HETEROCYCLIC ANALOGS OF PLEIADIENE.

45.* RECYCLIZATION OF 1-METHYLPERIMIDINE UNDER THE INFLUENCE OF FLUOROBENZOYL CHLORIDES. UNEXPECTED FORMATION OF TETRAFLUOROPHTHALOPERINONE IN THE CASE OF PENTAFLUOROBENZOYL CHLORIDE

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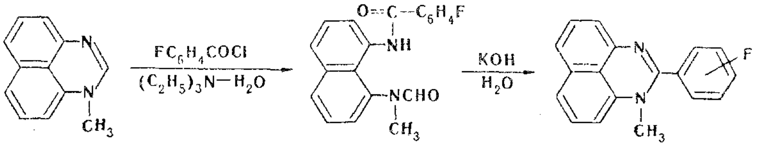
The action of isomeric fluorobenzoyl chlorides on 1-methylperimidine in the presence of triethylamine gave N-methyl-N-formyl-N'-fluorobenzoyl-1,8-naphthalenediamines, which on treatment with a solution of alkali are converted smoothly to 1-methyl-2-fluorophenylperimidines. Pentafluorobenzoyl chloride does not undergo this reaction but under absolute conditions at high temperatures forms 11,12,13,14-tetrafluorophthaloperin-10-one.

Continuing our study of recyclization [2] in the perimidine series, in the present research we investigated the reaction of 1-methylperimidine (I) with the chlorides of isomeric fluorobenzoic acids, as well as with pentafluorobenzoyl chloride. We found that the reaction of I with fluorobenzoyl chlorides in the presence of moist triethylamine proceeds just as smoothly as in the case of other aroyl chlorides. The reaction products are colorless 1,8-naphthalenediamine derivatives (II). When they are heated with alkali, they undergo cyclization to give yellow 1-methyl-2-fluorophenylperimidines (III) in good yields:



I
II a,c
III a–c

II, III a *o*-F; b *m*-F; c *p*-F

However, under the same conditions pentafluorobenzoyl chloride did not react with I. The positive charge on the carbonyl carbon atom in the initially formed [3] N-acylperimidinium salt (IV) is evidently greater than on the μ-carbon atom of the heteroring, as a result of which the action of hydroxide ions is directed toward the acyl group and leads to its elimination (see [3]). Taking this fact into account, we carried out the reaction of I with pentafluorobenzoyl chloride in the presence of triethylamine under absolute conditions and obtained extremely unexpected results. When we used two equivalents of triethylamine and perfluorobenzoyl chloride, the reaction product (46%) turned out to be a bright-red substance with the composition $C_{18}H_6F_4N_2O$ with a molecular weight of 342 (by mass spectrometry), which forms an extremely stable crystalline monohydrate. According to the data from the PMR spectrum, the substance obtained did not contain a CH_3 group; its IR spectrum did not contain the absorption of an NH group but did contain a $\nu_{C=O}$ band at 1732 cm^{-1}, which is typical for N-acylperimidines [3]. The properties of the compounds obtained coincided surprisingly closely with the properties of the known [4] phthaloperinone (IX). In fact, the two compounds have virtually identical $\nu_{C=O}$ frequencies and electronic absorption spectra (Fig. 1); when they are dissolved in strong acids (CF_3COOH and HCl but not in CH_3COOH), their color changes from red to dark-violet, and the absorption maximum of the long-wave band is shifted ∿90 nm bathochromically. In the case of dilution of acidic solutions with water, both perinones are regenerated unchanged. An important characteristic of both perinones is the fact that in their PMR spectra the 9-H proton, as a consequence of the

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*See [1] for Communication 44.

