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Abstract

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ON THE STRUCTURE OF SALTS OF DIPHENYLCYCLOPROPENONE AND TROPONE

(Presented by Academician M. M. Shemyakin, 28 XII 1960)

A characteristic feature of nonbenzenoid aromatic ketones—diphenylcyclopropenone (I) and tropone (II)—is their ability to form salts with strong acids (^{1,2}).

(structure of diphenylcyclopropenone)	(structure of tropone)
C_6H_5–△–C_6H_5	seven-membered ring
O (I)	O (II)

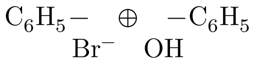
To elucidate the structure of such salts we synthesized the hydrobromide salts of diphenylcyclopropenone and tropone and investigated their infrared spectra.

The starting diphenylcyclopropenone was obtained by the reaction of tolane with dichlorocarbene (^{2}), m.p. 121—121.5°, and purified by chromatography on Al_2O_3. The anhydrous hydrobromide salt of diphenylcyclopropenone was obtained by passing hydrogen bromide, dried over P_2O_5, into a solution of the ketone in abs. benzene. The precipitate that formed was quickly separated, washed with absolute benzene and petroleum ether, and dried over paraffin at atmospheric pressure with brief evacuation at the end of drying, m.p. 121—121.5° (with decomposition). The substance is unstable; it eliminates hydrogen bromide on heating and on storage in vacuo, with formation of diphenylcyclopropenone. It is more stable in the form of the monohydrate $C_{15}H_{11}OBr \cdot H_2O$, m.p. 148.5—149° (decomp.), into which it passes on standing in air.

The hydrobromide salt of tropone was obtained by passing dry hydrogen bromide into a solution of tropone in dry benzene. The precipitate was washed with benzene and dried analogously to the salt of diphenylcyclopropenone.

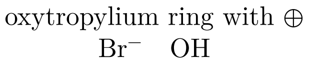
The IR spectra of the synthesized salts in the crystalline state are characterized by the disappearance of the bands of the carbonyl groups of the starting ketones and by the appearance of hydroxyl bands. Thus, in the spectrum of the hydrobromide salt of diphenylcyclopropenone there is no 1855 cm^{-1} band, associated with the stretching vibration of the $C = O$ group in diphenylcyclopropenone (^{3}), nor the 1621 cm^{-1} band, which, evidently, should be regarded as the stretching-vibration band of a largely localized $C = C$ double bond in the three-membered ring. At the same time, an intense broad band at 2976 cm^{-1} appears in the spectrum of the salt; it is undoubtedly due to the presence in the molecule of a hydroxyl group which, in the crystals, participates in the formation of very strong hydrogen bonds. The spectrum lacks bands that could be regarded as characteristic of an H—Br bond (2300—2800 cm^{-1}).

These data are in good agreement with the assumption that the salt has structure (III), i.e., is a salt of the nonbenzenoid aromatic cation diphenyloxycyclopropenylium.



$$\begin{array}{c} C_6H_5-\quad \oplus \quad -C_6H_5 \\ Br^- \quad OH \end{array}$$

(III)



$$\begin{array}{c} \text{oxytropylium ring with } \oplus \\ Br^- \quad OH \end{array}$$

(IV)

The spectrum of the hydrobromide salt of tropone differs from the spectrum of the initial tropone by the absence of the band at 1582 cm^{-1}, which is the most intense band in the spectrum of tropone. This fact confirms the correctness of assigning precisely this band to the carbonyl group of tropone, as was done earlier in our work (^{3}) and in the work of Borod' ko and Syrkin (^{4}). The band at 1635 cm^{-1} in the spectrum of tropone, which had previously been taken as the carbonyl band (^{1}), in our opinion belongs to vibrations of the double bonds of the ring; it is retained in the spectrum of the salt, being shifted only somewhat toward lower frequencies (to 1611 cm^{-1}), which is quite consistent with further equalization of the bonds in the ring on going from tropone to the oxytropylium ion. This is also supported by the fact that in the Raman spectrum of tropylium $C_7H_7^+$ a band at 1594 cm^{-1} is observed, assigned to symmetric vibrations of the aromatic ring (^{5}).

