

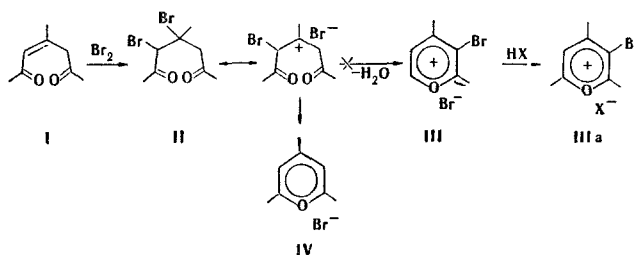
3-BROMOPYRYLIUM SALTS

S. V. Krivun, S. V. Sayapina,
and S. N. Baranov

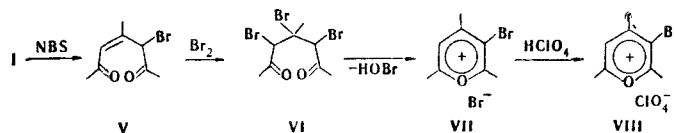
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Three new methods have been proposed for the synthesis of 3-bromopyrylium salts. An unsaturated 1,5-diketone is converted into a 3-bromopyrylium salt by allyl bromination and the addition of bromine to the double bond. 3-Bromopyrone, obtained by the bromination of dibenzoylacetone is converted by treatment with Grignard reagents into 3-bromopyrylium salts. Similar compounds have also been synthesized by the pyrylation of aromatic and heterocyclic compounds with 3-bromo-4-chloropyrylium salts obtained from 3-bromopyrone.

The present paper considers possible variants of the syntheses of 3-bromopyrylium salts. It is known that 2,4,6-triarylpyrylium salts form unsaturated 1,5-diketones on being heated in aqueous ethanol in the presence of sodium acetate or bicarbonate [1]. It appeared probable that this addition of bromine to the double bond of the diketone (I) would lead to the spontaneous cyclization of the dibromide (II) with the formation of the 3-bromopyrylium salt (III) in the following way:



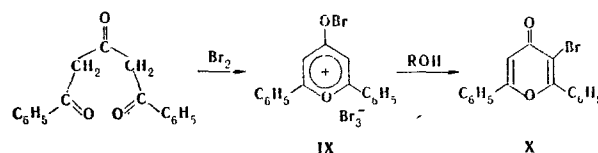
However, when (II) was heated in an inert polar solvent, the triarylpyrylium salt (IV), and not (III), was found. Similarly, an attempt to synthesize a 3-bromo-2,4,6-triphenylpyrylium salt (IIIa) from benzylideneacetophenone, ω -bromoacetophenone, and trityl perchlorate under conditions given in the literature [2] ended in the production of triphenylpyrylium perchlorate. Both these facts permit the assumption that the cyclization of the dibromo 1,5-diketone (for example, II) formed as an intermediate takes place not by dehydration but by the splitting out of HOBr . For this reason, we performed the bromination of (I) by the Wohl-Ziegler method, added bromine to the resulting compound (V) in chloroform, and converted the precipitate of (VII) (on heating, VI is converted into VII) into the perchlorate (VIII) by the action of perchloric acid on a solution of the bromide in nitromethane.



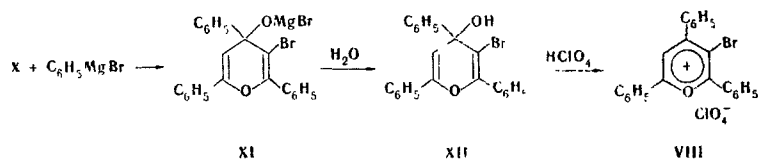
In this way, we obtained triaryl-3-bromopyrylium salts with yields of 20-25%. The laboriousness of this method and the low yield of the end product induced us to search for other methods of synthesizing the required compounds.