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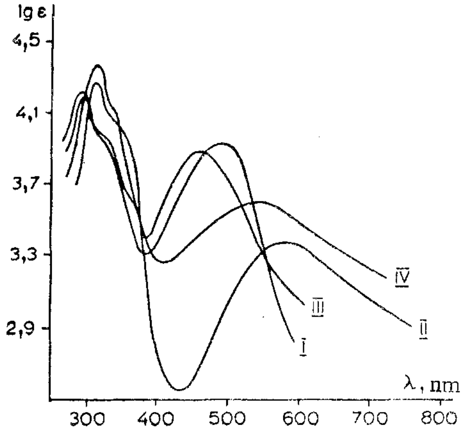
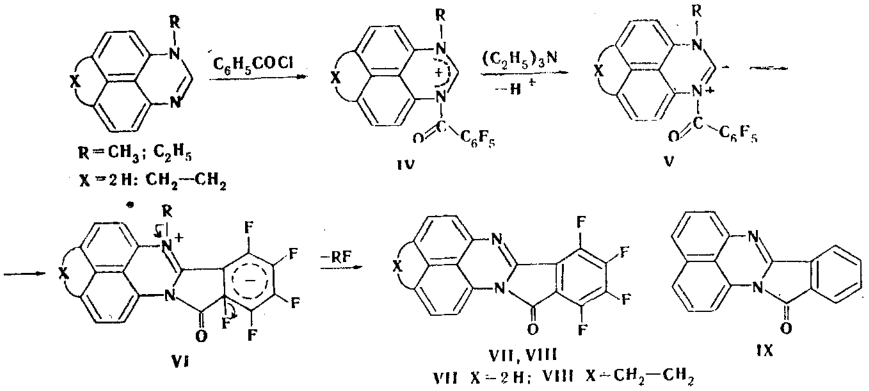


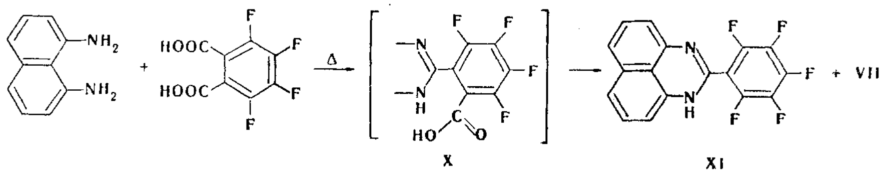
Fig. 1. UV spectra of 11,12,13,14-tetrafluorophthaloperin-10-ones (I, II) and phthaloperin-10-ones (III, IV): I and III in CH_3OH; II and IV in CF_3COOH.

deshielding effect of the carbonyl oxygen atom, is shifted to weak field as compared with the other protons and shows up at 8.0 ppm in solution in CF_3COOH and at 8.26 ppm in acetone.

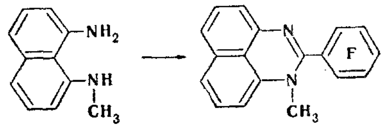
The mechanism of the formation of VII can be represented in the following way. The initially formed N-perfluorobenzoylperimidinium salt (IV) under the influence of triethylamine loses the 2-H proton and is converted to ylid V (the necessity for this step explains why the process takes place only in an anhydrous medium). Since reactions with nucleophiles are characteristic for polyfluorinated aromatic rings [5], in the next step the carbanion center intramolecularly attacks the o-carbon atom of the perfluorophenyl ring to give σ complex VI, and the latter is converted to final product VII by splitting out a molecule of CH_3F. It is apparent that in conformity with this scheme other 1-alkylperimidines under these conditions should also be converted to tetrafluorophthaloperinones. We actually confirmed this for 1-ethylperimidine although the yield of VII in this case was only 12%. 1-Methylaceperimidine also undergoes a similar transformation to give dark-red VIII.



We also obtained tetrafluorophthaloperinone by alternative synthesis. Fusion of 1,8-naphthalenediamine with tetrafluorophthalic acid led to the formation of two substances, viz., VII (34%) and the previously unknown 2-(2',3',4',5'-tetrafluorophenyl)perimidine (XI) (22%). It is apparent that the precursor of both compounds is the intermediately formed carboxylic acid X.



If the reaction of 1-methylperimidine with pentafluorobenzoyl chloride were to proceed via the usual recyclization scheme, we would have obtained 1-methyl-2-pentafluorophenylperimidine (XII). In this connection, it seemed of interest to synthesize this compound by another method. We obtained it in high yield by the reaction of N-methyl-1,8-naphthalenediamine with pentafluorobenzoyl chloride:



XII

EXPERIMENTAL

The IR spectra were measured with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) on the δ scale with hexamethyldisiloxane as the internal standard. The UV spectra were measured with a Specord UV-vis spectrophotometer. The mass spectra were obtained with a Heol JMS-01-JC-2 spectrometer with direct introduction of the samples into the ion source; the ionizing voltage was 75 eV, the cathode emission current was 300 μA, the accelerating voltage was 8 kV, and the ionization-chamber temperature was 120-130°C. Chromatography was carried out on Brockmann activity IV aluminum oxide.

