2-BENZOPYRILIUM SALTS.

38.* A NOVEL VARIANT OF THE CANNIZZARO REACTION

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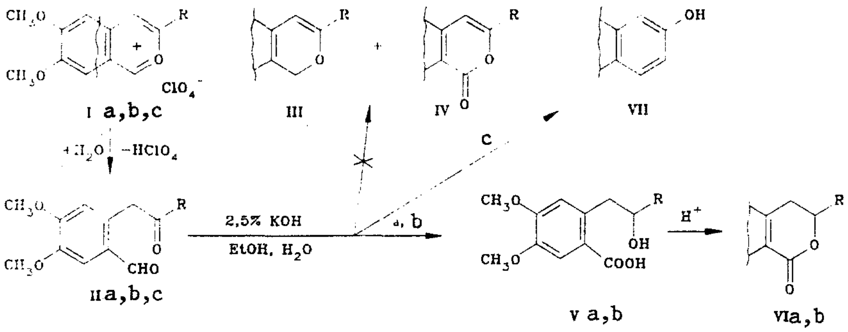
1,5-Aldehydoketones (the ring-opened forms of 2-benzopyrylium salts) under the conditions of the Cannizzaro reaction, when intramolecular aldol condensation is not possible, undergo intramolecular disproportionation.

The disproportionation of heterocyclic cations is regarded as being a special case of the Cannizzaro reaction [2]. We have recently observed disproportionation in 1,4-unsubstituted 2-benzopyrylium salts, involving prior dimerization, which is not in accordance with this view [3]. Since the 1,5-dicarbonyl compounds (IIa-c), which are ring-opened forms of the salts (Ia-c), contain an aromatic aldehyde group, they would be expected to disproportionate under the conditions of the Cannizzaro reaction. It was expected that there would thus be obtained, at least in the cases of (IIa) and (IIb), the isochromenes (IIIa, b) and the isocoumarins (IVa, b), these being the products of the disproportionation of the starting cations.

It was, however, found that on heating the aldehydoketones (IIa) and (IIb) with 2.5% aqueous-alcoholic potassium hydroxide, they underwent intra-, rather than intermolecular hydride transfer, to give high yields of the hydroxyacids (Va, b), which cyclize readily on heating to the lactones (VIa, b).



I—VI a R=3,4-$(CH_3O)_2C_6H_3$, b R=C_6H_5, c R=CH_3

The PMR spectrum of (VIa) shows a complex multiplet for the protons of the prochiral methylene grouping at 2.82-3.25 ppm, signals for the four methoxy groups, a double doublet for the secondary proton at 5.42 and 5.55 ppm, and a multiplet for five aromatic protons. The IR spectrum showed strong absorption for the ester group at 1705 cm^{-1}. These findings, taken with the reverse formation of the hydroxyacid (Va), the structure of which was also confirmed by IR and PMR spectroscopy, are in full agreement with the structure proposed for the lactone (VIa).

This reaction constitutes a novel variant of the Cannizzaro rearrangement [4, p. 198]. The ease of hydride transfer to the ε-position, even when donor substituents are present in the aromatic ring conjugated to the keto-group, is probably due to favorable steric factors. The originally expected intermolecular disproportionation does not take place at all,

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*For Communication 37, see [1].

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and the yields of intermolecular aldol condensation products do not exceed 10%. However, when intramolecular condensation is possible, as in the aldehydoketone (IIc), quantitative yields of the β-naphthol (VII) were obtained.*

Hence, the disproportionation of 2-benzopyrylium cations and their ring-opened forms differ not only in their mechanism, but also in the final outcome.

EXPERIMENTAL

IR spectra were obtained on a Specord 75 spectrophotometer in vaseline grease, and PMR spectra on a Tesla BS-487 (80 MHz) instrument, at 20°C in solution in $CDCl_3$, C_5D_5N, or CF_3COOH, internal standard HMDS. The purities of the products were checked by TLC on alumina, in chloroform. The elemental analyses were in agreement with the calculated values.

3-Phenyl-6,7-dimethoxy-2-benzopyrylium Perchlorate (Ib, $C_{17}H_{15}ClO_7$). A solution of 2.56 g (10 mmole) of 3,4-dimethoxybenzoin [5] in 10 ml of chloroform was cooled to 0°C, and 2.6 g (20 mmole) of $AlCl_3$ added with stirring, followed by the dropwise addition of 3.2 g (20 mmole) of dichloromethyl butyl ether. Stirring was continued until the vigorous evolution of HCl had ceased, then kept for a day at room temperature, and poured onto ice and hydrochloric acid. The solid was filtered off, and washed with water, acetic, acid, and ether to give 2.56 g (70%) of yellow crystals, mp 248°C (from formic acid). IR spectrum 1633, 1606, 1220, 1100 cm^{-1}. PMR spectrum (CF_3COOH): 3.70 (s, OCH_3); 3.85 (s, OCH_3); 7.12 (s, $5H_{arom}$); 7.57 (s, $2H_{arom}$); 7.82 (s, $1H_{arom}$); 9.23 ppm (s, $1H_{arom}$).

2-Formyl-3',4,4',5-tetramethoxybenzoin (IIa, $C_{19}H_{20}O_6$). To a suspension of 0.43 g (1 mmole) of the perchlorate (Ia) [7] in 5 ml of ethanol was added 0.15 g (2 mmole) of sodium acetate, and the mixture heated until the salt dissolved. After cooling, the solution was diluted with 30 ml of cold water, to give 0.31 g (90%) of colorless product, mp 182°C (from ethanol), R_f 0.66, IR spectrum: 1680, 1675, 1570, 1150 cm^{-1}. PMR spectrum ($CDCl_3$): 3.80 (s, $2OCH_3$); 3.82 (s, $2OCH_3$); 4.55 (s, 2H, $-CH_2-$); 6.65-7.65 (m, $5H_{arom}$); 9.82 ppm (s, 1H, CHO).

