \rightleftharpoons [\text{C}_7\text{H}_7]^+\text{X}^- + \text{H-C(-)}$$

The reversibility of the tropylation reaction makes it possible to explain a number of previously obscure facts—the decrease in the rate of tropylation with increasing acidity of the medium ([6]), the need for a base to bring tropylation to completion ([3]), etc. In view of the reversibility of the tropylation reaction, the interpretation of data on the kinetics of tropylation ([6]) must also be reconsidered.

The data presented above on the facile cleavage of the cycloheptatrienyl–carbon bond made it possible to expect that the cycloheptatrienyl residue could migrate from cycloheptatrienylmalonic acid to other compounds containing mobile hydrogen. Indeed, it was found that upon heating cycloheptatrienylmalonic acid with an excess of acetylacetone or acetoacetic ester, rapid retropylation occurs with formation of cycloheptatrienylacetylacetone or cycloheptatrienylacetoacetic ester:

$$\text{(cycloheptatrienyl)CH(COOH)}_2 + \text{CH}_3\text{COCH}_2\text{COCH}_3 \rightleftharpoons \text{(cycloheptatrienyl)CH(COCH}_3)_2 + \text{CH}_2\text{(COOH)}_2$$

Similarly, upon treatment of cycloheptatrienylmalonic acid with vinyl ethyl ether in water, the formation of cycloheptatrienylacetaldehyde could be observed:

$$\text{(cycloheptatrienyl)CH(COOH)}_2 + \text{CH}_2{=}\text{CHOR} \xrightarrow{\text{H}_2\text{O}} \text{(cycloheptatrienyl)CH}_2\text{CHO}$$

Thus, in a number of reactions it has been possible to show that the cycloheptatrienyl derivatives studied are distinguished by an unusual propensity, for carbon–carbon bonds, toward heterolytic cleavage with formation of the tropylium ion and, in this connection, by a high mobility of the cycloheptatrienyl residue.

In general terms, the relationships in the tropylium–substituted cycloheptatriene system are determined by two opposing tendencies. On the one hand, the presence of a positive charge accounts for the "alkylating" properties of the tropylium system and the ease of its conversion into the substituted cycloheptatriene system. On the other hand, the tendency toward formation of an

energetically favorable aromatic system determines the extraordinary ease of heterolysis not only of tropyl–oxygen and tropyl–hydrogen bonds, but also of the tropyl–carbon bond.

As a result, processes both of loss of aromaticity and of formation of the aromatic tropylium system proceed quite readily and in a number of cases are reversible:

$$[C_7H_7]^+X^- + R{:}Y \rightleftharpoons C_7H_7(R)(H) + YX$$

Experimental Part

Reaction of cycloheptatrienylmalonic acid with bromine. To 0.19 g (0.0098 mole) of cycloheptatrienylmalonic acid in 3 ml of chloroform, with vigorous stirring, a solution of 0.16 g (0.01 mole) of bromine in 3 ml of chloroform was added dropwise. The oily precipitate that separated was washed with chloroform and dissolved in 2 ml of abs. alcohol. To the alcoholic solution was added an alcoholic solution of chloroplatinic acid. The precipitate formed was centrifuged, washed with alcohol, then with ether, and dried. 0.24 g of tropylium hexachloroplatinate was obtained (83% of theory).

Found, %: C 28.45, 28.54; H 2.39, 2.49; Pt 32.57, 32.36; Cl 36.26, 36.12
$C_{14}H_{14}PtCl_6$. Calculated, %: C 28.50; H 2.36; Pt 33.05; Cl 36.10

The UV spectrum is identical with the UV spectrum of an authentic sample of tropylium hexachloroplatinate.

Reaction of cycloheptatrienylmalonic acid with sulfuric acid. 0.19 g of cycloheptatrienylmalonic acid was dissolved in 0.2 ml of conc. sulfuric acid. The solution was diluted with 3 ml of abs. alcohol and an alcoholic solution of H_2PtCl_6 was added. 0.29 g (99%) of tropylium hexachloroplatinate was obtained.

Found, %: C 28.02, 27.99; H 2.47, 2.45; Pt 32.82, 32.99; Cl 35.66, 35.96
$C_{14}H_{14}PtCl_6$. Calculated, %: C 28.50; H 2.36; Pt 33.05; Cl 36.10

The UV spectrum is identical with the UV spectrum of an authentic sample of tropylium hexachloroplatinate.

Reaction of cycloheptatrienylmalonic acid with hydrogen chloride. A solution of 0.19 g of cycloheptatrienylmalonic acid in ether was saturated with dry hydrogen chloride. The oil that separated was washed with abs. ether. The ethereal extracts were dried, the solvent was distilled off, and chromatography on alumina plates showed that the residue contained malonic acid. In the usual manner, from the precipitate insoluble in ether, 0.099 g (66%) of tropylium hexachloroplatinate was obtained. The UV spectrum is analogous to the UV spectrum of an authentic hexachloroplatinate.

The remaining experiments on the cleavage of tropylmalonic acid were carried out analogously to those described above.

Cycloheptatrienylacetylacetone and cycloheptatrienylacetoacetic ester form a platinate with an alcoholic solution of chloroplatinic acid at room temperature in a yield of ~ 12%; in the presence of acetic acid the platinate is formed in yields of 75 and 28%, respectively.

The retropylation reaction of cycloheptatrienylmalonic acid.

1. Reaction with acetylacetone. 0.4 g of cycloheptatrienylmalonic acid was heated on a water bath with 3 ml of acetylacetone for 3 h. The reaction mixture was extracted with ether. The ether extracts were washed with a solution of soda and with water. After removal of the solvent, 0.2 g of a substance with m.p. 122° was isolated from the ethereal solution. After recrystallization from petroleum ether, m.p. 125.5°. It does not give a melting-point depression with authentic cycloheptatrienylacetylacetone.

2. Reaction with acetoacetic ester. 0.3 g of cycloheptatrienylmalonic acid was heated with 4 ml of acetoacetic ester on a water bath for 2 h. The solution was diluted with ether and extracted with a soda solution. After drying and removal of the ether and acetoacetic ester, 0.09 g of a substance with b.p. 130–140°/5 mm was isolated. According to the literature, the b.p. of cycloheptatrienylacetoacetic ester is 121.5°/3 mm (5). The substance gives a platinate on treatment with chloroplatinic acid in the presence of acetic acid.

The IR spectrum of the substance is identical with the IR spectrum of authentic cycloheptatrienylacetoacetic ester.

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Note: Figure translations are in progress. See original paper for figures.