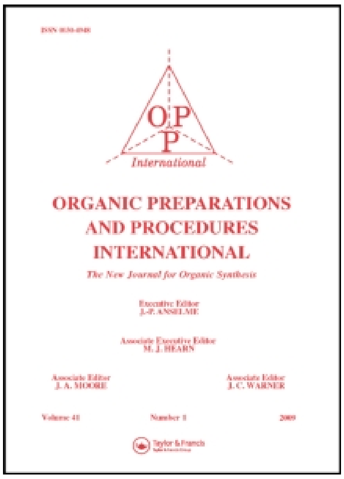

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OPPI BRIEFS

A CONVENIENT ONE-STEP SYNTHESIS OF DIALKYLBENZO[k]FLUORANTHENES AND TETRAETHYL *bis*-BENZO[k][k']FLUORANTHENES

Submitted by (10/16/95

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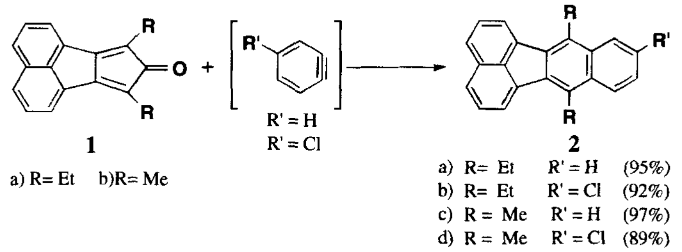
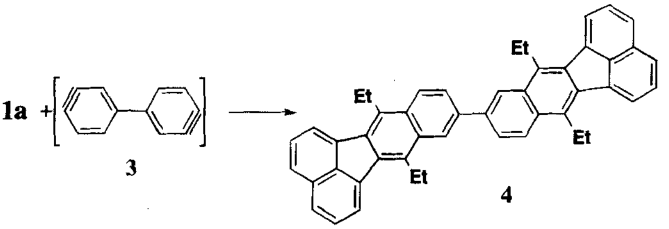
Benzo[b]fluoranthenes and benzo[k]fluoranthenes are of considerable interest because they are among the most commonly detected polycyclic aromatic hydrocarbons (PAH) in a large variety of combustions in the environment.[1] The availability of the methylated and ethylated and other derivatives would facilitate analytical studies of their possible presence in combustion pollutants. 7,9-Dialkyl-8-cyclopentan[a]acenaphthylene-8-one which exist as dimers were converted, by heating, to their monomeric forms **1a** and **1b** and reacted with benzyne and 4-chlorobenzyne in refluxing 1,2-dichloroethane. This paper describes the one step synthesis of 7,12-dialkylbenzo[k]fluoranthenes and their chloro derivatives **2a-2d** in high yields; they were fully characterized by ^{1}H NMR, IR, UV and elemental analysis. All the resulted PAH,s except the dimethyl derivative are new compounds. The synthesis of 7,12-dimethylbenzo[k]fluoranthene **2c** has been reported in four steps in less than 30% yield.[2] The reaction of cyclone **1a** with *bis*-benzyne **3** generated from 3,3'-dicarboxy-4,4'-diaminobiphenyl gave the decarbonylated bis-adduct **4**. The carbonyl-bridged *bis*-adduct is not stable at the reaction temperature and it lost carbon monoxide to give the *bis*-adduct **4**. The IR, ^{1}H NMR spectra and elemental analysis **4** are in agreement with structure **4**. Solutions of **4** in chloroform, methanol and other solvents showed intense violet fluorescence. 7,8-Dialkylbenzo[k]fluoranthenes, their chloro derivatives and tetraethyl *bis*-benzo[k][k']fluoranthene can be readily prepared in one step. These very strongly fluorescent polycyclic aromatic hydrocarbons may be used as a standard reference compound in environmental research.



1
a) R= Et b)R= Me

2

a) R= Et R' = H (95%)
b) R= Et R' = Cl (92%)
c) R = Me R' = H (97%)
d) R = Me R' = Cl (89%)



3

4

EXPERIMENTAL SECTION

All melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by Research Institute of Petroleum Industry,Tehran, I. R. Iran. Infrared spectra were recorded as KBr pellets on a Shimadzu 435 infrared spectrophotometer. Vibrational transition frequencies are reported in cm^{-1}. Band intensities are assigned as weak (w), medium (m), strong (s). 1H NMR (90MHz) spectra were determined in $CDCl_3$ using TMS as astandard on a Varian EM-390 instrument. Ultraviolet and visible spectra were measured with a Shimadzu 240 UV-visible spectrophotometer. All the λmax in, nm were recorded in chloroform and ε lit.mol^{-1}.cm^{-1} are shown in parentheses. Thin layer chromatography (TLC) on commercial plates of silica gel 60 F254 on aluminum was used to monitor the progress of reaction. Column chromatography was carried out using silica gel 60 (Riedel de Haen AG). 7,9-Diethyl and 7,9-dimethyl-8-cyclopenta[a]acenaphthylene-8-one (**1a-b**) were synthesized as a dimer from a reported procedure.[3]