2-Formyl-4,5-dimethoxybenzoin (IIb, $C_{17}H_{16}O_4$) was obtained similarly, as colorless crystals (80%), mp 152°C (from ethanol), R_f 0.68, IR spectrum: 1693, 1680, 1606, 1580 cm^{-1}. PMR spectrum ($CDCl_3$): 3.81 (s, OCH_3); 3.82 (s, OCH_3); 4.57 (s, 2H, $-CH_2-$); 6.60-7.95 (m, $7H_{arom}$); 9.80 ppm (s, 1H, CHO).

2-[2-(3,4-Dimethoxyphenyl)-2-hydroxyethyl]-4,5-dimethoxybenzoic Acid (Va, $C_{19}H_{22}O_7$). To a suspension of 0.34 g (1 mmole) of the aldehydoketone (IIa) in 10 ml of ethanol was added 10 ml of 5% KOH, and the mixture heated for 30 min. After cooling, the mixture was diluted with 20 ml of cold water, the solid which separated was filtered off, and the mother liquors cautiously acidified with 15% HCl to give 0.26 g (72%) of colorless product, mp 186°C (from ethanol). IR spectrum: 3405, 3365, 1695, 1606, 1573 cm^{-1}. PMR spectrum (C_5D_5N): 3.55 (s, OCH_3); 3.57 (s, $3OCH_3$); 3.77-4.22 (m, 2H, $-CH_2-$); 5.35 and 5.44 (2d, J = 5 Hz, 1H); 6.67-7.75 ppm (m, $5H_{arom}$).

3-(3,4-Dimethoxyphenyl)-3,4-dihydro-6,7-dimethoxycoumarin (VIa, $C_{19}H_{20}O_6$). Recrystallization of the hydroxyacid (Va) from acetic acid gave 90% of colorless crystals, mp 179°C, R_f 0.74. IR spectrum: 1705, 1606, 1067 cm^{-1}. PMR spectrum ($CDCl_3$): 2.82-3.25 (m, 2H, $-CH_2-$); 3.85 (s, $2OCH_3$); 3.89 (s, $2OCH_3$); 5.42 and 5.55 (2d, J = 4 Hz, 1H); 6.67-7.57 ppm (m, $5H_{arom}$). M^+ 344.

3-Phenyl-3,4-dihydro-6,7-dimethoxyisocoumarin (VIb, $C_{17}H_{16}O_4$). To a suspension of 0.28 g (1 mmole) of the aldehydoketone (IIb) in 6 ml of ethanol was added 6 ml of 5% KOH, and the mixture heated for 30 min. After cooling, the mixture was diluted with 15 ml of cold water, the solid which separated was filtered off, and the mother liquors acidified with 15% HCl. The resulting precipitate was filtered off, dried, and recrystallized from acetic acid to give 0.19 g (70%) of colorless crystals, mp 177°C, R_f 0.80. IR spectrum: 1713, 1610, 1073 cm^{-1}. PMR spectrum ($CDCl_3$): 2.97-3.20 (m, 2H, $-C\ _2-$); 3.85 (s, $2OCH_3$); 5.40 and 5.52 (2d, J = 5 Hz, 1H); 6.62-7.52 ppm (m, $7H_{arom}$).

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*The absence of the naphthol (VII) when the aldehydoketone (IIc) is obtained by the method given in [6] is due to the formation of an adduct of the 2-benzopyrylium salt with the alkoxide anion which is stable under basic conditions.

6,7-Dimethoxy-2-naphthol (VIII, $C_{12}H_{12}O_3$). To a suspension of 0.22 g (1 mmole) of the aldehydoketone (IIc) [6] in 4 ml of ethanol was added 4 ml of 5% KOH, and the mixture heated for 10 min. After cooling, the mixture was diluted with 15 ml of cold water and acidified with 15% HCl. The resulting precipitate was extracted with ether (3 × 5 ml), and the extracts evaporated to give 0.20 g (90%) of colorless product, mp 154°C (from hexane–benzene, 2:1), R_f 0.33. IR spectrum: 3460, 1640, 1620, 1593 cm^{-1}. PMR spectrum ($CDCl_3$): 3.70 (s, OCH_3); 3.75 (s, OCH_3); 5.20 (br.s, 1H, OH); 6.67-7.37 ppm (m, $5H_{arom}$).

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DISSOCIATION OF THE (4H-FLAVEN-4-YL)TRIPHENYLPHOSPHONIUM CATION IN ACETONITRILE

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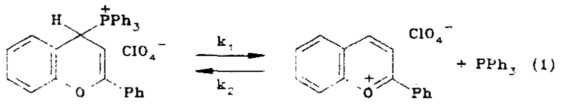
The thermodynamic and kinetic parameters of the reversible dissociation of (4H-flaven-4-yl)triphenylphosphonium perchlorate in acetonitrile were determined.

In the study of the electrochemical properties of phosphonium salts – the pyrylium derivatives were first described by S. V. Krivun in [1] – we found that some of them can dissociate into the initial components: the corresponding pyrylium cation and the phosphine. Thus, the peaks, for which the values of the potentials correspond to the reduction of the flavylium cation (F) [2] and the oxidation of triphenylphosphine (T) [3], are observed on the cyclic voltamperograms of the flavenylphosphonium salt (FT) in dilute solutions of acetonitrile. The temperature of the medium significantly, but completely reversibly, influences the ratio of the peak heights of all three components of the equilibrium (1) (Fig. 1, a, b).



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