

with sodium bicarbonate and extracted with ethyl acetate. The extract was washed successively with a saturated solution of sodium bicarbonate and water until the wash water was neutral, after which it was dried with magnesium sulfate. The ethyl acetate was removed by distillation *in vacuo*, and the residue was recrystallized to give IVa. Nitrofurans IVb,c (Table 1) were similarly obtained.

2-(3-Nitro-4-acetamidophenyl)-3,4-bis(carbomethoxy)-5-nitrofurans (VIa). A 1.3-ml sample of nitric acid (sp. gr. 1.4) was added dropwise with stirring to 5 ml of cooled (to -5°C) acetic anhydride, 1.4 g (4.5 mmole) of IIa was added in portions at 0°C to the resulting solution, and the reaction mixture was stirred at this temperature for 3 h. The resulting precipitate was removed by filtration. Dinitrofurans VIb (Table 1) was similarly obtained.

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REACTIONS OF HETEROCYCLIC CATIONS WITH NITROGEN-CONTAINING NUCLEOPHILES.

10.* SYNTHESIS OF 3,5,7-TRIARYL-1,2-OXAZEPINIUM PERCHLORATES BY THE REACTION OF 2,4,6-TRIARYLPYRYLIUM SALTS WITH NITRONES AND SUBSTITUTED HYDROXYLAMINES

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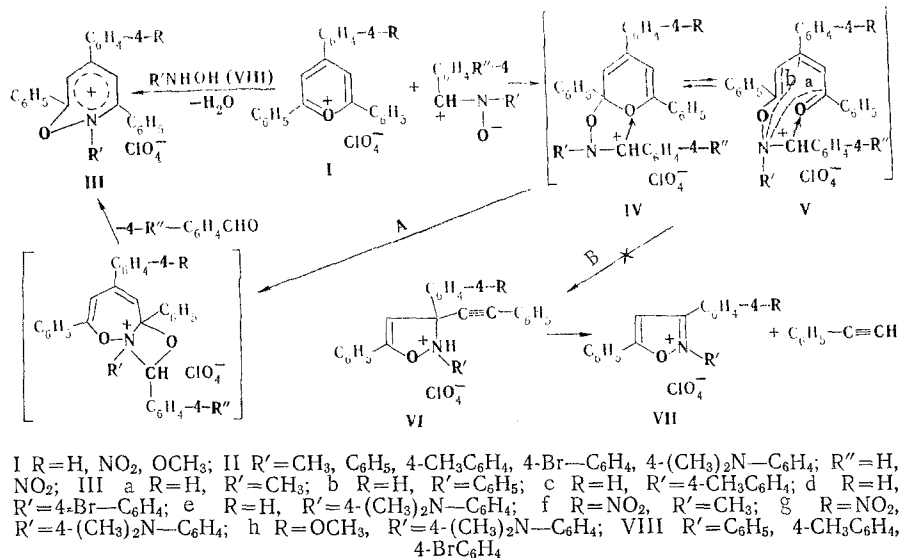
2-Substituted 3,5,7-triaryl-1,2-oxazepinium perchlorates were obtained by the reaction of 2,4,6-triarylpopyrylium salts in dimethylformamide with nitrones and N-arylhydroxylamines. The products are the first representatives of seven-membered cations with eight π electrons.

We have studied the reaction of 2,4,6-triarylpopyrylium salts (I) in dimethylformamide (DMF) with nitrones II, which are 1,3-bipolar compounds [2], as a result of which we obtained 2-substituted 3,5,7-triaryl-1,2-oxazepinium salts (III) — the first representatives of seven-membered cations with eight π electrons.

The mechanism of the reaction of pyrylium salts with various nucleophiles has been thoroughly studied [3-5]. On the basis of this mechanism it may be assumed that the oxide center of the nitron molecules with its increased electron density [6] attacks the 2 position of the pyrylium ring. The positively charged carbon atom probably reacts with the electronegative oxygen atom in intermediates IV and V, which may exist in equilibrium. This is confirmed by the formation of benzaldehyde in the reaction. The subsequent cyclization of V should proceed via scheme A or B. Alternative pathway B is not realized, since bands that are characteristic for the $\text{C}\equiv\text{C}$ bond and the NH group of expected perchlorate VI are absent in the IR spectra of the products. However, the structure of VII (which could have been obtained from salts VI by splitting out of phenylacetylene) must be excluded from the results of elementary analysis.

