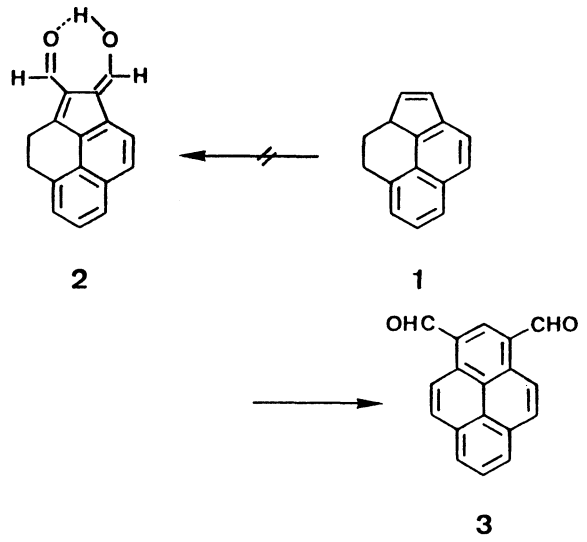
A Convenient Synthesis of 1,3-Pyrenedicarbaldehyde

Michael GOLTZ† and Ichiro MURATA*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
(Received April 14, 1988)

Synopsis. A convenient and preparatively useful access to the unknown 1,3-pyrenedicarbaldehyde is presented. When treated with an excess amount of *N,N*-dimethylformamide and phosphoryl chloride, 3,4-dihydro-2a*H*-cyclopenta[*cd*]phenalene was smoothly converted into dialdehyde in 57% yield. A plausible mechanism for this transformation was suggested from a labeling experiment using *N,N*-dimethylformamide-d_7.

Although pyrene is a reactive aromatic hydrocarbon and readily gives mono-, di-, tri-, and tetra-substitution in positions 1-, 1,6-, (and 1,8-), 1,3,6-, and 1,3,6,8-, respectively, by various electrophilic substitution reactions,[1] 1,3-disubstituted derivatives are hardly accessible. Quite recently, Harvey et al. reported that the acetylation of pyrene produced a mixture of 1,6- and 1,8-diacetylpyrene together with the 1,3-derivative, which was difficult to separate.[2] However, a selective introduction of carbon functionalities in these positions has not been reported so far. The only known 1,3-dialkyl derivatives are the 1,3-dimethylpyrene, which has been isolated together with its 1,8-isomer from a Vilsmeier formylation and reduction sequence of 1-methylpyrene,[3] and the 1,3-dipropylpyrene derived from 1-(2-chloro-1,3-dipropyl-2-cyclopropenyl)-1*H*-phenalene in poor yield.[4] During the course of our studies on nonalternant polycyclic hydrocarbons, we have found a convenient access to 1,3-pyrenedicarbaldehyde (**3**).

In order to synthesize the tetracyclic aldehyde **2** as a potential building block for the construction of various nonalternant hydrocarbons including a phenalene ring system,[5] the Vilsmeier reaction of 3,4-dihydro-2a*H*-cyclopenta[*cd*]phenalene (**1**)[6] was carried out. When treated with a large excess of *N,N*-dimethylformamide and phosphoryl chloride at room temperature for 14 h, compound **1** was smoothly converted into a stable crystalline product, yellow needles, mp 245—246 °C as the sole product in 57% yield. In contrast to our expectation, the structure of the obtained product was unambiguously established not as **2** but as 1,3-pyrenedicarbaldehyde (**3**), as shown in Scheme 1, from an elemental analysis and the following spectroscopic data. The electronic spectrum of **3** exhibits absorption bands similar to those of 1-pyrenecarbaldehyde.[7] Its IR spectrum shows the characteristic absorptions of aromatic aldehydes at 2700 and 1650 cm^{-1}. The presence of two formyl groups was established by its mass spectral fragmentation of m/z 258 (M^+, 33%), 229 (M^+ −CHO, 25%), and 200 (M^+ −2CHO, 100%). The NMR spectra reflect the C_{2v} symmetry. Thus, in $CDCl_3$ at 500 MHz, the two aldehyde protons appear as one singlet at δ 10.78 and the aromatic protons show an AB-quartet (4H) at δ 8.46 (H-5 and 9) and 9.49 (H-4 and 10) with J= 9.15 Hz, AX_2 pattern (3H) at δ 8.19 (H-7) and 8.43 (H-6 and 8) with J= 7.63 Hz, and 1H singlet at δ 8.83 (H-2). Its eleven carbon types was also revealed by the ^{13}C NMR spectrum (see Experimental).



