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NEW MUTUAL CONVERSION OF AROMATIC SYSTEMS

TROPILIUM SALTS AND BENZENE

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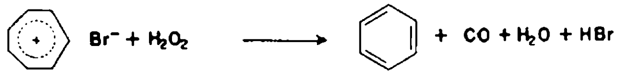
Abstract—The present work reports on the effected direct conversion of the aromatic tropilium cation to benzene and that of benzene to tropilium cation.

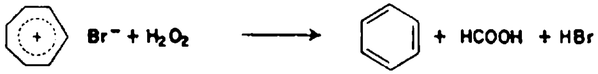
Numerous rearrangements of tropone and tropolone derivatives[1] as well as oxidation of tropilium salts with chromic acid or silver oxide[2] give rise to substituted benzene with the same number of carbon atoms as in the parent compound.

We have recently discovered a reaction of direct conversion of tropilium salts to unsubstituted benzene accompanied by elimination of one carbon atom.

The formation of benzene from tropilium takes place under the action of aqueous hydrogen peroxide at room temperature, the main products of the reaction other than benzene being carbon monoxide and formic acid (almost in equal amounts). See Table 1.

The process is seen to be going mainly in two directions:





We have investigated the kinetics of the former reaction (accompanied by evolution of carbon monoxide). It follows a second order equation with a second order velocity constant (at 20·05° in aqueous solution) 10·4 ± 0·3 l. mole^{-1} min^{-1}. The Arrhenius parameters over the 20–50° range are E 10·5 kcal/mole, lg A 8·89.

Considerably increasing the acidity of the media (if the reaction is carried out in 1 N H_2SO_4) only negligibly reduces the reaction rate (velocity constant 7·7 at 20°). The reaction stops already in slightly alkaline media, that is under the conditions when, according to Doering and Knox,[3] the tropilium ion concentration sharply falls due to the right hand shift of the equilibrium $C_7H_7^+ + 2H_2O \rightleftarrows C_7H_7OH + H_3O^+$. In passing from aqueous to alcoholic solutions the reaction rate increases by one order, possibly owing to the tropilium ion being less solvatized. Substituting perchlorate for tropilium bromide does not affect the reaction course.

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[1] P. Pauson, *Chem. Rev.* 55, 9 (1955).

[2] W. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* 79, 352 (1957).

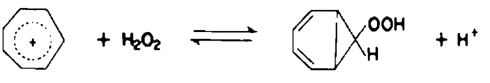
[3] W. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* 76, 3203 (1954).

The reaction of tropilium salts with hydrogen peroxide does not appear to involve free radicals. Thus, equimolecular addition of ferric sulphate and sulphuric acid (favouring the hydrogen peroxide and organic peroxide decomposition into free radicals) markedly hinders the reaction, the rate falling two to threefold and the termination of the reaction necessitating a considerable excess of hydrogen peroxide.

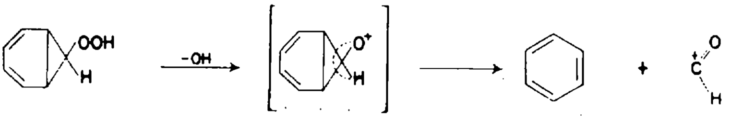
Table 1

	g-mole	Calc. for C_7H_7Br (%)
Starting compounds		
$C_7H_7{}^+Br^-$	0·0780	100
H_2O_2	0·0780	100
Reaction products		
C_6H_6	0·0644	82·5
CO	0·0393	50·4
HCOOH	0·0390	50·0
C_6H_5CHO		(~1·0)
C_6H_5OH		(~0·1)

The data obtained suggest the first bimolecular reaction step to proceed due to the reaction of the tropilium ion and hydrogen peroxide to yield unstable hydroperoxide (I) that either directly decomposes into reaction products, or is first converted into cation II to be split into benzene and cation HCO^+ as follows:



I



II

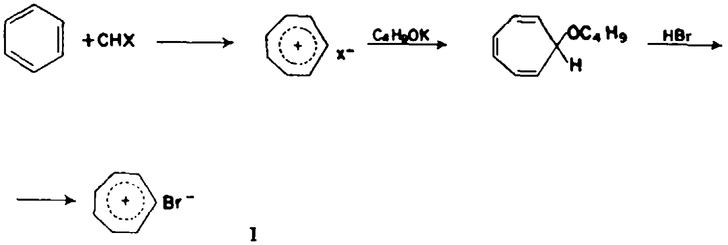
$$H\overset{+}{C}=O \longrightarrow H^+ + CO; \quad H\overset{+}{C}=O + H_2O \longrightarrow HCOOH + H^+$$

One could have also thought the reaction to proceed via the intermediate formation of tropone. But tropone does not decompose into benzene and carbon monoxide, neither does it react with hydrogen peroxide under studied conditions. Similar considerations lead to suggest that the reaction does not proceed through benzaldehyde as an intermediate. It will be seen that the above cycle contraction reaction is characterized by a simultaneous cleavage of two C—C bonds to give an unsubstituted benzene ring.

