ISSN 1070-4272, Russian Journal of Applied Chemistry, 2006, Vol. 79, No. 8, pp. 1384–1385. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.P. Stankevičius, L.N. Janušiene, P.B. Terent'ev, M.S. Saprogoniene, 2006, published in Zhurnal Prikladnoi Khimii, 2006, Vol. 79, No. 8, pp. 1397–1398.

BRIEF COMMUNICATIONS

A Procedure for Preparing 4-Cyanofluoren-9-one

A. P. Stankevičius, L. N. Janušiene, P. B. Terent'ev, and M. S. Saprogoniene

Institute of Cardiology, Kaunas Medical University, Kaunas, Lithuania
Lomonosov Moscow State University, Moscow, Russia

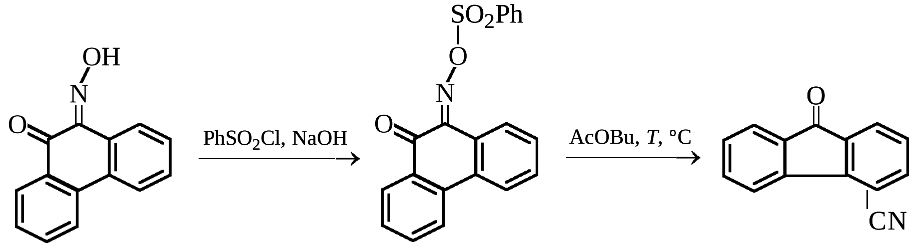
Received June 19, 2006

Abstract—A procedure was developed for preparing 4-cyanofluoren-9-one by intramolecular cyclization of 9,10-phenanthrenequinone monooxime benzenesulfonate.

DOI: 10.1134/S1070427206080362

Fluorenones, mainly 2- and 4-substituted, are widely used in electrophotography [1] and as drugs [2]. In particular, Grintsev et al. studied a series of fluorenones [3] and synthesized a novel antiviral agent, Florenal [4]. It is widely used in medical practice against herpesis and adenoviruses. However, the lack of facile routes to 4-substituted fluorenones hinders the development of this novel group of antiviral agents.

Fluorenones are usually prepared from 2-arylbenzoic acids by the Friedel–Crafts reaction or its modifications [1]. Even 2'-cyanodiphenyl-2-carboxylic acid in thionyl chloride forms, along with the corresponding acid chloride, also 4-cyanofluoren-9-one [2]. Experiments on the Beckmann rearrangement of the second kind of 9,10-phenanthrenequinone monooxime **1** have shown that suspensions of this compound in ether under the action of PCl_5 give 4-cyanofluoren-9-one **3** in a low yield [3]. Proceeding with studies of *o*-quinone monooxime sulfonates, we found that 9,10-phenanthrenequinone monooxime benzenesulfonate **2**, when melted (~215°C) or crystallized from ethyl acetate, forms traces of a new substance with mp 238–240°C (dec.), whose mass spectrum was consistent with the structure of 4-cyanofluoren-9-one. Prolonged refluxing of **2** in ethyl acetate or (which is better) in butyl acetate always gives fluorenone **3** in a good yield:



1 **2** **3**

An attempt to perform the reaction with 9,10-phenanthrenequinone monooxime propionate or benzoate resulted in the recyclization.

EXPERIMENTAL

The purity of the compounds was checked by TLC on Silufol UV-254 plates, solvent system tetrachloromethane–ethyl acetate, 3 : 1; the spots were developed with iodine vapor. The mass spectra were recorded on MAT-1303 and MAT-212 devices (Varian-MAT) at ionizing electron energies of 50 and 70 eV, respectively, with direct sample input. The elemental composition of the major ions was determined with an MAE-212 device at high resolution ($M/\Delta M$ = 10 000).

9,10-Phenanthrenequinone monooxime 1 was prepared by the procedure described in [4]; mp 157°C. Mass spectrum, *m/z* (*I*, %): 223 (96), 207 (20), 206

(100), 179 (11), 178 (34), 177 (15), 166 (7), 165 (40), 164 (149), 163 (20), 151 (18).

9,10-Phenanthrenequinone monooxime benzenesulfonate 2. To a solution of 22.3 g (0.1 mol) of **1** and 17.66 g (0.1 mol) of benzenesulfonyl chloride in 50 ml of acetone was added, with cooling to 0–5°C, a solution of 4.8 g (0.12 mol) of NaOH in 50 ml of water. The mixture was stirred for 10 min and then diluted with 50 ml of cold water. The precipitate was separated by vacuum filtration, washed with ice-cold water, and dried at room temperature. Yield 21 g (78%); yellow-orange compound, mp 140–141°C (from methyl ethyl ketone); R_f = 0.58.

Found (%): C 66.27, H 3.41, N 3.92, S 8.54.
$C_{20}H_{13}NO_4S$.
Calculated (%): C 66.11, H 3.58, N 3.85, S 8.81.

Mass spectrum, *m*/*z* (*I*, %): 363 (6) M, 299 (4) (M – SO_2), 222 (7) (M – $PhSO_2$), 206 (100) (M – $PhSO_3$), 179 (11) (M – $PhSO_3$ – HCN), 178 (24) (M – $PhSO_3$ – CO), 177 (21), 163 (6), 151 (20), 141 (9), 77 (43).

9,10-Phenanthrenequinone monooxime propionate was prepared similarly to **2** from 4.46 g (0.02 mol) of **1** in 40 ml of acetone, 2.8 g (0.03 mol) of propionyl chloride, and 1.6 g (0.04 mol) of NaOH in 10 ml of water. Yield 4.45 g (80%), mp 109.5–110°C (acetonitrile), R_f = 0.46.

Found (%): C 73.40, H 4.65, N 4.86.
$C_{17}H_{13}NO_3$.
Calculated (%): C 73.11, H 4.69, N 5.02.

9,10-Phenanthrenequinone monooxime benzoate was prepared similarly to **2** from **1** and benzoyl chloride; yield 60%, mp 172–174°C (butanone), R_f = 0.70.

Found (%): N 4.32.
$C_{21}H_{13}NO_3$.
Calculated (%): N 4.28.

4-Cyanofluoren-9-one 3. A mixture of 3.63 g (0.01 mol) of **2** and 30 ml of anhydrous butyl acetate was refluxed on an oil bath at 100°C for 6 h until sulfonate **2** was completely consumed (chromatographic monitoring). The solvent was distilled off by half, the mixture was cooled, and the precipitate was separated by vacuum filtration and crystallized from benzene. Yield 1.23 g (60%), mp 238–240°C (published data: mp 240°C [1]), R_f = 0.43. Mass spectrum, *m*/*z* (*I*, %): 205 (100) M, 177 (57) (M – CO), 176 (8), 175 (5), 150 (17) (M – CO – HCN), 149 (5), 127 (4), 124 (3), 89 (10), 75 (16), 74 (9).

REFERENCES

1. Borsche, W. and Sander, W., *Ber.*, 1914, vol. 47, pp. 2815–2826.
2. Rapoport, H. and Williams, A.R., *J. Am. Chem. Soc.*, 1949, vol. 71, pp. 1774–1778.
3. Fuson, R., *Reactions of Organic Compounds: A Textbook for the Advanced Student*, New York: Wiley, 1962.
4. Terent’ev, P.B. and Stankiavicius, A.P., *Khim. Geterotsikl. Soedin.*, 1988, pp. 1518–1521.