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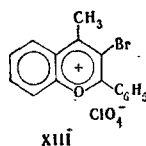
We have found that an excess of dioxane dibromide in dioxane brominates dibenzoylacetone mildly with the formation of an orange crystalline product to which we ascribe structure (IX). On trituration with a small amount of ethanol, compound (IX) loses its color, forming pure 3-bromo-2,6-diphenyl- γ -pyrone (X) [monitoring by thin-layer chromatography; alumina, benzene-chloroform (3:1)].



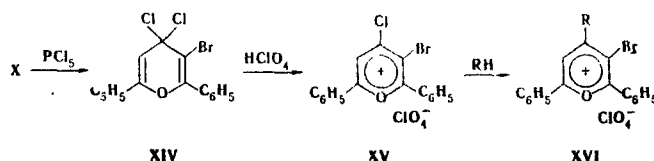
In this case, also, it is appropriate to assume that both methylene groups of the triketone are brominated and cyclization takes place with the splitting out of HOBr , and not with dehydration. This is shown indirectly by the absence of the dibromo derivative of the pyrone in the reaction product. In a similar manner to the syntheses of simple pyrylium salts from pyrones, the 3-bromo-2,6-diphenyl- γ -pyrone (X) obtained adds Grignard reagents (from alkyl halides, bromobenzene, etc.) with the formation of the corresponding pyranols which, with perchloric acid, give bromine-substituted pyrylium salts. Thus, phenylmagnesium bromide reacts with the bromopyrone (X) in benzene to give (XI), which, after hydrolysis by acidified water forms the pyranol (XII), which is converted by the action of HClO_4 into the perchlorate of the pyrylium cation (VIII), identical with that obtained from an unsaturated 1,5-diketone.



Thus, phenylmagnesium bromide reacts with 3-bromo-4,6-diphenylcoumalin [3], giving, in the final account, 3-bromo-2,4,6-triphenylpyrylium perchlorate, identical with (VIII). 3-Bromo-4-methylcoumarin, synthesized as described by Zagorevskii and Kirsanova [4], forms 3-bromo-4-methyl-2-phenylbenzopyrylium perchlorate (XIII) under similar conditions.



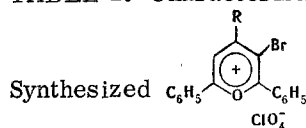
On the basis of the capacity of 4-chloropyrylium salts for adding nucleophilic organic compounds [5, 6], yet another method of synthesizing 3-bromopyrylium cations has been developed. As is well known (for example, [7]), pyrones, on reacting with phosphorus pentachloride with subsequent treatment of the intermediate dichloropyran (of the type of XIV) with perchloric acid, form chloropyrylium perchlorates. The latter, on being heated with reactive organic compounds, give new pyrylium perchlorates with the substituent corresponding to the nucleophile taken. In a similar manner, the bromopyrone (X) yielded (XV), and when the latter was heated with nucleophilic organic compounds (N-alkylindoles, trimethylazulene, etc.) pyrylium salts containing bromine in position 3 of the heterocyclic ring (XVI) were obtained in the following way:



This method is fairly general, but no 3-bromopyrones other than (X) are known. Thus, three methods for the synthesis of 3-bromopyrylium salts have been proposed, the last two methods being simpler and more general than the first and supplementing one another in that compounds that can be obtained by the second method are not obtained by the third, and conversely.

All the heteroaromatic salts obtained consist of colored crystalline substances similar in properties (solubility, stability, etc.) to 2,4,6-trisubstituted pyrylium salts. However, they melt at lower temperatures

