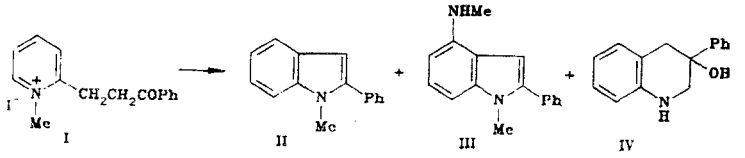
RECYCLIZATION OF 1-METHYL-2-(2-BENZOYLETHYL)PYRIDINIUM IODIDE

V. I. Terenin, A. N. Rumynatsev,
P. V. Nosyrev, L. G. Yudin,
S. P. Gromov and Yu. G. Bundel'

UDC 547.823'821.3'754.07

It is known that 1,2-dialkylpyridinium salts recyclize into N-alkylanilines by the action of nucleophilic reagents [1]. To determine the influence of structural factors on the recyclization of pyridinium salts, we studied the rearrangement of a pyridinium salt containing at the 2-position an alkyl chain with a carbonyl group at the γ-position by the action of various nucleophiles.

In the reaction of 1-methyl-2- (2-benzoylethyl)pyridinium iodide (I) with an alcoholic solution of methylamine (heating in a sealed ampule (150°C, 30 h) the known 1-methyl-2-phenylindole (II) was isolated in 7% yield. This compound is formed in accordance with the Kost—Sagitullin rearrangement scheme, followed by cyclization of the intermediate 2-phenacyl-N-methylaniline. When the alcoholic methylamine solution was replaced by an aqueous methylammonium sulfite solution, not only indole (II) (3%), but also unusual transformation products of the pyridine ring were isolated from the reaction mixture: 1-methyl-4-methylamino-2-phenylindole (III) (yield, 6%), the structure of which was confirmed by an alternate synthesis, and a compound, in a 6% yield, to which, the structure of 3-hydroxy-3-phenyl-1,2,3,4-tetrahydroquinoline (IV) was ascribed from the spectral data.



The formation of aminoindole III may take place by the Kost—Sagitullin rearrangement scheme, but with inclusion of a methylamine fragment in the molecule at the intermediate stage. Compound IV is formed as a result of removal of a proton from the N-methyl group of the pyridine ring, followed by closure of the quinolizine ring and its recyclization.

The use of a mixture of methylamine and sodium sulfite as the reagent led to increase in the yield of indole II (35%) and tetrahydroquinoline IV (13%), while the yield of aminoindole III was 6%. The yield of aminoindole III could be increased to 17% when a mixture of an alcoholic solution of methylamine and an aqueous solution of methylammonium sulfite was used as the reagent.

1-Methyl-4-methylamino-2-phenylindole (III), mp 108-109°C. IR spectrum: 3400 cm^{-1} (NH). PMR spectrum [$(CD_3)_2CO$]: 2.73 (1H, br. s, NH); 2.70 (3H, s, NCH_3); 3.64 (3H, s, 1-CH_3); 6.13 (1H, d, J = 8 Hz, 5-H); 6.55 (1H, s, 3-H); 6.67 (1H, d, J = 8 Hz, 7-H); 6.98 (1H, m, J = 8 Hz, 6-H); 7.31 (1H, m, J = 8 Hz, J = 1.5 Hz, H_p); 7.40 (2H, m, J = 8 Hz, J = 1.5, H_m); 7.47 ppm (2H, d, t, J = 8 Hz, J = 1.5 Hz, J = 1Hz, H_o). Mass spectrum: 236 (100), 235 (15), 221 (37), 207 (19), 194 (17), 165 (10), 118 (12), 110 (7), 77 (7).

3-Hydroxy-3-phenyl-1,2,3,4-tetrahydroquinoline (IV), mp 115-116°C. IR spectrum: 3495 (OH), 3400 cm^{-1} (NH). PMR spectrum [$(CD_3)_2CO$]: 2.71 (1H, d, d, J = 16 Hz, J = 3 Hz, 4-H); 3.09 (1H, d, t, J = 11.5 Hz, J = 3 Hz, 2-H); 3.14 (1H, d, J = 16 Hz, 4-H), 3.40 (1H, d, J = 11.5 Hz, 2-H), 3.86 (1H, s, OH), 5.25 (1H, br. s, NH); 6.49 (1H, t, d, J = 8 Hz, J = 11 Hz, 7-H); 6.55 (1H, d, J = 8 Hz, 8-H); 6.87 (1H, d, J = 8 Hz, 5-H); 6.88 (1H, d, J = 8 Hz, 6-H); 7.18 (1H, t, t, J = 8 Hz, J = 1.15 Hz, H_p), 7.20 (2H, t, t, J = 8 Hz, J = 1.5 Hz, H_m); 7.52 ppm (2H, d, t, J = 8 Hz, J = 1.5 Hz, J = 1 Hz, H_o). Mass spectrum: 225 (30), 205 (10), 120 (100), 118 (17), 106 (13), 105 (20), 9 (15), 77 (20).

