of 70 eV, and inlet temperatures of 70°C (V-XVI) and 80°C (I-IV). Compounds I-XVI were synthesized according to previously described methods [1-4]. Their purities were assessed by TLC, GLC, IR, PMR, and mass spectroscopy. Mass spectra of the deuteroanalogs VIII, X, and XIII were obtained under conditions of spontaneous deuterium exchange between compounds VII, IX, and XII in the vapor phase with CD_3OH vapor in the ionizing chamber of the mass spectrometer.

LITERATURE CITED

1. N. S. Prostakov, L. A. Gaivoronskaya, N. M. Mikhailova, and L. M. Kirilova, Zh. Obshch. Khim., 33, 2573 (1963).
2. N. S. Prostakov, L. M. Kirilova, L. A. Shakhparonova, V. P. Zvolinskii, and D. É. Provensal, Khim. Geterotsikl. Soedin., No. 9, 1225 (1970).
3. N. S. Prostakov, A. T. Soldatenkov, A. P. Krapivko, A. A. Fomichev, A. I. Mikaya, and A. A. Ustenko, Zh. Org. Khim., 18, 1106 (1982).
4. N. S. Prostakov, A. P. Krapivko, A. T. Soldatenkov, N. D. Sergeeva, and Khadu Kheir, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 22, 548 (1979).
5. N. S. Prostakov, A. P. Krapivko, A. T. Soldatenkov, A. A. Savina, and I. Romero, Khim. Geterotsikl. Soedin., No. 3, 384 (1979).
6. N. S. Prostakov, A. P. Krapivko, A. T. Soldatenkov, and N. D. Sergeeva, Khim. Geterotsikl. Soedin., No. 5, 677 (1980).
7. N. S. Prostakov, A. P. Krapivko, A. T. Soldatenkov, K. Furnasis, and A. A. Savina, Khim. Geterotsikl. Soedin., No. 3, 365 (1976).
8. P. B. Terent'ev, R. A. Khmel'nitskii, N. A. Klyuev, A. B. Belikov, and V. V. Dorogov, Khim. Geterotsikl. Soedin., No. 1, 70 (1973).
9. R. A. Khmel'nitskii and P. B. Terent'ev, Usp. Khim., 48, 854 (1979).
10. I. H. Bowie and T. K. Brandshaw. Aust. J. Chem., 23, 1431 (1970).
11. V. K. Shevtsov, P. I. Zakharov, V. P. Zvolinskii, V. G. Pleshakov, G. V. Grigor'ev, Abeuir Zainul Md. and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 7, 941 (1981).
12. E. E. Robin, G. B. Thomas, and I. M. Vernon, J. Chem. Soc., B, No. 6, 1273 (1971).
13. C. S. Barnes, R. J. Goldrack, and E. J. Halbert, Tetrahedron Lett., No. 8, 705 (1972).
14. E. V. Brown and M. B. Shambhu, Org. Mass. Spectrom., 6, 479 (1972).
15. P. B. Terent'ev, R. A. Khmel'nitskii, and N. A. Kost, Zh. Org. Khim., 7, 1777 (1971).
16. P. I. Zakharov, V. P. Zvolinskii, A. T. Soldatenkov, A. P. Krapivko, and N. S. Prostakov, Zh. Org. Khim., 16 2330 (1980).
17. S. Meyerson, H. Drews, and E. K. Fields, J. Am. Chem. Soc., 66, 4964 (1964).
18. S. Meyerson, I. Puskas, and E. K. Fields, J. Am. Chem. Soc., 68, 4974 (1966).

QUATERNIZATION OF PYRIDINES WITH HALOADAMANTANES

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UDC 547.68'821.3.07

The quaternization of pyridine and its 3- and 4-derivatives with 1-haloadamantanes has been carried out in the presence of a small quantity of water in the pyridines.

The quaternization reaction of pyridines with alkyl halides is well known [1]. However, its use for quaternization of compounds with a halogen atom at the bridgehead has received virtually no study. It is known that under severe conditions 1-bromoadamantane reacts with pyridine [2], 4-methylpyridine and isoquinoline [3].