TABLE 1. Characteristics of the 3-Bromopyrylium Salts



R	Synthesis method	Mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
				C	H	Br	Cl	C	H	Br	Cl	
Methyl	A	197—198	C ₁₈ H ₁₄ BrClO ₅	50,5	3,5	18,7	8,6	50,8	3,3	18,8	8,3	74
Ethyl	A	222—223	C ₁₉ H ₁₆ BrClO ₅	51,6	3,9	18,4	8,2	51,9	3,6	18,2	8,1	82
Isopropyl	A	224—225	C ₂₀ H ₁₈ BrClO ₅	52,7	4,0	17,9	8,0	52,9	4,0	17,6	7,8	74
Butyl	A	197—198	C ₂₁ H ₂₀ BrClO ₅	54,2	4,5	16,6	7,6	53,9	4,3	17,2	7,6	51
Phenyl	A	215—216	C ₂₃ H ₁₆ BrClO ₅	56,9	3,4	16,7	7,5	56,6	3,3	16,4	7,3	67
p-Dimethyl-aminophenyl	B	206—207	C ₂₅ H ₂₁ BrClNO ₅	57,0	3,8	15,2	6,9	56,7	3,9	15,0	6,7	25
N-Methylindol-3-yl	B	260—261	C ₂₆ H ₁₉ BrClNO ₅	57,5	3,6	14,5	6,5	57,7	3,5	14,8	6,5	65
N-Ethylindol-3-yl	B	200—201	C ₂₇ H ₂₁ BrClNO ₅	58,6	3,8	14,3	6,4	58,4	3,8	14,4	6,4	68
N-Methyltetrahydro-quinolin-5-yl	B	200—201	C ₂₇ H ₂₃ BrClNO ₅	58,3	4,2	14,2	6,5	58,3	4,1	14,4	6,4	33
4,6,8-Trimethyl-azulenyl	B	232—233	C ₃₀ H ₂₄ BrClO ₅	62,3	4,3	13,7	6,1	62,1	4,1	13,6	6,1	74

* A) From 3-bromopyrones and Grignard reagents; B) by pyrylation with 3-bromo-4-chloropyrylium salts.

than, and not so sharply as, the analogous bromine-free salts and crystallize more poorly from polar organic solvents. This is probably connected with the asymmetry of the molecule.

The IR spectra of the pyrylium salts obtained each have a series of bands of the stretching and deformation vibrations of the pyrylium ring. These bands are fairly strong and can be used to identify the pyrylium cation (according to Balaban [8]). This applies primarily to the absorption in the 1435–1420- and 1485–1470-cm⁻¹ regions. In the case of the bromine-substituted cations, absorption in the 1545–1520-cm⁻¹ region is less pronounced and frequently appears in the form of inflections, and strong bands in the 1640–1620-cm⁻¹ region – the most characteristic absorption for 2,4,6-trisubstituted pyrylium salts [8] – is shifted to the 1600-cm⁻¹ region and is overlapped by the absorption bands of the phenyl substituents in the 3-bromopyrylium salts. There is also a series of less well-defined bands characterizing the pyrylium ring, and also absorption bands of the substituents of the ClO₄⁻ anion, etc. The structure of 3-bromo-2,6-diphenyl-γ-pyrone is also shown by IR spectra in which an absorption band at 1650 cm⁻¹ confirms the presence of a pyrone ring.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer in KBr tablets.

3-Bromo-2,4,6-triphenylpyrylium Perchlorate. A mixture of 9.8 g (0.03 mole) of 1,3,5-triphenylpent-2-ene-1,5-dione and 6.25 g (0.035 mole) of bromosuccinimide in 10 ml of dry carbon tetrachloride was boiled until the bromosuccinimide had dissolved completely (30–40 min) and a precipitate of succinimide had formed. The precipitate was filtered off and, with cooling, 1.5 ml (4.8 g) of bromine in 3 ml of CCl₄ was added. A yellow precipitate of 3-bromo-2,4,6-triphenylpyrylium bromide formed. Part of the product was precipitated from the filtrate with ether. The total yield was 3.37 g (24.1%). Mp 198–200°C (from acetic acid with the addition of acetic anhydride). The bromide obtained was dissolved in 50 ml of chloroform, and the solution was treated with 1.5 ml of 70% perchloric acid in 5.5 ml of acetic anhydride and was boiled for 5 min. On standing, a yellow crystalline product deposited which was precipitated completely with ether. Yield 3.32 g (22.7% on the diketone). The analysis and constants of the substance are given in Table 1.