It seemed of interest to effect the reverse conversion of benzene directly to tropilium cation. To this end we attempted to add dihalocarbenes CCl_2 and CBr_2 to benzene but the Doering and Hoffmann's reaction of $CHCl_3$ and CHBr with potassium t-butylate[4] when carried out in the presence of benzene did not yield the expected tropone.

Believing our failure to be due to the activity of dihalocarbenes CX_2 not being high enough and bearing in mind that unsubstituted methylene readily adds on to benzene we postulated that monohalocarbenes CHX could readily react with benzene. Indeed, we succeeded in showing that the reaction of methylene chloride, bromide or iodide with potassium t-butylate in benzene leads in all cases to tropilium salts, though in poor yields. This may be accounted for by the formation of monohalocarbenes as intermediates and their reaction with benzene, according to the following scheme:

$$CH_2X_2 + C_4H_9OK \longrightarrow CHX + C_4H_9OH + KX$$



I

with X being Cl, Br or I. The tropilium salt thus formed reacts with potassium *tert*.-butylate to give butoxycycloheptatriene that, in turn, leads to tropilium bromide when treated with hydrogen bromide. The concentration of starting compounds and the reaction time do not essentially affect the tropilium salt yield, the temperature rise somewhat increasing it.

There are no indications in the literature on the formation of unsubstituted monohalocarbenes. According to Hine *et al.*[5] the reaction of methylene halides and sodium methoxide in methanol follows the S_N2 mechanism, alcoholysis proceeding successively faster in the following sequence $CH_2Cl_2 < CH_2Br_2 < CH_2I_2$. On the other hand the tropilium salt yield rises in a reverse order, or $CH_2I_2 < CH_2Br_2 < CH_2Cl_2$. This is in accordance with the data obtained by Hine[6] on the readiness of dihalocarbene formation from haloformes depending on the halogen ($I < Br < Cl$). The evidence obtained allows us to suggest that alcoholysis of methylene halides by potassium t-butylate partly proceeds with intermediate formation of monohalocarbenes that may add to benzene to give tropilium derivatives.

EXPERIMENTAL

To a solution of tropilium bromide (13·34 g, 0·0780 mole) in water (100 cc) with cold water cooling, 5% hydrogen peroxide was added. An equivalent amount of hydrogen peroxide having been added, the solution contained no tropilium bromide, as evidenced by absence of precipitate when adding chloroplatinic acid solution.[7] Stirring was continued for 30 more min and the reaction mixture extracted with n-octane (previously distilled on a column). As to the aqueous solution (A) see below.

Organic extracts were washed with water, 10% NaOH, again with water, dried with magnesium

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[4] W. E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.* **76**, 6162 (1954).

[5] J. Hine, C. H. Thomas and S. J. Eherenson, *J. Amer. Chem. Soc.* **77**, 3886 (1955).

[6] J. Hine, D. C. Duffy, P. B. Langford and J. J. Porter, *Angew. Chem.* **69**, 682 (1957).

[7] M. E. Volpin, S. I. Zhdanov and D. N. Kursanov, *Dokl. Akad. Nauk SSSR* **112**, No. 2, 264 (1957).

sulphate, and distilled on the column (10 theoretical plates), 4·90 g benzene being obtained, b.p. 79·6–80·1°/746 mm, n_D^{20} 1·5005.

(Found: C, 92·14, 92·12; H, 7·71, 7·81. C_6H_6 requires: C, 92·21; H, 7·74%).

The intermediate fraction (0·95 g), b.p. 80·1–123°, n_{20}^D 1·4123, contains additional 0·12 g benzene, the overall benzene yield amounting to 5·02 g (82·5%).

Benzene was identified by ultra-violet spectrum and nitration (with mixture of H_2SO_4 and HNO_3) to nitrobenzene to give further aniline by zinc dust reduction in HCl. Aniline was converted into benzanilide, m.p. 160–161°. (lit. m.p. 162°). The mixed melting point with the authentic sample showed no depression.

Aqueous solution. (A) was vapour distilled, the distillate containing 0·0390 mole formic acid (as ascertained by potassium permanganate titration), the latter identified as *p*-bromophenacyl ester, m.p. 141–142° (lit. m.p. 142°) showed no melting point depression with the authentic sample.

The reaction was accompanied by evolution of 1000 cc gas (at 19·6°/746 mm over NaCl saturated solution) that contained 98·6% CO and 1·4% O_2, the latter apparently at the expense of the partial decomposition of hydrogen peroxide.

