# 2-BENZOPYRYLIUM SALTS

# XIII.* SYNTHESIS OF 2-BENZOPYRYLIUM SALTS BY THE REACTION OF ALKYL AND ARYL BENZYL KETONES WITH ACETALS

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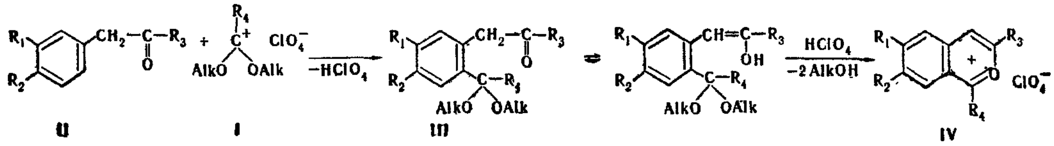
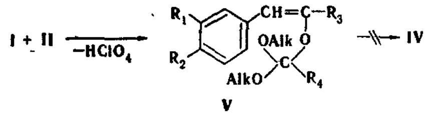
The reaction of alkyl and aryl benzyl ketones with acetals of aliphatic, aromatic, and heterocyclic aldehydes in the presence of triphenylmethyl perchlorate leads to 2-benzopyrylium perchlorates with substituents in positions 1, 3, 6, and 7. The influence of substituents in the benzyl ketones and the acetals on the ease of formation of the salts has been studied. The mechanism of the reaction is discussed.

The dialkoxycarbonium ions (I) formed in the reaction of acetals with triphenylmethyl perchlorate that we have recently discovered [1] possess a comparatively high reactivity. In the present work it has been found that the reaction of (I) with alkyl and aryl benzyl ketones leads to 2-benzopyrylium salts with substituents in positions 1, 3, 6, and 7. The first stage of the reaction is apparently the detachment by the trityl perchlorate of a hydride ion from the acetal with the formation of (I), which attacks the alkyl or aryl benzyl ketone molecule (II) in the ortho position to the methyl group, giving the ketal (III). Under the conditions of acid catalysis, compound (III) rearranges into the enolic form which cyclizes with the splitting out of ethanol to form the 2-benzopyrylium salt (IV).



The possibility of the occurrence of the reaction through the stage of the acylation of (II) by the cation (II) at the carbonyl oxygen with the formation of the corresponding enol acetate (V) was refuted by our investigation of the dependence of the yields of 2-benzopyrylium salts on the electronic nature of the substituents $R_1$ and $R_2$, which obviously influence the reactivity of the hydrogen atom in the ortho position of the nucleus to a far greater extent than the carbonyl group. This conclusion is confirmed by previous work [3].



As the oxo components we took phenylacetone, benzyl ethyl ketone, p-anisylacetone, 3,4-dimethoxyphenylacetone, and deoxybenzoin, which were caused to react with acetals of aliphatic aldehydes (formaldehyde, acetaldehyde, butyraldehyde), aromatic aldehydes (benzaldehyde, anisaldehyde, veratraldehyde, and p-nitrobenzaldehyde), and a heterocyclic aldehyde (thiophene-α-carbaldehyde). The reaction takes

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* For communication XII, see [2].

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TABLE 1. 2-Benzopyrylium Perchlorates

