UDC 547.81 + 547.821 + 542.95

SYNTHESIS OF CYCLOALKENOPYRYLIUM SALTS

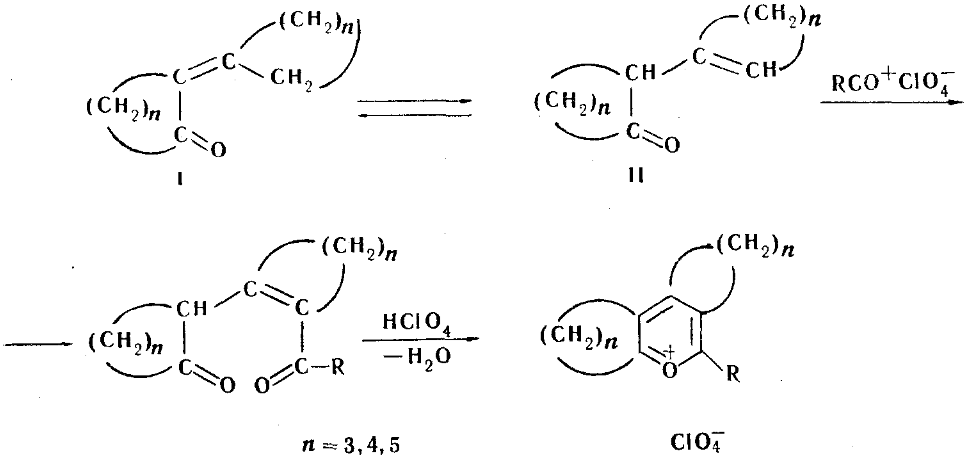
G. N. Dorofeenko, Yu. A. Zhdanov, V. I. Dulenko, V. A. Palchkov, and
N. V. Kovalenko

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 2, pp. 172-175, 1966

Acylation of cyclopentylidenecyclopentanone, cyclohexenylcyclohexanone, and cycloheptenylcycloheptanone with anhydrides of aliphatic acids in the presence of 70% perchloric acid is studied. A simple method of synthesis of 2-alkyl-3, 4; 5, 6-bicycloalkenopyrylium salts is given. Treatment of the pyrylium salts with ammonia gives 2-alkyl-3, 4; 5, 6-bicyclopenteno- and cycloheptenopyridine in good yields.

In extending work on the synthesis of pyrylium salts by acylation of aliphatic, aliphatic-aromatic [1], and β,γ-unsaturated ketones [2, 3], we have made a study of the acylation of products of crotonaldehyde-type autocondensation of cyclic ketones, cyclopentanone, cyclohexanone, and cycloheptanone. The crotonaldehyde-type condensations of cyclopentanone and cyclohexanone were effected using potassium hydroxide [4], and of cycloheptanone with potassium tert-butoxide [5].

It was not possible to isolate pure pyrylium salts by acylating cyclopentylidenecyclopentanone with acid anhydrides in the presence of 70% perchloric acid, but treatment of the reaction products with ammonia gave 35-40% of 2-alkyl-3, 4; 5, 6-bicyclopentenopyridines (n = 3). The structures of the compounds are analogous to that of the recently isolated alkaloid actinidine [6]. The comparatively low yield of 2-aklyl-3, 4; 5, 6-bicyclopentenopyridines can be ascribed to isomerization of the cyclopentylidenecyclopentanone to a β, γ-unsaturated ketone (cyclopentenylcyclopentanone, I → II) being hindered on account of the strain in the 5 membered ring.



On the other hand, in the case of the products of crotonaldehyde-type condensation of cyclohexanone and cycloheptanone, equilibrium is shifted towards the β,γ-unsaturated ketone, so that good yields are obtained, (65-87%), and the pyrylium salts are readily isolated crystalline. It did not prove possible to obtain the corresponding octahydrophenanthridines by treating the 2-alkyl-3, 4; 5, 6-bicyclohexenopyrylium perchlorates with aqueous or ethanolic ammonia. Under similar conditions the 2-alkyl-3, 4; 5, 6-bicycloheptenopyrylium salts give good yields of the 2-alkyl-3, 4; 5-6-bicycloheptenopyridines.

The homogeneity of the compounds synthesized was confirmed by thin-layer chromatography using gypsum or aluminum oxide. The structures of the pyrylium salts were confirmed by their exhibiting intense absorption bands in the 1630-1615 and 1540-1530 cm^{-1} regions, these being characteristic vibrations of the pyrylium cation [7].

Experimental

2-Methyl-3, 4; 5, 6-bicyclopentenopyridine. A mixture of 40 g acetic anhydride, and 4 ml $HClO_4$ was prepared with cooling, and added, with stirring, to 15 g cyclopentylidenecyclopentanone. After an hour 100 ml water was added to the cooled reaction products, and with cooling and stirring, excess concentrated aqueous ammonia added gradually. The organic layer was extracted with ether, and the ether solution shaken with 40 ml 10% HCl. The hydrochloric acid solution of the pyridine was separated off, washed with ether, and made alkaline with KOH. The pyridine which separated was extracted with ether, the ether extract dried over KOH, then distilled, to give 5.2 g (30%) of a compound bp 276–278° (760 mm) [8], or 142–145° (5 mm). Found: N 8.00, 8.05%. Calculated for $C_{12}H_{15}N$: N 8.08%. Picrate mp 137° (ex EtOH) [8]. Found: N 14.45, 14.67%. Calculated for $C_{12}H_{15}N \cdot C_6H_3N_3O_7$: N 14.43%. Hydrochloride mp 186–188° (ex Me_2CO). Found: N 6.60, 6.53%. Calculated for $C_{12}H_{15}N \cdot HCl$: N 6.68%.