General Method for the Preparation of N-Methyl-N-formyl-N'-fluorobenzoylnaphthalenediamines (IIa-c). A 2.1-g (0.015 mole) sample of the corresponding fluorobenzoyl chloride was added with stirring to a solution of 1.8 g (0.01 mole) of I in 50 ml of benzene. After 5 min, 1.65 g (0.015 mole) of triethylamine was added to the resulting yellow 1-methyl-3-fluorobenzoylperimidinium salt, and the mixture was refluxed for 4 h. It was then cooled, and the resulting precipitate was removed by filtration. The filtrate was diluted with a fivefold volume of petroleum ether, and the resulting precipitate was separated and combined with the initial precipitate. The combined precipitates were treated with 300 ml of water to remove the triethylammonium chloride, and the colorless crystals that were obtained after drying were recrystallized from benzene—petroleum ether.

N-Methyl-N-formyl-N'-(o-fluorobenzoyl)-1,8-naphthalenediamine (IIa). The yield of this compound, with mp 147-148°C, was 2.6 g (83%). Found: C 70.4; H 4.7; N 8.9%. $C_{19}H_{15}FN_2O_2$. Calculated: C 70.8; H 4.7; N 8.7%.

N-Methyl-N-formyl-N'-(m-fluorobenzoyl)-1,8-naphthalenediamine (IIb). The yield of this compound, with mp 170-171°C, was 2.7 g (84%). Found: C 70.6; H 4.6; N 8.9%. $C_{19}H_{15}FN_2O_2$. Calculated: C 70.8; H 4.7; N 8.7%.

N-Methyl-N-formyl-N'-(p-fluorobenzoyl)-1,8-naphthalenediamine (IIc). The yield of this compound, with mp 226-228°C, was 2.8 g (86%). Found: C 70.7; H 4.7; N 8.7%. $C_{19}H_{15}FN_2O_2$. Calculated: C 70.8; H 4.7; N 8.7%.

General Method for the Preparation of 1-Methyl-2-fluorophenylperimidine (IIIa-c). A suspension of 1 g (3 mmole) of the corresponding IIa-c in 20 ml of 10% potassium hydroxide solution was refluxed with stirring for 1 h. The color of the reaction mixture changed from white to yellow. The mixture was cooled, and the resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from ethanol. Compounds IIIa-c were obtained in quantitative yields.

1-Methyl-2-(o-fluorophenyl)perimidine (IIIa). This compound was obtained as yellow crystals with mp 141-141.5°C. Found: C 78.2; H 4.5; N 9.9%. $C_{18}H_{13}FN_2$. Calculated: C 78.3; H 4.7; N 10.1%.

1-Methyl-2-(m-fluorophenyl)perimidine (IIIb). This compound was obtained as yellow crystals with mp 143-144°C. Found: C 78.3; H 4.8; N 10.1%. $C_{18}H_{13}FN_2$. Calculated: C 78.3; H 4.7; N 10.1%.

1-Methyl-2-(p-fluorophenyl)perimidine (IIIc). This compound was obtained as yellow crystals with mp 187-188°C. Found: C 78.1; H 4.6; N 10.1%. $C_{18}H_{13}FN_2$. Calculated: C C 78.3; H 4.7; N 10.1%.

11,12,13,14-Tetrafluorophthaloperin-10-one* (VII). A) A mixture of 0.13 g (1 mmole) of I, 0.2 g (2 mmole) of dry triethylamine, and 0.46 g (2 mmole) of pentafluorobenzoyl chloride in 2 ml of dry benzene was heated in a sealed ampul at 130°C for 3 h, after which it was cooled and diluted to a volume of 40-50 ml with benzene. This mixture was heated to the boiling point, and the undissolved precipitate was removed by filtration and washed on the filter with 15-20 ml of benzene. Chromatography of the mother liquor on aluminum oxide (elution with benzene) gave 0.16 g (46%) of VII as red crystals with mp 237-238°C (from acetic acid). UV spectrum, λ_{max} (log ε): 292 (4.21) and 4.82 nm (3.94) (in methanol); 318 (4.28) and 580 nm (3.38) (in CF_3COOH). PMR spectrum (in acetone): 7.4 (m, 5H and 8.26 ppm (d, 9-H, J_{9-8} = 7.5 Hz). Found: C 63.4; H 2.0; F 21.9; N 7.9%. $C_{18}H_6F_4N_2O$. Calculated: C 63.2; H 1.8; F 22.2; N 8.2%.

