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SYNTHESES IN THE METHYL-2 FURYLKETONE SERIES

IX. ω-Ammonium Derivatives of Methyl-5-nitro-2 furylketone

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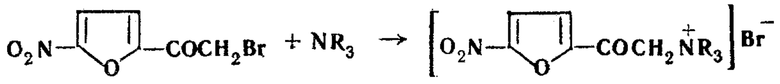
Reaction of bromoethyl-5-nitro-2-furylketone with tertiary nitrogen bases, i.e., pyridine, picolines, quinoline, 1-methyl-morpholine, trimethylamine, and triethylamine, serves for preparation of the corresponding 5-nitro 2-furacylammonium bromides, from which the perchlorates and picrates are obtained.

It is known [2-5] that various compounds can be prepared starting from α-ketoammonium salts. In this connection, ω-ammonium derivatives of methyl-5 nitro-2-furylketone are also of great interest for preparing a series of 5-nitrofuran derivatives.

The appropriate 5-nitro-2-furacylammonium bromides are prepared by reacting 5-nitro-2-furylketones with tertiary nitrogen bases, pyridine, picolines, quinoline, 1-methylmorpholine, trimethylamine, and triethylamine, in dry organic solvents (ether, benzene, chloroform and carbon tetrachloride), the yields being 75-95%. The last two derivatives can also be prepared in ethanol solution.



Save in the case of the trialkylammonium derivatives, the products which are isolated directly from the reaction mixtures are quite sensitive to moisture in the air, and when slowly filtered they undergo considerable resinification although in a desiccator, they can be kept a long time. After purifying they become more stable; that is especially true of those forming crystalline hydrates. Such hydrates are formed by 5-nitro-2-furacylquinolinium bromide, and by the 2- and 3-picolinium compounds when crystallized from water, or a mixture of water and organic solvent. These crystalline hydrates do not lose water on drying in air, but they readily dehydrate when dried over phosphorus pentoxide or sulfuric acid. Nitrofuracylammonium bromides, with the exception of the trialkyl derivatives, are readily soluble in water and ethanol. Trimethyl- and triethylnitrofuracylammonium bromides have low solubilities in water and ethanol, and they are decomposed by prolonged treatment with ethanol or acetic acid. The triethyl compound is the more labile, and among its decomposition products has been isolated triethylamine hydrobromide. We also observed formation of the hydrobromide of the starting amine when bromoethyl-5-nitro-2-furylketone was treated with quinaldine in benzene. Though quinaldine is known [6] to react similarly with other α-bromoketones, the labilities of α-ketoammonium salts obviously depend not only on the nature of the amine moiety, but also on the nature of the substituent and that of the keto group. It can be considered that the ease of splitting of ω-ammonium derivatives of 5-methyl-2-furylketones, particularly of trialkyl ammonium derivatives, is determined by the specific effect of the nitrofuryl group, since the closest aromatic analog which we have prepared, p-nitrophenacyltriethylammonium bromide, and the previously described [7] furacyltrialkylammonium halides, are stable under the same conditions. A detailed study of the natures of the products of conversion of ω-ammonium derivatives of methyl-5-nitro-2-furylketone by solvents, will form the subject of a separate communication.

Treatment of the appropriate bromides with perchloric acid or magnesium perchlorate gives the crystalline 5-nitro-2-furacylpyridinium and 5-nitro-2-furacylquinolinium perchlorates, which are considerably less soluble in water than the starting bromides. N-(5 Nitro-2-furacyl)-substituted N-methylmorpholinium, α-, β- and γ-picolinium bromides do not form crystalline products with perchloric acid, but oily ones.

The picrates of ω-ammonium derivatives of methylnitrofurylketone are stable, and crystallize well. The compounds synthesized are listed in the table.

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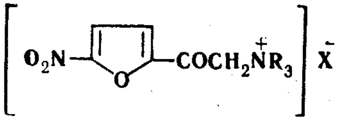
* For Part VIII see [1].

