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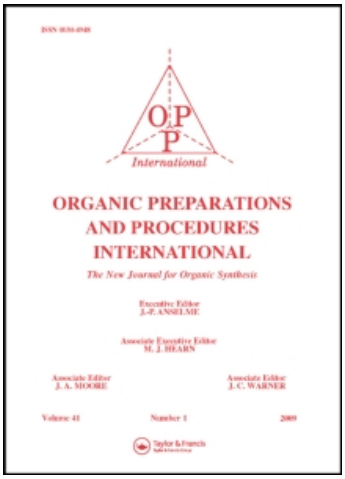

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THE FRIEDEL-CRAFTS ACYLATION AND BENZOYLATION OF PYRENE

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THE FRIEDEL-CRAFTS ACYLATION AND BENZOYLATION OF PYRENE

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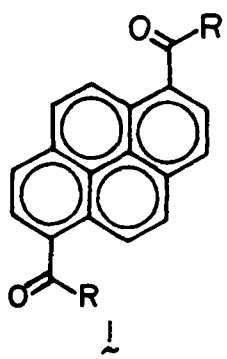
Reaction of pyrene with chloroacetyl chloride and $AlCl_3$ in CS_2 was reported by Vollmann et al.[1] to afford 1,6- and 1,8-bis(chloroacetyl)pyrene (1b, 2b), while analogous benzoylation of pyrene gave a mixture of 1,6- and 1,8-dibenzoylpyrene (1c, 2c).



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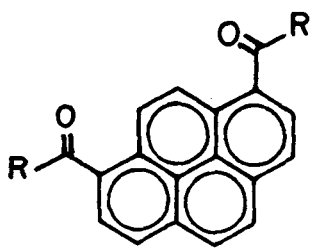

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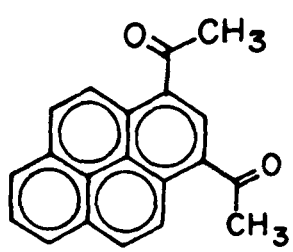

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a: R = CH_3, b: R = CH_2Cl, c: R = C_6H_5

We now report that acetylation of pyrene with acetyl chloride and $AlCl_3$ in CS_2 under similar conditions affords three isomeric diacetylpyrenes in the approximate ratio of 1:1:3. Analysis of the 500 MHz high resolution NMR spectra of these isomers permits their identification as 1,3-, 1,6-, and 1,8-diacetylpyrene (3, 1a, and 2a), respectively. These assignments are further confirmed by comparison of their physical and spectral properties with those of the isomeric diacetylpyrenes obtained through reduction of 1,6- and 1,8—bis(chloroacetyl)pyrene synthesized by the method of Vollmann et al.[1]

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The high resolution 500 MHz NMR spectrum of the major isomer (mp 162-163°) was consistent with only the highly symmetrical 1,8-diacetylpyrene structure (2a), exhibiting singlets at δ 9.04 and 8.09 ppm assigned to the $H_{9,10}$ and $H_{4,5}$ protons, respectively, and a pair of doublets at δ 8.36 and 8.18 ($J_{2,3}$ = 8.0 Hz) for the $H_{2,7}$ and $H_{3,6}$ protons, respectively. The low field displacement of the $H_{9,10}$ (Δδ = 0.97) and $H_{2,7}$ (Δδ = 0.36) peaks relative to the chemical shifts of the analogous protons of pyrene (δ 8.07 and 8.00, respectively)[2] is consistent with their location peri and ortho to the carbonyl functions. This NMR spectral pattern is also consistent with the reported spectrum of 1,8-dibromopyrene.[3]

The 1,6-diacetylpyrene structure was the only isomeric assignment consistent with the NMR spectral pattern of the highest melting isomer (mp 206.5-207.5°). Thus, the pair of low field doublets at δ 9.06 and 8.39 ppm were assigned to the protons adjacent to the carbonyl functions, $H_{5,10}$ and $H_{2,7}$, respectively. The second pair of doublets at δ 8.22 and 8.17 were assigned to the remaining protons, $H_{3,8}$ and $H_{4,9}$, respectively, on the basis of their coupling constants ($J_{2,3}$ = 8.0 and $J_{4,5}$ = 9.3 Hz). Again, no other diacetylpyrene isomer structures are consistent with this NMR spectral pattern.