B) A mixture of 1.5 g (7.6 mmole) of 1-ethylperimidine, 3.6 g (15 mmole) of pentafluorobenzoyl chloride, and 1.5 g (15 mmole) of dry triethylamine in 7 ml of absolute benzene was heated in a sealed ampul at 140°C for 4 h. The reaction product was isolated and purified by the method described above to give 0.32 g (12%) of red crystals with mp 238°C (from acetic acid). This product was identical to the product obtained from I with respect to its spectral and other characteristics.

C) A mixture of 0.3 g (2 mmole) of 1,8-naphthalenediamine and 0.48 g (2 mmole) of tetrafluorophthalic acid was fused with stirring for 15 min while raising the temperature from 150 to 220°C, during which all of the liberated water was removed by distillation, and the melt turned red-brown. The mixture was cooled and dissolved in 50 ml of benzene, and the solution was chromatographed on silica gel (elution with benzene). The first fraction (R_f 0.82) consisted of 0.22 g (34%) of red crystals of VII with mp 237-238°C (from acetic acid). The second fraction (R_f 0.67) consisted of 0.13 g (22%) of orange crystals of 2-(2',3',4',5'-tetrafluorophenyl)peridimine (XI) with mp 213-214°C (from octane). IR spectrum (in $CHCl_3$): 3460 cm^{-1} (N—H). UV spectrum, λ_{max} (log ε): 235 (4.604), 340 (4.065), 438 nm (3.127). Mass spectrum, m/e (intensity, %): 316.1 (100); 167.0 (12.74); 166 (87.32); 158.0 (10.26); 148.0 (13.67); 140 (28.18); 114.1 (15.22); 113.1 (17.32); 84.1 (17.30); 69.1 (10.25); 57.1 (14.68); 55.1 (10.91); 41.1 (11.91); 40.0 (26.82). Found: C 64.3; H 2.9; N 8.4%. $C_{17}H_8F_4N_2$. Calculated: C 64.6; H 2.5; N 8.7%.

11,12,13,14-Tetrafluorophthaloaceperin-10-one (VIII). A 0.2-g (2 mmole) sample of dry triethylamine and 0.46 g (2 mmole) of pentafluorobenzoyl chloride were added to a suspension of 0.2 g (1 mmole) of 1-methylaceperimidine in 3 ml of absolute benzene, and the mixture was heated in a sealed ampul at 130°C for 3 h. Compound VIII was isolated and purified in the same way as perinone VII to give 0.06 g (17%) of violet-red crystals with mp 259-260.5°C (from acetic acid). PMR spectrum (in CF_3COOH): 2.95 (s, 4H), 6.80 (m, 3H), and 7.63 ppm (d, 9-H, J_{9-8} = 7.5 Hz). Found: C 65.2; H 1.9; N 7.5%. $C_{20}H_8F_4N_2O$. Calculated: C 65.2; H 2.2; N 7.6%.

1-Methyl-2-pentafluorophenylperimidine (XII). A solution of 2.3 g (0.01 mole) of pentafluorobenzoyl chloride in 15 ml of dry benzene was added at 20°C in the course of 5 min to a solution of 1.7 g (0.01 mole) of N-methyl-1,8-naphthalenediamine in 50 ml of dry benzene, and the reaction mixture was refluxed with stirring for 1.5 h. At the end of the reaction, the solvent was evaporated, and the residual orange-red powder was stirred for 30 min with 100 ml of water. The mixture was filtered to give 2.6 g (76%) of bright-yellow crystals of a product with mp 207-208°C (from octane). Found: C 62.1; H 2.8; N 7.9%. $C_{18}H_9F_5N_2$. Calculated: C 62.1; H 2.6; N 8.0%.

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*The nomenclature for perinones used here was proposed by Sachs [4] and is also used by Mosher and Banks [6]. It is convenient in that the usual character of the numbering of the atoms of the perimidine ring is retained in it. In conformity with the more precise IUPAC rules, VII should be called 13-H-1,2,3,4-tetrafluoro-13-oxoisoindolo[2,1-a]perimidine.

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