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | Mp, °C | Empirical formula | Found, % |  |  | Calculated, % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | C | H | Cl | C | H | Cl |  |
| H | H | $CH_3$ | 3,4-$C_6H_3(OCH_3)_2$ | 249 | $C_{18}H_{17}ClO_7$ | 57,1 | 4,7 | 9,1 | 56,8 | 4,5 | 9,3 | 4,8 |
| H | H | $C_2H_5$ | $C_6H_5$ | 193 | $C_{17}H_{15}ClO_5$ | 60,7 | 4,8 | 10,6 | 61,0 | 4,5 | 10,6 | 1,9 |
| H | H | $C_2H_5$ | 3,4-$C_6H_3(OCH_3)_2$ | 238 | $C_{19}H_{19}ClO_7$ | 57,5 | 5,1 | 8,6 | 57,7 | 4,9 | 9,0 | 1,2 |
| H | $CH_3O$ | $CH_3$ | $CH_3$ | 168 | $C_{12}H_{13}ClO_6$ | 49,6 | 4,8 | 12,1 | 49,9 | 4,5 | 12,3 | 3,2 |
| H | $CH_3O$ | $CH_3$ | $C_6H_5$ | 221 | $C_{17}H_{15}ClO_6$ | 58,0 | 4,5 | 9,7 | 58,2 | 4,3 | 10,1 | 5,0 |
| H | H | $C_6H_5$ | H | 206 | $C_{15}H_{11}ClO_5$ | 58,6 | 3,5 | 11,7 | 58,8 | 3,6 | 11,6 | 4,2 |
| H | H | $C_6H_5$ | $CH_3$ | 214 | $C_{16}H_{13}ClO_5$ | 60,1 | 4,3 | 10,9 | 59,9 | 4,1 | 11,0 | 3,0 |
| H | H | $C_6H_5$ | $C_6H_5$ | 246* | — | — | — | — | — | — | — | 7,2 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | H | 241* | — | — | — | — | — | — | — | 63,2 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | $CH_3$ | 224* | — | — | — | — | — | — | — | 36,3 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | $C_3H_7$ | 210* | — | — | — | — | — | — | — | 22,9 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | $C_6H_5$ | 217* | — | — | — | — | — | — | — | 30,4 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | 4-$C_6H_4OCH_3$ | 244* | — | — | — | — | — | — | — | 18,0 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | 3,4-$C_6H_3(OCH_3)_2$ | 265* | — | — | — | — | — | — | — | 13,2 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | 4-$C_6H_4NO_2$ | 258 | $C_{18}H_{16}ClNO_9$ | 50,6 | 4,0 | 8,3 | 50,8 | 3,8 | 8,3 | 26,3 |
| $CH_3O$ | $CH_3O$ | $CH_3$ | α-Thienyl | >300* | — | — | — | — | — | — | — | 39,8 |

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*The melting points of these salts correspond to those given in the literature [4-8].

place when a mixture of the ketone, the acetal, and triphenylmethyl perchlorate (in a molar ratio of 1:1:1) in glacial acetic acid solution is heated briefly.

The reaction of phenylacetone with benzaldehyde acetal, of benzyl ethyl ketone with the acetals of aliphatic aldehydes, and of p-anisylacetone with butyraldehyde acetal did not give satisfactory results.

It can be seen from Table 1 that the yield and, consequently, the ease of formation of the 2-benzopyrylium salts in this reaction depend on two factors: the influence of the substituents in positions 3 and 4 of the alkyl or aryl benzyl ketone, and the reactivity of the dialkoxycarbonium cations (I). For benzyl ketones having electron-donating methoxy groups in the nucleus (3,4-dimethoxyphenylacetone), it is easy to see that with an increase in the positive inductive effect of $R_4$ in the aliphatic acetals the yield of (IV) decreases; the same is observed with an increase in the positive mesomeric effect of the substituents in the aromatic acetals. It must be noted that the influence of $R_4$ on the properties of the cations (I) is twofold; facilitating the formation of (I) through an increase in the electron density of the C—H bond of the acetal; at the same time, electron-donating substituents decrease the activity of the resulting cation (I) through the partial cancellation of the positive charge and the stabilization of the cation. The two phenomena are shown differently in the interaction of (I) with benzyl ketones of different activities. In the case of 3,4-dimethoxyphenylacetone, the yields of the 2-benzopyrylium salts are fairly high, since the electron-donating methoxy groups in the benzyl ketone facilitate the electrophilic attack of the cation (I) in the ortho position of the phenyl nucleus of the benzyl ketone.

