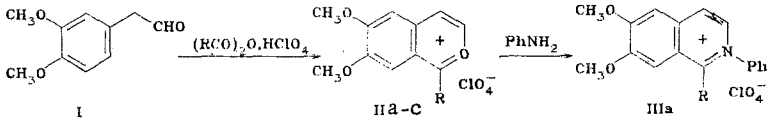
SYNTHESIS OF 3-UNSUBSTITUTED 2-BENZOPYRYLIUM SALTS

I. V. Shcherbakova, V. G. Brovchenko, and E. V. Kuznetsov

UDC 547.813.833.9.07

The ability of 2-benzopyrylium salts to undergo conversion to isoquinoline bases is widely known [1, 2]. Of particular interest in this respect are 3-unsubstituted 2-benzopyrylium salts, which can serve as key compounds in the synthesis of natural alkaloids of the salsolidine and papaverine series. However, the multistep method for their synthesis, which is realized by oxidation of indenes [3], does not make it possible to introduce the necessary alkyl or benzyl groups into the 1 position.

We have shown that 1-alkyl-2-benzopyrylium salts IIa-c are obtained in 35-70% yields in the acylation of homoveratraldehyde (I) [4] with aliphatic acid anhydrides in the presence of 70% perchloric acid.



I IIa-c IIIa

IIa, III a R=CH_3; b R=C_2H_5; c R=C_3H_7

Compound IIa, with mp 235-237°C (from acetic acid), was obtained in 70% yield. PMR spectrum (CF_3COOH): 2.93 (s, CH_3), 3.80 (s, OCH_3), 3.88 (s, OCH_3), 7.18 (s, 1H), 7.38 (s, 1H), 7.63 (d, 1H), and 8.28 ppm (d, 1H). Compound IIb, with mp 176°C, was obtained in 40% yield. PMR spectrum (CF_3COOH): 1.15 (t, CH_3), 3.88 (q, CH_2), 3.75 (s, OCH_3), 3.83 (s, OCH_3), 7.10 (s, 1H), 7.33 (s, 1H), 7.08 (d, 1H), and 8.23 ppm (d, 1H). Compound IIc, with mp 155°C, was obtained in 35% yield. The IR spectra of IIa-c contained characteristic absorption bands at 1615-1620, 1600, 1260-1275, and 1100 cm^{-1}.

Possible products of dimerization [5] or acylation of aldehyde I at the methylene group [6] were not detected under the described conditions.

Isoquinolinium salt IIIa, with mp 272°C (from acetic acid), was formed in 80% yield when salt Ia was heated with aniline in ethanol. PMR spectrum (CF_3COOH): 2.53 (s, CH_3), 3.78 (s, OCH_3), 3.80 (s, OCH_3), and 7.10-7.69 ppm (m, 9H, aromatic).

The results of elementary analysis of the compounds for their C, H, Cl, and N content were in agreement with the calculated values.

LITERATURE CITED

1. G. N. Dorofeenko, E. V. Kuznetsov, and S. V. Krivun, Zh. Org. Khim., No. 2, 1499 (1966).
2. G. N. Dorofeenko, E. I. Sadekova, S. V. Krivun, and Yu. A. Zhdanov, Dokl. Akad. Nauk SSSR, No. 2, 345 (1968).
3. A. Müller, El-Sawy, M. Meszaros, and F. Ruff, Acta Chim. Hung., 52, 261 (1967).
4. I. K. Stamos, Tetrahedron Lett., 23, 459 (1982).
5. M. E. Jung and S. J. Miller, J. Am. Chem. Soc., 103, 1984 (1981).
6. E. V. Kuznetsov, A. I. Pyshchev, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 2, 152 (1972).

Scientific-Research Institute of Physical and Organic Chemistry. M. A. Suslov Rostov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, p. 702, May, 1984. Original article submitted July 14, 1983; revision submitted September 13, 1983.

 0009-3122/84/2005-0570$08.50