The NMR spectrum of the remaining isomer (mp 184.5-185.5°) supports its assignment as the unusual 1,3-diacetylpyrene isomer (3). Thus, the appearance of a triplet at δ 8.10 assigned to H_7 indicates the presence of an unsubstituted ring with three adjacent protons. The location of the second acetyl group in the 3-position is supported by the presence of a relatively low field singlet (δ 8.69) assigned to H_2 and a doublet at δ 8.97 ($J_{4,5}$ = 9.3 Hz) associated with $H_{4,10}$ located peri to the carbonyl functions. The chemical shifts and couplings of the remaining protons are also consistent with their assignments.[2] Other possible diacetylpyrene isomers may be ruled out, since they lack similar symmetry and may be expected to exhibit more complex NMR spectral patterns.

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Chloroacetylation of pyrene with chloroacetyl chloride and $AlCl_3$ in CS_2 according to the procedure of Vollmann et al.[1] gave two isomeric bis(chloroacetyl)-pyrenes melting at 288° and 202°, identified previously on the basis of chemical evidence as 1b and 2b, respectively. Reduction of 1b with BF_3 etherate and LiI in tetrahydrofuran[4] furnished a diacetylpyrene isomer whose NMR spectrum was identical with 1,6-diacetylpyrene (1a). Similarly, reduction of 2b gave 1,8-diacetylpyrene identical by NMR with 2a obtained by direct acetylation. These findings confirm the prior assignments of 1,6- and 1,8-bis(chloroacetyl)pyrene made by Vollmann et al.[1] on the basis of chemical evidence.

Analogous benzoylation of pyrene gave two isomeric dibenzoylpyrenes, (1c and 2c) melting at 243.5-245° and 168-169°, identified previously as 1,6- and 1,8-dibenzoylpyrene (lit.[1] mps 239° and 167°), respectively. The NMR spectra of 1c and 2c were consistent with their assignments. The aromatic protons of the benzoyl groups appeared at highest field (a doublet and two triplets, in the expected 2:2:1 ratio) outside the range of the other aromatic protons. Other features of the NMR spectra of 1c and 2c were essentially identical with those of 1a and 2a.

1,3-Diacetylpyrene (3) is the first example of a 1,3-disubstituted pyrene derivative formed by electrophilic substitution.[5] While analogous 1,3-isomeric products were not isolated from the benzoylation or chloroacetylation reactions of pyrene, minor amounts of these isomers may be present in the mother liquors.

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EXPERIMENTAL SECTION

Diacetylation of Pyrene . - To a stirred solution of pyrene (16.18 g, 80 mmol) in CS_2 (325 ml) was added anhydrous $AlCl_3$ (32.5 g, 244 mmol). The dark solution was cooled in an ice bath, and acetyl chloride (13.9 g, 177 mmol) was added with stirring over 10 min. Stirring was continued for 2 hrs at room temperature. The reaction mixture was poured into ice-water, stirred for 2 hrs, then allowed to stand overnight. The yellow