M. V. Lomonosov State University, Moscow 119899. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, p. 855, June, 1988. Original article submitted October 20, 1987.

Compounds III and IV have satisfactory analytical characteristics.

LITERATURE CITED

1. R. S. Sagitullin, S. P. Gromov, and A. N. Kost, Dokl. Akad. Nauk SSSR, 243, 937 (1978).
2. H. M. Kissman, D. W. Farnswort, and B. Witkop, J. Am. Chem. Soc., 74, 3948 (1952).

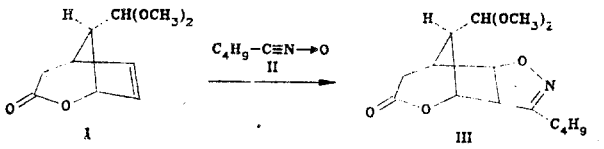
STEREO- AND REGIOSPECIFIC CYCLOADDITION OF NITRILE OXIDE TO 8-syn-DIMETHOXYMETHYL-3-OXO-2-OXABICYCLO[3.2.1]OCT-6-ENE

N. F. Bondar', R. V. Skupskaya, and F. A. Lakhvich

UDC 547.786.3'514.7'239.2.07

2-Isoquazoline intermediates, which are obtainable by cycloaddition of nitrile oxides to olefins, recently gained a wide synthetic application through the variant of a selective transformation of the heterocycle into different functional open-chain derivatives, developed for these compounds [1, 2]. The cycloaddition of nitrile oxides to substituted bicycloheptenes proceeds stereospecifically into an exo position, but with the formation of regio-isomers, the ratio of which is not much dependent on the character of the substituents in the dipolarophile and in dipole [3].

In the course of study of the isoxazole variant of the introduction of side chains into the bicyclic precursors of prostanoids, we have found that the cycloaddition of nitrile oxide II to the unsaturated lactone I proceeds regiospecifically with the formation of adduct III:



I III

Triethylamine (4 drops) was added to a mixture of 0.47 g (4 mmoles) of nitropentane, 0.16 g (0.8 mmole) of bicycloalkene I, and 0.95 g (8 mmoles) of phenyl isocyanate in 6 ml of benzene, and the reaction mixture was stirred for 48 h at room temperature. The precipitate was filtered, the solvent was removed on a rotary evaporator, and the residue was chromatographed on a silica gel with a gradient elution by a mixture of ether and hexane. The yield of 11-syn-dimethoxymethyl 5-butyl-9-oxo-3,8-dioxa-4-azatricyclo[5.3.1.$0^{3,5}$]undec-4-ene (III) was 0.18 g (75%), colorless crystals, mp 89°C. IR spectrum (thin layer): 1040, 1065, 1100, 1140, 1190, 1630, 1755, 2835 cm^{-1}. PMR spectrum ($CDCl_3$): 0.96 (t, 3H, J = 7.2 Hz, CH_3), 1.41 (sext., 2H, CH_2); 1.53-1.77 (m, 2H, CH_2); 2.30 (m, 1H, $CH_2C{=}N$); 2.45-2.56 (m, 2H, 11-H, CH_2-C=N); 2.65 (d, 1H, J_{gem} = 18 Hz, 10-H_{endo}); 2.88 (d, 1H, J = 6.2, Hz, 1-H); 2.94 (d.d, 1H, J_{gem} = 18 Hz, J = 6.2 Hz, 10-H_{exo}); 3.32 (s, 3H, CH_3O), 3.44 (s, 3H, CH_3O), 4.00 (d, 1H, J = 9.0 Hz, 6-H); 4.32 [d, 1H, J = 8.6 Hz $CH(OCH_3)_2$]: 4.84 (br. d, 1H, 7-H); 4.97 (d, 1H, J = 9.0 Hz, 2-H). M 297 (mass spectrometrically).

LITERATURE CITED

1. A. A. Akhrem, F. A. Lakhvich, and V. A. Khripach, Khim. Geterotsikl. Soed., No. 9, 1156 (1981).
2. A. P. Kozikowski, Acc. Chem. Res., 17, 410 (1984).
3. W. Adam, N. Carballeira, E. Cramer, V. Lucchini, E.-M. Peters, and H. G. von-Schnering, Chem. Ber., 120, 695 (1987).

Institute of Bioorganic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. 220045.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, p. 856, June, 1988. Original article submitted November 10, 1987.

0009-3127/88/2406-0706$12.50