We have previously obtained adamantylpyridinium salts by a conjugated haloamination reaction of 1,3-dehydroadamantane and 3,7-dimethylenebicyclo[3.3.1]nonane [4, 5] and also by interaction of 3,7-dimethylenebicyclo[3.3.1]nonane with pyridine hydrochloride [6].

Institute of Chemistry and Chemical Technology, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk 660049. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 817-819, June, 1987. Original article submitted January 22, 1986.

0009-3122/87/2306-0675$12.50

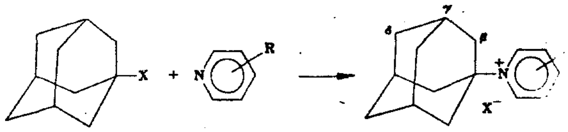
TABLE 1. Properties of Compounds IIIa-f

Compound	Reaction time, h	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	Hal	N		C	H	Hal	N	
IIIa	6	246—248	61,1	6,8	27,2	4,6	$C_{15}H_{20}BrN$	61,2	6,8	27,2	4,8	97
IIIb	4	250—251	52,2	6,1	—	4,0	$C_{15}H_{20}IN$	52,8	5,9	37,2	4,1	96
IIIc	6	187—189	61,9	7,1	25,9	4,5	$C_{16}H_{23}BrN$	62,3	7,2	25,9	4,5	62
IIId	6	223—224	62,3	7,5	25,7	4,2	$C_{16}H_{23}BrN$	62,3	7,2	25,9	4,5	80
IIIe	6	206—208	62,5	8,1	19,3	6,5	$C_{22}H_{34}BrN_2O$	62,5	8,1	18,9	6,6	70
IIIf	4	308—309	64,2	6,2	21,4	7,3	$C_{20}H_{23}BrN_2$	64,7	6,2	21,5	7,5	98

TABLE 2. Values of PMR Spectra of Adamantylpyridinium Salts

Compound	Solvent	PMR spectrum, δ, ppm							
		adamantane fragment		protons of pyridinium ring					other protons
		6-H, H_σ	9-H, $H_\gamma + H_\beta$	2-H	3-H	4-H	5-H	6-H	
IIIa IIIb	CF_3COOH	1,83	2,33	9,00	8,07	8,40	8,07	9,00	
IIIc	CF_3COOH	1,86	2,33	8,76	—	8,20	7,96	8,83	2,60 (3H, CH_3)
IIId	CF_3COOH	1,86	2,33	8,80	7,80	—	7,80	8,80	2,66 (3H, CH_3)
IIIe	D_2O	1,66	2,00	9,10	—	8,46	8,10	9,16	1,0 and 1,1 (6H, CH_3); 3,13 and 3,43 (4H, CH_2)
IIIf	D_2O	1,81	2,30	9,18	8,32	—	8,32	9,18	8,71 (2′-H, 6′-H); 7,88 (3H′, 5H′)

In this work* we have investigated the quaternization reaction of pyridine derivatives with haloadamantanes in order to develop a preparative method of obtaining the corresponding salts and also to determine the effect of the substituents in the pyridine ring on the reaction. It transpired that the quaternization reaction of pyridine and its 3- and 4-derivatives occurs only with 1-bromoadamantane (Ia) and 1-iodoadamantane (Ib), while 1-chloroadamantane does not react with pyridine up to a temperature of 300°C.



I a,b II a–e III a–f

Ia X=Br, b X=I; IIa R=H, b R=3-CH_3, c R=4-CH_3, d R=3-CON(C_2H_5)$_2$, e R==4-(4′-pyridyl); III a, b R=H, c R=3-CH_3, d R=4-CH_3, e R=3-CON(C_2H_5)$_2$, f R=4-(4′-pyridyl); a,c–f X=Br, b X=I

In this reaction an important part is played by water. If pyridine is completely dehydrated the yields of products are small and the temperature needed for carrying out the reaction is high. When water is added (0.2% of the quantity of pyridine) the reaction temperature is reduced to 50-70°C and the yields of pyridinium salts are substantially increased (compare [2, 3]). We determined the content of water in the pyridines by means of PMR and supplemented it to a level of ~0.2%. The property of water to accelerate the ionization of 1-haloadamantanes was used by Stetter [8] when alkylating toluene with 1-bromoadamantane.