precipitate was collected, washed with CS_2 and H_2O and dried. The crude mixture of diacetylated products (21.75 g, 95%) was stirred with CH_2Cl_2 (125 ml) for 15 min and filtered to yield 6.45 g of a yellow solid, mp 168-190°. This solid was stirred with CH_2Cl_2 (50 ml) for 20 min, and filtered to afford 3.38 g of an insoluble residue which melted at 203-207°. The mother liquors were evaporated to dryness, and again triturated with CH_2Cl_2 (25 ml) to give an additional 100 mg of the least soluble diacetylpyrene isomer, mp 205-206.5°. The product fractions (3.48 g) melting above 200° were combined and recrystallized from benzene to yield pure 1,6-diacetylpyrene (3.04 g), mp 206.5-207.5°. NMR (500 MHz, $CDCl_3$, standard Me_4Si): δ 9.05 (d, 2H, $H_{5,10}$), 8.39 (2H, d, $H_{2,7}$), 8.22 (2H, d, $H_{3,8}$), 8.17 (2H, d, $H_{4,9}$), 2.90 (6H, s, Me); $J_{2,3}$ 8.0, $J_{4,5}$ 9.3 Hz.

The combined mother liquors were evaporated to dryness, and the residue (17.86 g) was chromatographed on Florisil (800 g). Initial elution with benzene-ether (95.5) gave a mixture of 1a and 3 (5.26 g). Fractional crystallization of this mixture from benzene gave pure 1,3-diacetylpyrene (2.52 g), mp 184.5-185.5°. NMR (500 MHz): δ 8.97 (2H, d, $H_{4,10}$), 8.69 (1H, s, H_2), 8.32 (2H, d, $H_{5,9}$), 8.30 (2H, d, $H_{6,8}$), 8.10 (1H, t, H_7); $J_{4,5}$ 9.3, $J_{6,7}$ 7.6 Hz.

Elution of the column with decreasing ratios of benzene-ether to 1:1 gave 10.45 g of crude 1,8-diacetylpyrene. Recrystallization from benzene gave pure 2a (8.24 g), m.p. 162-163°: NMR (500 MHz): δ 9.04 (2H, d, $H_{9,10}$), 8.36 (2H, d, $H_{2,7}$), 8.18 (2H, d, $H_{3,6}$), 8.09 (2H, s, $H_{4,5}$), 2.89 (3H, s, Me); $J_{2,3}$ 8.0 Hz.

Attempted separation of the diacetylpyrene isomers by chromatography without prior trituration with CH_2Cl_2 to remove 1a gave an initial fraction which crystallized in beautiful orange needles, and melted sharply at 166-167°. Despite the narrow range of its melting point, its NMR spectrum revealed it to be a mixture of the 1,3-and 1,6-diacetylpyrene isomers. Interestingly, the individual pure isomers are lemon yellow rather than orange.

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Synthesis of 1,6- and 1,8-diacetylpyrene (1a, 2a) via reduction of 1,6- and 1,8-bis (chloroacetyl) pyrene (1b,2b) . - To a stirred suspension of 1b[1] (533 mg, 1.5 mmol) in a solution of $BF_3 \cdot Et_2O$ (0.46 ml, 3.7 mmol) in anhydrous THF (40 ml) under N_2 a solution of anhydrous LiI (1.34 g, 10 mmol) in dry THF (30 ml) was added dropwise over 20 min. Stirring was continued for 90 min, then the dark solution was poured into 350 ml of 0.5% $Na_2S_2O_3$ solution. The yellow precipitate was filtered, washed with water, and dissolved in CH_2Cl_2. The solution was dried and concentrated to a small volume and adsorbed on 6 g of Florisil which was added to the top of a column of Florisil. Elution with CH_2Cl_2 gave 1a (330 mg, 77%), mp 186.5-190°; recrystallization from $EtOH/CHCl_3$ and from benzene raised the mp to 204-205°; mixed mp with authentic 1a did not depress; the NMR spectrum was identical with that of 1a obtained from direct acetylation of pyrene.

Analogous reduction of 2b (1.07 g, 3 mmol) furnished 2a (530 mg, 61%), mp 157-159°; recrystallization from ethanol raised the mp to 160-161°; mixed mp with authentic 2a did not depress; the NMR spectrum was identical with authentic 2a.

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