In the absence of activating substituents in (II) (phenylacetone, benzyl ethyl ketone, deoxybenzoin), the reaction takes place with lower yields; nevertheless, the nature of the acetal is shown in the same way as described above. But in this case, the greatest influence is shown by the relative stability of (I) under the experimental conditions (boiling in $CH_3COOH$), which permits the cation (I) to take part in a reaction with the poorly active benzyl ketone. Thus, in the reaction of phenylacetone with the acetal of veratraldehyde the 2-benzopyrylium salt was obtained, while with the more active but less stable cation obtained from the acetal of benzaldehyde no salt was formed. Furthermore, the acylation of deoxybenzoin with acetyl perchlorate on boiling in $CH_3COOH$ was unsuccessful. The low yields of the 2-benzopyrylium salts with the use of benzyl ketones unsubstituted in the nucleus are also explained by the predominant acylation of the latter not in the ortho but in the para position of the nucleus, as was shown by the isolation from the reaction mixture of the para-substituted acylation products, and also by the synthesis of 3,4-dimethoxyacetophenone from veratrole and acetaldehyde and of 4-methoxybenzophenone from anisole and benzaldehyde acetal (reaction conditions similar with the exception that the mixture was boiled for 3 h).

On the basis of the facts presented, we consider that the activity of the dialkoxycarbonium cations (I) is somewhat lower than the activity of the corresponding acylium cations (from a comparison of the yields of salts), but the stability of the former is considerably greater because of the influence of the substituent $R_4$ and also because of the delocalization of the charge between the carbon atom and the neighboring oxygen atoms of the alkoxy groups.

A feature of the proposed method of synthesizing 2-benzopyrylium salts is the accessibility of the initial acetals, which fundamentally broadens the possibilities of synthesis. The methods known hitherto for obtaining (IV) were based on the use of acylating agents of acid anhydrides and chlorides [4] and of the acids themselves [9] in the presence of $HClO_4$, $AlCl_3$, or polyphosphoric acid. However, the use of these reagents is limited by the difficulty of obtaining some of them, particularly those with functional substituents. This limitation is removed by the use of acetals. The reaction of (II) with formaldehyde acetal gives the fairly difficultly accessible 1-unsubstituted 2-benzopyrylium salts [6]. By this method we have obtained for the first time 2-benzopyrylium salts unsubstituted in the phenyl nucleus by the reaction of acetals with benzyl ketones containing no activating substituents in the aromatic nucleus. The method is completely suitable for preparative purposes, since the yields of many salts are fairly high and the salts themselves are obtained in the fairly pure state.

The IR spectra of the 2-benzopyrylium salts synthesized have a number of absorption bands characteristic for this class of compounds [4]. The structure of the salts described in the literature was shown by a number of independent syntheses, by the preparation of the products of ring opening — alkyl and aryl o-acylbenzyl ketones, by the synthesis of the corresponding isoquinolines, by a comparison of IR spectra, and also by melting-point determinations and mixed melting points with authentic samples of the salts, showing no depression of the melting points.*

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* The work was performed with the participation of the fourth-year student E. A. Murad'yan.

## EXPERIMENTAL

All the syntheses were performed by a common method.

Reaction of Alkyl and Aryl Benzyl Ketones with Acetals. A mixture of a benzyl ketone (0.01 mole), and acetal (0.01 mole), triphenylmethyl perchlorate (3.4 g, 0.01 mole) and acetic acid (13 ml) was carefully heated. The mixture darkened and soon boiled vigorously. The boiling, due to the evolution of ethanol, lasted about a minute, and in this process the solid trityl perchlorate dissolved. The reaction mixture was heated for another 5 min, cooled, and diluted with dry ether (~100 ml). The precipitate that deposited was filtered off, washed with dry ether, dried, and recrystallized from glacial acetic acid. If a highly contaminated product was obtained, it was found desirable to purify it through recrystallization by boiling in glacial $CH_3COOH$ or acetone with activated carbon, adding 1-2 drops of concentrated $HClO_4$. If an oily product was formed, the mother liquid was decanted off and the salt was reprecipitated with ether from acetone solution.

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