It should be noted that the quaternization reaction of pyridine derivatives with 1-haloadamantanes is sensitive to steric factors. Thus, with pyridine derivatives having a substituent at the 2-position reaction does not take place, while increasing the water content in such pyridines only leads to hydrolysis of the haloadamantanes. Adamantyl salts are not obtained from 2-picoline, 2,3-lutidine, 2,4,6-collidine, or quinoline, although the corresponding salts have been obtained [5] by a conjugated haloamination reaction of 3,7-dimethylenebicyclo[3.3.1]nonane with quinoline and 2-picoline. A quaternary salt is not formed when the reaction is attempted with triethylamine, evidently also because of steric factors.

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*For previous communication, see [7].

Thus, by quaternization of pyridine and its 3- and 4-derivatives with 1-bromo- and 4-iodoadamantanes in the presence of a small quantity of water it is possible to obtain the corresponding adamantylpyridinium salts (see Tables 1 and 2). Pyridine derivatives having substituents at the 2-position do not undergo a quaternization reaction with haloadamantanes.

EXPERIMENTAL

The reaction was conducted in sealed ampuls; PMR spectra were recorded on a Tesla BS-467 (60 MHz) spectrometer, with D_2O and CF_3COOH as solvents and TMS as external standard.

1-Bromoadamantane [9] and 1-iodoadamantane [10] were obtained according to known methods.

1-(1-Adamantyl)pyridinium Iodide (IIIb). General Method. 0.01 mole of compound Ib in a tenfold excess of pyridine containing 0.2% water was heated for 4 h at 180°C. The reaction mixture was poured into ether, and the precipitate was filtered off and crystallized from a benzene–ethanol mixture.

LITERATURE CITED

1. J. Joule and G. Smith, Heterocyclic Chemistry, Van Nostrand Reinhold (1972).
2. F. N. Stepanov, N. L. Dovgan', and A. G. Yurchenko, Zh. Org. Khim., 6, 1823 (1970).
3. E. V. Krumkalns and W. Pfeifer, J. Med. Chem., 11, 1103 (1968).
4. V. A. Sokolenko and B. E. Kogai, Zh. Org. Khim., 12, 1370 (1976).
5. B. E. Kogai, V. K. Gubernatorov, V. A. Sokolenko, Zh. Org. Khim., 20, 2554 (1984).
6. V. K. Gubernatorov, B. E. Kogai, and V. A. Sokolenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1203 (1983).
7. V. A. Sokolenko and N. M. Svirskaya, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1677 (1984)
8. H. Stetter, J. Weber, and C. Wulff, Chem. Ber., 97, 3488 (1964).
9. H. Stetter, M. Schwarz, and A. C. Hirschhorn, Chem. Ber., 92, 1629 (1959).
10. P. R. Schleyer and R. D. Nicholas, J. Am. Chem. Soc., 83, 2700 (1961).

SYNTHESIS AND SPECTRAL LUMINESCENT PROPERTIES OF CERTAIN PYRIDINE AND QUINOLINE ANALOGS OF ISOMERIC DISTYRYLNAPHTHALENES AND STYRYL- AND DISTYRYLANTHRACENES

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UDC 547.652'672'831.2.07:542.953.3:535.37

A series of pyridine and quinoline analogs of isomeric distyrylnaphthalenes and styryl- and distyrylanthracenes has been synthesized. Their spectral-luminescent properties were studied. Compounds whose structures are sterically hindered in the ground state have the highest Stokes' shift.

1,4-Distyrylbenzene, 2,6-distyrylnaphthalene, and certain heterocyclic analogs of these compounds are known as organic luminophores, which effectively transform laser emission [1-3]. In continuation of the study of the hetero analogs of styrylarenes, we synthesized quinoline analogs of isomeric 2,6-, 1,5-, and 2,7-distyrylnaphthalenes (I-III), and also pyridine and quinoline analogs of 9,10-distyrylanthracene (IVa,b) and 9-styryl anthracene (Va,b), and studied their spectral luminescent properties.

All the compounds were obtained by the method described in [4], in analogy to the preparation of 1,4-di[β-(2-quinolyl)vinyl]benzene (VI), by the condensation of 4-picoline or quin-

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0009-3122/87/2306-0677$12.50