Synthesis of 7,12-dialkybenzo[k]fluoranthenes. General Procedure.- one equivalent of dimeric cyclone was dissolved in minimum amount of 1,2-dichloroethane and was heated to reflux. Solutions of one equivalent of anthranilic acid in a minimum amount of 1,2-dichloroethane and 4 equivalents of isoamyl nitrite in the same amount of 1,2-dichloroethane were added dropwise separately and simultaneously to the refluxing mixture over a period of 2 hrs. Reflux was continued for 40 min. The solvent was removed under reduced pressure. The residue was triturated with methanol to give yellow solids.

7,12-Diethylbenzo[k]fluoranthene (2a), yield 95% (from EtOH), mp. 184-185°. IR (KBr): 3030 (w), 2950 (m), 2900 (m), 2850 (w), 1578 (s), 1510 (w), 1478 (w), 1425 (s), 820 (w), 775 (m), 760 (m), 670 (w) cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.05 (t, 6H, J = 7.5Hz), 3.55 (q, 4H, J = 7.5Hz), 7.41-7.80 (m, 6H), 8.00-8.22 (m, 4H). UV-vis: 416 (21235), 392 (20448), 373 (11533).

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.40; H, 6.80

9-Chloro-7,12-diethylbenzo[k]fluoranthene (2b), yield 92% (from EtOH), mp. 175-176°. IR (KBr) 2960 (m), 2900 (m), 2840 (m), 1590 (s), 1475 (s), 1460 (m), 1445 (m), 1420 (s), 1115 (w), 1100 (w), 1050 (w), 950 (w), 920 (w), 885 (w), 865 (w), 820 (s), 785 (w), 765 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$,TMS):

δ 1.40 (t, 6H, J = 7.5Hz), 3.40 (q, 4H, J = 7.5Hz), 7.30-7.80 (m, 3H), 7.95-8.20 (m, 6H). UV-vis: 416 (15889), 392 (14871), 372 (8685).

Anal. Calcd. for $C_{24}H_{19}$ Cl: C, 84.07; H, 5.59. Found: C, 84.40; H, 5.90

7,12-Dimethylbenzo[k]fluoranthene (2c), yield 97% (from EtOH), mp. 185-186°, lit.[2] 194-195°. IR (KBr): 3050 (w), 2900 (w), 2900 (w), 2850 (w), 1615 (m), 1430 (m),1380 (m) 1010 (w), 820 (m), 775 (s), 750 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): δ 2.95 (s ,6H), 7.35-7.80 (m, 6H), 7.90-8.10 (m, 4H). UV-vis: 415 (19116), 392 (18678), 372 (11144).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.60; H, 5.50

9-Chloro-7,12-dimethylbenzo[k]fluoranthene (2d), yield 89% (from 2-propanol), mp. 178-179°. IR (KBr): 3030 (w), 2900 (w), 1590 (s), 1495 (m),1420 (m),1380 (m), 1210 (w), 1115 (m), 1095 (m), 900 (w), 880 (m), 860 (m),800 (m),760 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$,TMS): δ 2.95 (s, 6H), 7.50-7.90 (m, 6H), 8.20-8.30 (m, 3H) . UV-vis: 414 (16936), 392 (15850), 372 (9223).

Anal. Calcd. for $C_{22}H_{25}Cl$: C, 83.94; H, 4.80. Found: C, 83.60; H, 4.60

Synthesis of 7,12,7',12'-Tetraethyl-9,9'-*bis*[k][k']fluoranthene (4).- A solution of 3,3'-dicarboxy-4,4'-diaminobiphenyl[4a-c] in dimethoxyethane and minimum amount of dimethyl sulfoxide (DMSO) and a solution of isoamyl nitrite in 1,1,2-trichloroethane were added dropwise to a refluxing solution of cyclone **1a** in 1,1,2-trichloroethane. The crude product was triturated with methanol and was chromatographed on silica gel with carbon tetrachloride (R_f = 0.83) and was recrystallized from ethanol to give yellow crystals. Yield (crude) 99%, mp. 300-303°. IR (KBr): 3040 (W), 2900 (m), 2850 (m), 1605 (w), 1455 (w), 1425 (w),1370 (w), 820 (m), 765 (s) cm^{-1}. The insolubility of compound **9** precluded any NMR measurements.

Anal. Calcd. for $C_{48}H_{38}$: C, 93.77; H, 6.23. Found: C, 93.40; H, 6.30

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