In the spectrum of the crystalline salt of tropone an intense band appears at 3125 cm^{-1}. This band undoubtedly indicates, as in the case of diphenyloxycyclopropenylium bromide, the presence of a hydroxyl group in the molecule. The spectrum also shows two bands of medium intensity at 2387 and 1876 cm^{-1}, which are apparently connected with the presence, in the crystalline state, of hydrogen bonds of the type $O - H \cdots Br$. The assignment of these bands to $H - Br$ bonds, and hence also the content of free hydrogen bromide in the solid salt, is excluded because of the absence in the spectrum of the band at 1582 cm^{-1}, characteristic of the free ketone.

All these data convincingly show that the tropone salt studied has structure (IV) and is a salt of the nonbenzenoid aromatic oxytropylium cation. Thus, under the action of strong acids on diphenylcyclopropenone and tropone, addition of a proton to the carbonyl group occurs, with conversion of the latter into a hydroxyl group and formation of the corresponding nonbenzenoid aromatic system.

Fig. 1. IR spectra: diphenylcyclopropenone (1), bromodiphenylhydroxycyclopropenylium (2), tropone (3), bromooxytropylium (4). 1, 2, 4 –crystalline state; 3 –liquid

Figure 1: Fig. 1. IR spectra: diphenylcyclopropenone (1), bromodiphenylhydroxycyclopropenylium (2), tropone (3), bromooxytropylium (4). 1, 2, 4 –crystalline state; 3 –liquid

This reaction is reversible; under the action of bases on the salts, the initial ketones are formed:

$$\text{diphenyloxycyclopropenylium cation} \rightleftharpoons \text{diphenylcyclopropenone} + \mathrm{HBr}$$

$$\text{oxytropylium cation} \rightleftharpoons \text{tropone} + \mathrm{HBr}$$

Elimination of HBr from the salts also occurs to a considerable extent under the action of solvents.

In the IR spectra of solutions of the salts in chloroform, dioxane, nitromethane, etc., bands appear that are characteristic of the initial ketones (1855 and 1621 cm^{-1} in solutions of diphenyloxycyclopropenylium bromide and 1582 cm^{-1} in solutions of oxytropylium bromide), but the intensity of these bands is somewhat lower than in the ketones themselves.

It is evident that the stability of such salts characterizes the tendency of the ketones under consideration to pass from a partially delocalized system of π-electrons in the ring to complete delocalization of π-electrons, with formation of an aromatic system in the salts.

We measured the instability constants of the salts under investigation in chloroform using data on the integral intensity of the carbonyl bands in solutions of ketones and their salts. The integral intensities of the carbonyl bands of diphenylcyclopropenone and tropone in chloroform solutions, according to our measurements, are $5.9 \cdot 10^4\ \mathrm{mol} \cdot \mathrm{l}^{-1} \cdot \mathrm{cm}^{-2}$ and $3.5 \cdot 10^4\ \mathrm{mol} \cdot \mathrm{l}^{-1} \cdot \mathrm{cm}^{-2}$, while the intensities of the carbonyl band in the spectra of the salts of these ketones in the same solutions (at a concentration of $\sim 10^{-2}\ \mathrm{mol} \cdot \mathrm{l}^{-1}$) are $5.0 \cdot 10^4$ and $2.6 \cdot 10^4\ \mathrm{mol} \cdot \mathrm{l}^{-1} \cdot \mathrm{cm}^{-2}$, respectively. Hence the instability constant for bromodiphenylhydroxycyclopropenylium is $7.5 \cdot 10^{-2}$, and for bromooxytropylium $1.8 \cdot 10^{-2}$.

Fig. 1. IR spectra: diphenylcyclopropenone *(1)*, bromodiphenylhydroxycyclopropenylium *(2)*, tropone *(3)*, bromooxytropylium *(4)*. *1, 2, 4* –crystalline state; *3* –liquid.

Thus, tropone has a somewhat greater tendency to form a completely aromatic bond system than diphenylcyclopropenone.

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