*See [1] for Communication 9.

[†]Deceased.



It follows from the information set forth above that the reaction proceeds via pathway A to give perchlorates III. The existence of a heteroatomic cation was confirmed by absorption in the IR spectra at 1627-1650, 1600-1608, and 1560-1570 cm^{-1} .

The PMR spectrum of IIIa in trifluoroacetic acid contains singlets of three protons of a 2-methyl group at 3.55 ppm, 15 aromatic protons at 7.30 ppm, and two methylydyne 4- and 6-H protons of a seven-membered ring at 7.67 ppm. The PMR spectrum of IIIc in trifluoroacetic acid contains a singlet of three methyl protons of the CH₃ group of a p-tolyl substituent at 1.75 ppm, a multiplet of 19 aromatic protons at 6.25-7.62 ppm, and a singlet of 4- and 6-H protons (2H) at 7.75 ppm.*

In the PMR spectra of the remaining compounds the signals of the methylydyne protons of the seven-membered ring are covered by the multiplet of aromatic protons (see Table 1).

We also studied the reaction of salts I with N-substituted hydroxylamines. The reaction does not take place in alcohol, but when salt Ia is refluxed in dimethylformamide (DMF) with methylhydroxylamine, it undergoes decomposition to give 1-methyl-2,4,6-triphenylpyridinium perchlorate and 2,4,6-triphenylpyridine. The reaction of salt Ia in DMF with the corresponding N-substituted arylhydroxylamines (VIII) leads to IIIb-d. The yields of the latter are approximately the same as in the reaction of salt Ia with nitrones.

The transformations discovered in this research cannot be carried out with methyl-containing pyrylium salts - a deeply colored mixture of substances that cannot be separated is formed in DMF.

It is interesting to note that the reaction of salt Ia with hydroxylamine leads to 3,5-diphenyl-5-phenacyl-2-isoxazoline [4], hydrazine forms 3,5,6-triphenyl-4H-1,2-diazepine [4], while methyl- and phenylhydrazines give pyrazole and pyrazoline derivatives [4, 7].

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71 IR spectrometer. The PMR spectra were recorded with a Tesla BS 467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The purity of the compounds obtained was monitored by means of thin-layer chromatography (TLC) on Silufol plates or plates with silicic acid. Data on all of the compounds obtained are presented in Table 1. Pyrylium salts Ia-c were obtained by known methods [8, 9]. All of the nitrones were also synthesized by the methods described in [10-13].

Reaction of Perchlorate Ia with N-(p-Nitrobenzylidene)methylamine N-Oxide (IIa). A 0.36-g (2 mmole) sample of IIa was refluxed with 0.65 g (1.6 mmole) of perchlorate Ia in 5 ml of dry DMF for 1 h, after which the mixture was allowed to stand overnight. It was then treated with ether, and the liberated oil was crystallized by treatment with water to give

*The equivalence of the 4-H and 6-H protons of IIIa,c is retained in various solvents (acetone, acetonitrile, methylene chloride, and dimethyl sulfoxide).

TABLE I. 1,2-Oxazepinium Perchlorates (III)