3-Bromo-2,6-diphenyl-γ-pyrone. With vigorous stirring, a mixture of 5.2 ml (16 g, 0.1 mole) of bromine and 50 ml of dioxane was added to a solution of 13.3 g (0.05 mole) of dibenzoylacetone in 150 ml of dioxane. After 10–15 min, a yellow crystalline precipitate appeared in the dark solution that had been formed. After 7–10 h, the precipitate was filtered off and triturated with ethanol. The crystals decolorized in this way were separated off, washed with a small amount of ethanol, and dried. The yield of the end product was 12.2 g (74.5%). Mp 141–142°C (from methanol). Found, %: C 62.3; H 3.5; Br 23.8. C₁₇H₁₁O₂Br. Calculated, %: C 62.5; H 3.4; Br 24.2.

3-Bromo-2,4,6-triphenylpyrylium Perchlorate. a) With vigorous stirring, the phenylmagnesium bromide obtained from 2.4 g of bromobenzene and 1.5 g of magnesium was added to a solution of 3.27 g (0.01 mole) of 3-bromo-2,6-diphenyl- γ -pyrone in 0.5 liter of absolute ethanol, the mixture was stirred for 30 min, and the suspension formed was treated with 100 ml of water acidified with 1.5 ml of acetic acid. The ethereal layer was separated off, washed with water, and dried, and to it was added 1 ml of 70% perchloric acid dropwise. Yellow crystalline 3-bromopyrylium perchlorate precipitated. Yield 2.45 g (64.3%).

b) The substance was obtained similarly from 3.27 g of 3-bromo-4,6-diphenylcoumalin in 100 ml of dry benzene with a yield of 1.47 g (30%). Mp 215-216°C (from acetic acid and methanol).

Pyrylium salts with alkyl substituents were obtained similarly (Table 1).

3-Bromo-4-methylflavylum Perchlorate. With stirring, the phenylmagnesium bromide obtained from 1.5 g of magnesium and 2.4 g of bromobenzene was added dropwise to 2.39 g (0.1 mole) of 3-bromo-4-methylcoumarin in 250 ml of absolute ether, the mixture was stirred for 30 min, and the light-yellow precipitate formed was decomposed with acidified water. The ethereal layer was separated off, washed with water, and dried, and to it was added 1 ml of 70% HClO_4 . The yellow crystalline perchlorate formed was separated off and washed with ether. Yield 1.6 g (40.0%). Mp 208°C (from acetic acid). Found, %: C 48.1; H 3.1; Br 20; Cl 8.9. $\text{C}_{16}\text{H}_{12}\text{BrClO}_5$. Calculated, %: C 48.1; H 3.0; Br 19.9; Cl 8.9.

3-Bromo-4-chloro-2,6-diphenylpyrylium Perchlorate. A mixture of 9.8 g (0.3 mole) of 3-bromo-2,6-diphenyl- γ -pyrone and 10.5 g (0.05 mole) of phosphorus pentachloride in 50 ml of dry chloroform was boiled for 30 min. After cooling, the 3-bromo-4-chloro-2,6-diphenylpyrylium chloride was separated off, washed with a small amount of chloroform, and heated to 80°C in 20 ml of dry nitrobenzene. With stirring, 2.5 ml of 70% perchloric acid was added to the suspension, giving rise to a voluminous evolution of hydrogen chloride. After the pyrylium chloride had dissolved, a new crystalline precipitate of 3-bromo-4-chloro-2,6-diphenylpyrylium perchlorate separated out. This was filtered off and washed with dry ether. Yield 6.8 g (50.4%). Mp 209°C (from nitromethane).

3-Bromo-4(N-methylindol-3'-yl)-2,6-diphenylpyrylium Perchlorate. 3-Bromo-4-chloro-2,6-diphenylpyrylium perchlorate (1.35 g, 0.003 mole) was boiled with 0.65 g (0.05 mole) of N-methylindole in 8 ml of dry nitromethane for 20 min. To the cooled mixture was added 20-30 ml of ether and it was left to crystallize in the refrigerator. The orange crystals were separated off and were washed with acetic acid and ether. Yield 1 g (65%).

The other nucleophiles (see Table 1) were pyrylated similarly with the use of nitromethane or nitrobenzene as the reaction media.

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