Reaction of tropilium perchlorate and hydrogen peroxide

To 9·8 g of tropilium perchlorate (0·05 mole) 25% H_2O_2 (8 cc) in water (30 cc) was gradually added with cooling, and the reaction mixture extracted with ether. The extracts were washed with 10% alkaline solution (as to treatment of alkaline extracts see below) and water, dried over magnesium sulphate and distilled, yield 2·8 g (72%) benzene, b.p. 79·7–78·1°, n_D^{20} 1·5005, d_4^{20} 0·8748. The residue from distillation of benzene was dissolved in alcohol and 2,4-dinitrophenyl hydrazine alcoholic solution added to precipitate 2,4-dinitrophenylhydrazone benzaldehyde (0·11 g or 1%), m.p. 237° (lit. m.p. 237°); the mixed melting point determination with the authentic sample showed no depression.

The alkaline extracts (see above) were evaporated to a small volume, acidified and treated with iodine in potassium iodide solution and with soda. The precipitate was triiodophenol (0·11 g, 0·1%, m.p. 157–158°, lit. m.p. 157°); the mixed melting point determination with the authentic sample showed no depression.

The reaction yielded 820 cc CO (740·4 mm at 20·7° over saturated NaCl solution), or 0·031 mole (62%).

Kinetic study of the reaction of tropilium bromide and hydrogen peroxide

Equimolecular aqueous solutions of hydrogen peroxide and tropilium bromide were placed in a thermostat and vigorously shaken, the reaction rate being followed by the volume of the evolving gas (CO). It has previously been shown that the amount of gas formed (when shaken) is proportional to the amount of the reacted substances. The rate constant was calculated from the equation:

$$K = 1/tC_0(V_t/V_\infty - V_t)$$

where t is the time from the beginning of the reaction

V_∞—the amount of gas evolved after the end of the reaction (determined experimentally),

V_t—the amount of gas evolved measured in time,

C_0—initial concentration of reacting substances

To evaluate K use was made of the value V_t from the beginning of the reaction up to 60–70% conversion. Arrhenius parameters were evaluated over a 10–15° range in terms of $K_{10\cdot2^\circ} = 6\cdot12$, $K_{20\cdot05^\circ} = 10\cdot4$, $K_{30\cdot0^\circ} = 20$, $K_{40\cdot0^\circ} = 33$ and $K_{50\cdot0^\circ} = 61\cdot5$.

Reaction of benzene and methylene chloride

(a) To the boiling mixture of 8·4 g (0·075 mole) dry potassium t-butylate (not containing t-butyl alcohol) and absolute benzene (200 cc) 19·1 g (0·225 mole) methylene chloride were added with stirring. After addition, the mixture was stirred for 4 hr at 60° and left overnight. The solidified brownish mass was filtered off, the filtrate evaporated in vacuum and swept with dry hydrogen bromide. The precipitate was filtered off, washed with absolute benzene and dried in vacuum. The reaction yielded 0·24 g tropilium bromide. (1·9% accounted for by potassium t-butylate).

The substance obtained is soluble in water and after treating with sodium bicarbonate and benzene extraction is again precipitated by hydrogen bromide. Under the action of H_2PtCl_6 tropilium chloroplatinate is precipitated from the aqueous and alcoholic solutions. The infra-red and ultra-violet spectra of tropilium bromide are identical to those obtained by Doering and Knox.[3]

(b) To the mixture of 10·7 g (0·095 mole) potassium t-butylate and benzene (200 cc) 15·3 (0·18 mole) CH_2Cl_2 were added (30 min) at room temp with stirring. The reacting substance was stirred for seven days, the precipitate then filtered off and the filtrate swept with dry hydrogen bromide. The precipitate was treated with water and the aqueous solution made alkaline with sodium bicarbonate. The ditropyl ether was extracted with benzene. Sweeping the benzene solution with hydrogen bromide yielded tropilium bromide, (0·16 g, yield 1·4%).

Reaction of benzene and methylene bromide

(a) 8·9 g (0·08 mole) potassium t-butylate, 27·8 g (0·16 mole) CH_2Br_2 and benzene (200 cc) at room temp (under experimental conditions as above) resulted in 0·06 g tropilium bromide (yield 0·44%).

(b) 11·2 g (0·1 mole) potassium t-butylate, 22·6 g (0·13 mole) CH_2Br_2 and benzene (200 cc) under reflux gave 0·20 g of tropilium bromide (yield 1·2%).

Reaction of benzene and methylene iodide

10·3 g (0·09 mole) potassium t-butylate, 44·4 g (0·17 mole) CH_2I_2 and benzene (200 cc) at room temp yielded to 0·015 g tropilium bromide (yield 0·1%).