α -Ammonium Derivatives of Methyl-5-Nitro-2-furylketone 

NR₃	X	Mp, °C		Formula	Found, %				Calculated, %			
					C	H	N	Br	C	H	N	Br
Pyridine	Br	181—183*	(a)	$C_{11}H_9BrN_2O_4$	42.19	3.02	8.80	25.45	42.19	2.89	8.94	25.55
	ClO_4**	75—76	(b)	$C_{11}H_9ClN_2O_8 \cdot H_2O$	***	—	7.89	—	—	—	7.99	—
	ClO_4	114—116	(c)	$C_{11}H_9ClN_2O_8$	40.04	2.67	8.43	—	39.70	2.71	8.42	—
	Picrate	151—152	(d)	$C_{17}H_{11}N_5O_{11}$	44.26	2.38	15.18	—	44.26	2.38	15.18	—
2-Picoline	Br**	174—175	(e)	$C_{12}H_{11}BrN_2O_4 \cdot H_2O$	41.87	3.78	8.19	—	41.76	3.77	8.19	—
	Picrate	130—132	(d)	$C_{18}H_{13}N_5O_{11}$	45.91	2.61	14.45	—	45.48	2.74	14.73	—
3 Picoline	Br**	74—75	(e)	$C_{12}H_{11}BrN_2O_4 \cdot H_2O$	41.83	4.01	—	22.65	41.76	3.77	—	23.15
	Br	159—160	(a, f)	$C_{12}H_{11}BrN_2O_4$	43.90	3.36	8.39	—	44.08	3.36	8.56	—
	Picrate	129—131	(d)	$C_{18}H_{13}N_5O_{11}$	45.50	2.66	14.77	—	45.48	2.74	14.73	—
4-Picoline	Br	218—221	(a)	$C_{12}H_{11}BrN_2O_4$	44.06	3.39	—	23.92	44.08	3.36	—	24.13
	Picrate	144—145	(d)	$C_{18}H_{13}N_5O_{11}$	45.23	2.64	14.97	—	45.48	2.74	14.73	—
Quinoline	Br**	114—115	(b)	$C_{15}H_{11}BrN_2O_4 \cdot 2H_2O$	45,20	3.83	—	19.90	45.13	3.75	—	20.02
	Br	183—183.5	(a, c)	$C_{15}H_{11}BrN_2O_4$	49.32	3.34	7.72	22.20	49.60	3.05	7.71	22.00
	ClO_4	120—123	(b)	$C_{15}H_{11}ClN_2O_8$	47.20	3.04	7.39	—	47.07	2.90	7.32	—
	Picrate	199—200	(d)	$C_{21}H_{13}N_5O_{11}$	49.63	2.37	13.56	—	49.32	2.56	13.69	—
1-Methylmorpholine	Br	179—180	(a)	$C_{11}H_{15}BrN_2O_5$	39,27	4.57	8.25	—	39.41	4.51	8.36	—
	Picrate	166—167	(d)	$C_{17}H_{17}N_5O_{12}$	—	—	14.65	—	—	—	14.49	—
$N(CH_3)_3$	Br	235*	(g)	$C_9H_{13}BrN_2O_4$	36.71	4.69	10.02	26.99	36.87	4.47	9.56	27.26
	Picrate	141—142	(d)	$C_{15}H_{15}N_5O_{11}$	40.83	3.64	15.56	—	40.82	3.43	15.87	—
$N(C_2H_5)_3$	Br	171—172*	(g)	$C_{12}H_{19}BrN_2O_4$	42.76	5.48	—	24.11	43.00	5.71	—	23.84

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* Decomp. ** Crystalline hydrate. *** Found: H_2O 4.92% . . Calculated: H_2O 5.10% . a) Ex dry EtOH + ether, dried over H_2SO_4 or P_2O_5 . b) Ex water, air-dried. c) Ex water, dried over P_2O_5 d) Ex EtOH. e) Ex EtOH + + ether + H_2O, air-dried, f) Ex EtOH + ether + H_2O, dried over P_2O_5. g) Ex mixed glacial AcOH + ether.

Experimental

5-Nitro-2-furacylammonium bromides (except the trimethylammonium derivative). 0.02 mole of the appropriate tertiary nitrogen base was added to a solution of 4.68 g (0.02 mole) bromomethyl-5-nitro-2-furylketone in 25 ml dry benzene (or 100 ml dry ether, CCl_4, or $CHCl_3$), with cooling. After standing for 24 hr at room temperature, the precipitate was quickly filtered off, washed on the filter with dry ether, keeping it covered with solvent to prevent resin formation, and then immediately transferred to a desiccator, where it was dried over H_2SO_4 or P_2O_5. Colorless compound, yield 75–95%, for analysis purified by recrystallization from a suitable solvent and dried, as shown in the table. Anhydrous compounds formed hygroscopic needles, white to yellowish-brown, while the hydrated crystals were non-hygroscopic white needles.

Trimethyl-5-nitro-2-furacylammonium bromide. 6 ml 20% solution of Me_3N in EtOH (1.18 g, 0.02 mole) was added to 4.68 g (0.02 mole) bromomethyl-5-nitro-2-furylketone in 70 ml EtOH, after 24 hr the precipitate was filtered off, and washed with ether, yield 3.4 g (58%).

The triethylamine derivative was prepared by both methods, but with this last method it was much contaminated.

5-Nitro-2-furacylammonium perchlorate. A 50–60% aqueous solution of $HClO_4$, or a 50% aqueous solution of Mg perchlorate was added to an aqueous solution of the nitrofuracylammonium bromide, the precipitate filtered off, recrystallized from water, and dried over H_2SO_4.

5-Nitro-2-furacylammonium picrate. An aqueous or ethanol solution of the nitrofuracylammonium bromide or perchlorate was mixed with an ethanolic solution of picric acid, the precipitate filtered off, and recrystallized from EtOH.

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