Com- pound	mp, °C (from etha- nol)	Color	IR spectra, cm ⁻¹	PMR spectra, ppm, in CF ₃ COOH	Found, %				Calculated, %				Yields, % from the nitrones
					C	H	Cl	N	C	H	Cl	N	
IIIa	199—200	Yellow	1100, 1500, 1572, 1608, 1650	3.55 (s, 3H, 2-CH ₃); 7.30 (s, 15H, C ₆ H ₅); 7.67 (s, 2H, CH) and CH	65.9	4.4	8.3	3.3	65.9	4.6	8.0	3.2	48
IIIb	189—190	Yellow	1100, 1500, 1565, 1605, 1630	6.43—8.15 (m, 22H, C ₆ H ₅ and CH)	69.6	4.4	7.1	2.8	69.7	4.4	7.1	2.8	82
IIIc	169—170	Yellow	1100, 1500, 1573, 1608, 1628	1.75 (s, 3H, 4'-CH ₃); 6.25—7.62 (m, 19H, C ₆ H ₅); 7.75 (s, 2H, CH)	69.8	4.9	6.7	2.6	70.1	4.7	6.9	2.7	62
IIId	233—234	Light-beige	1100, 1500, 1560, 1605, 1627	—	60.4	3.9	19.9*	2.4	60.2	3.7	19.9*	2.4	64
IIIe	263—264	Dark-green	1100, 1500, 1560, 1600, 1640	2.90 (s, 6H, 2-CH ₃); 6.25—8.20 (m, 21H, C ₆ H ₅ and CH)	68.8	5.3	6.8	5.5	68.6	5.0	6.5	5.2	71
IIIf	166—167	Red	1100, 1350, 1500, 1530, 1570, 1600, 1630	3.60 (s, 3H, 2-CH ₃); 6.55—8.20 (m, 16H, C ₆ H ₅ CH)	60.0	4.3	7.6	5.8	59.7	4.0	7.4	5.8	55
IIIg	265—266	Greenish- brown	1100, 1350, 1500, 1530, 1570, 1600, 1630	2.90 (s, 6H, 2-CH ₃); 6.15—8.20 (m, 20H, C ₆ H ₅ and CH)	64.8	4.8	5.9	5.1	64.9	4.6	6.2	4.9	70
IIIh	184—185†	Dark-brown	1100, 1200, 1270, 1500, 1570, 1600, 1630	2.87 (s, 6H, 2-CH ₃); 3.55 (s, 3H, OCH ₃); 6.18— 8.10 (m, 20H, C ₆ H ₅ and CH)	66.7	5.3	6.2	4.9	67.0	5.1	6.2	4.9	69

*The overall percent of Cl and Br is indicated.

†Recrystallized from butanol.

IIIa. The ether mother liquor was evaporated to give 0.3 g (94%) of p-nitrobenzaldehyde with mp 106°C (from water).

Compounds IIIb,c,e-h were similarly obtained; however, the reaction was carried out for 3 h in the case of IIIc,g,h.

Reaction of Perchlorate Ia with N-(Benzylidene)-p-bromophenylamine N-Oxide (IIId). A 3.88-g (0.012 mole) sample of IIId was refluxed with 4.08 g (0.01 mole) of the perchlorate in 20 ml of dry DMF for 7 h, after which the mixture was allowed to stand overnight. It was then cooled to precipitate 0.32 g (8%) of the starting aldonitrone (IIId) and treated with ether, and the liberated oil was crystallized by treatment with water to give 2-(4-bromophenyl)-3,5,7-triphenyl-1,2-oxazepinium perchlorate hydrate [3.9 g (64%)] with mp 225°C (from ethanol). Found: C 56.9; H 4.4; Hal 18.7%. $C_{29}H_{21}BrClNO_5 \cdot 2H_2O$. Calculated: C 56.7; H 4.1; Br 12.8; Cl 5.6%. The product was dried *in vacuo* to constant weight to give perchlorate IIId.

Reaction of Perchlorate Ia with N-Methylhydroxylamine. A 0.41-g (1 mmole) sample of perchlorate Ia was refluxed with 0.3 g (6 mmole) of N-methylhydroxylamine in 5 ml of dry DMF for 1 h, after which the mixture was allowed to stand overnight. It was then treated with ether, and the liberated oil was crystallized by treatment with water to give 0.1 g (24%) of the perchlorate with mp 214°C (from glacial acetic acid), which did not depress the melting point of 1-methyl-2,4,6-triphenylpyridinium perchlorate [11]. Evaporation of the ether gave 2,4,6-triphenylpyridine, with mp 138°C (from ethanol) (mp 138°C [14]), in quantitative yield.

Reaction of Perchlorate Ia with N-Phenylhydroxylamine (VIIIa). A 1.2-g (3 mmole) sample of perchlorate Ia was refluxed with 0.44 g (4 mmole) of VIIIa in 10 ml of dry DMF for 1 h, after which the mixture was allowed to stand overnight. It was then treated with ether, and the liberated oil was crystallized by treatment with water to give IIIa.

The reaction of salt Ia with N-(p-tolyl)hydroxylamine (VIIIb) was carried out similarly, but the reaction time was 3 h. The reaction with N-(p-bromophenyl)hydroxylamine (VIIIc) was complete after 5 h.

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