2-Propyl-3, 4; 5, 6-bicyclopentenopyridine. This was prepared similarly, using butyric anhydride. Yield 25%, bp 293–296° (760 mm). Found: N 6.76, 6.77%. Calculated for $C_{14}H_{19}N$: N 6.95%. Picrate mp 111°. Found: N 12.98, 12.91%. Calculated for $C_{14}H_{19}N \cdot C_6H_3N_3O_7$: N 12.01%.

2-Propyl-3, 4; 5, 6-bicyclohexenopyrylium perchlorate. A mixture of 13.4 g butyric anhydride and 3 ml 70% $HClO_4$ was added to 6.4 g cyclohexenylcyclohexanone [4]; this was accompanied by a considerable evolution of heat. After an hour the reaction products were diluted with ether (about 15 ml), and cooled to 2–3°, when a crystalline precipitate formed, which was filtered off, washed with ether, and dried in air. Yield of 2-propyl-3, 4; 5, 6-bicyclohexenopyrylium perchlorate, 8.3 g (85%), mp 201–204° (ex EtOH). Similarly acylation of cyclohexenylcyclohexanone and cycloheptenylcycloheptanone with 5 other anhydrides of carboxylic acids in the presence of 70% $HClO_4$ gave the pyrylium salts listed in Table 1.

Table 1

Pyrylium salts

n	R in formula A	Mp, °C	Formula	Found, %			Calculated, %			Yield, %
				C	H	Cl	C	H	Cl	
4	CH_3	52—56	$C_{14}H_{19}ClO_5$	56.72	6.22	11.64	57.58	6.50	12.10	50
	C_2H_5	167—169	$C_{15}H_{21}ClO_5$	57.31	6.74	10.97	56.80	6.63	11.18	67
				57.12	6.78	10.81				
	n-C_3H_7	201—204	$C_{16}H_{23}ClO_5$	58.89	7.23	10.48	58.09	7.01	10.72	85
				58.83	7.15	10.70				
	i-C_4H_9	182—184	$C_{17}H_{25}ClO_5$	59.60	7.51	10.37	59.20	7.30	10.28	87
				59.68	7.65	10.52				
5	CH_3	Liquid	$C_{16}H_{23}ClO_5$	57.01	6.53	10.00	58.09	7.01	10.72	—
	C_2H_5	188—190	$C_{17}H_{25}ClO_5$	59.21	7.19	10.40	59.20	7.30	10.28	73
				59.02	7.14	10.01				
	n-C_3H_7	228—231	$C_{18}H_{27}ClO_5$	59.74	7.63	10.06	59.69	7.59	9.63	70
				59.79	7.74	10.16				

Table 2

2-R-3, 4; 5, 6-bicycloheptenopyridines

R	*Rf*	Formula	Found, %		Calculated, %		Yield, %
			C	H	C	H	
CH_3	0.50	$C_{16}H_{23}N$	83.24 83.42	10.54 10.31	83.78	10.18	90
C_2H_5	0.58	$C_{17}H_{25}N$	83.63 83.42	10.63 10.44	83.88	10.31	96
C_3H_7	0.66	$C_{18}H_{27}N$	83.68 83.61	10.68 10.61	83.98	10.57	95

2-Ethyl-3, 4; 5, 6-bicycloheptenopyridine. 5 ml concentrated aqueous ammonia was added to 1.72 g 2-ethyl-3, 4; 5, 6-bicycloheptenopyrylium perchlorate. After 24 hr, the organic layer was extracted with ether, the ether extract washed with water, and then shaken with 10 ml 10% HCl. The hydrochloric acid solution of the pyridine was separated off, washed with ether, and made alkaline with KOH. After evaporating off the ether the pyridine was chromatographed on an aluminum oxide column (benzene solvent). 1.6 g (96%) 2-ethyl-3, 4; 5, 6-bicycloheptenopyridine was obtained as a viscous yellow oil. The IR spectrum had ν_{max}: 1570, 1450, 1409 cm^{-1}, and R_f 0.58 (benzene solvent, visualizer iodine). The other 2-alkyl-3, 4; 5, 6-bicycloheptenopyridines (Table 2) were prepared similarly.

REFERENCES

1. G. N. Dorofeenko and S. V. Krivun, Ukr. Khim. Zh., 29, 1058, 1963.
2. G. N. Dorofeenko and V. I. Dulenko, DAN, 157, 361, 1964.
3. G. N. Dorofeenko, V. I. Dulenko, and L. V. Dulenko, ZhOKh, 32, 3445, 1962; 34, 4018, 1964.
4. I. Plešek, Chem. Listy, 50, 252, 1956.
5. W. I. Rosenfelder and D. Ginsburg, J. Chem. Soc., 2957, 1954.
6. Sakan, Fujito and Murai, Bull. Chem. Soc., Japan, 32, 315, 1959.
7. A. T. Balaban, G. D. Mateescu, and M. Elian, Tetrah., 18, 1083, 1962.
8. A. E. Chichibabin, Bull. Soc. Chim. France, 5, 4, 1826, 1937; 5, 6, 522, 1939.

16 July 1964

Rostov-on-Don State University

All-Union Scientific Research Institute for Reagents and Ultrapure Chemicals, Donetsk Branch