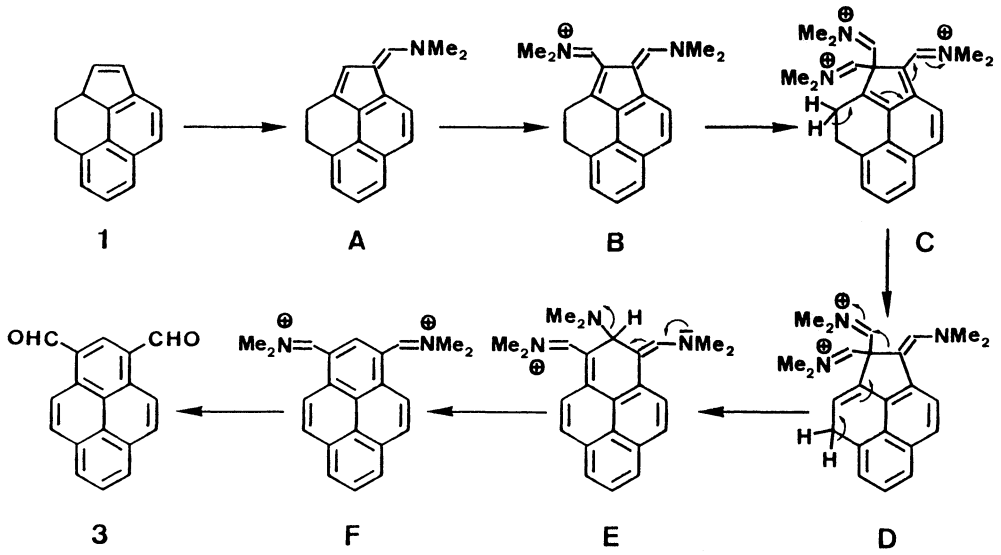
Scheme 1.

The mechanism for the transformation of **1** to **3** is of particular interest. It should be noted that one CH-unit was incorporated into the ring skeleton of **1** and that the dehydrogenation took place during a reaction at room temperature under nitrogen.

The origin of the additional carbon atom was confirmed by a Vilsmeier reaction of **1** using *N,N*-dimethylformamide-d_7. Thus, the ^1H NMR spectrum of product **3**-d_3 from this reaction clearly reveals the deuterium incorporation at the 2-position of the pyrene skeleton in addition to the two formyl groups. Hence, the CH-unit at the 2-position must have arisen from the Vilsmeier reagent.

From a labeling experiment, together with the well-documented Vilsmeier reaction of cyclopentadiene derivatives,[8] we propose a plausible mechanism that might account for the transformation of **1** to **3** involving multi-step reactions, as shown in Scheme 2. As for the first and second steps, several precedents for the formation of 6-dimethylamino-1-[dimethyliminiomethyl]fulvenes appear in the literature.[8] Regarding the third step, we postulate that the Vilsmeier reagent attacks at the 6-position of the ring system to produce the tri-substituted intermediate **C**, which readily expels a proton owing to the generation of a naphthalene conjugation (**C**→**D**). The second deprotonation can occur with an expansion of the five-membered ring, followed by an elimination of dimethylamine to form a pyrene skeleton **F** which leads to the observed

† JSPS postdoctral fellow. M.G. expresses gratefully his thanks for a grant to the Japan Society for the Promotion of Science.



Scheme 2.

product **3** after a workup.

In summary, we have demonstrated that the Vilsmeier reaction of readily available hydrocarbon **1** provides a convenient, preparatively useful approach to **3** which might be used for the synthesis of hardly accessible [2.2]metapyrenophanes,[9] triangulenequinone,[10] and various carcinogenic polycyclic aromatic compounds.[11] We hope to report on additional experiments along this line in the near future.

Experimental

All melting points are uncorrected. IR spectra were measured in KBr with a JASCO A-100 spectrophotometer. The UV spectrum was measured with a Hitachi 340 recording spectrophotometer. Mass spectra were determined on a JEOL JMS-01SG-2 spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on JEOL JNM-GX 500 spectrometer (500 MHz). ^{13}C NMR spectra were taken on JEOL FX-90Q spectrometer (22.5 MHz). All chemical shifts are reported in δ units downfield from internal Me_4Si, and the J values are given in hertz. All reactions were carried out under a nitrogen atmosphere.

1,3-Pyrenedicarbaldehyde (3). To a stirred solution of 3,4-dihydro-2a*H*-cyclopenta[*cd*]phenalene (3.00 g, 15.6 mmol) (**1**) in tetrahydrofuran (20 cm^3, distilled from benzophenone ketyl) is added under nitrogen at room temperature a mixture of *N*,*N*-dimethylformamide (18.8 g, 0.25 mol, distilled from CaH_2) and phosphoryl chloride (19.8 g, 0.13 mol). The solution warms and iminium salt precipitates. After 14 h the solvent was removed under reduced pressure, 2 mol dm^{-3} sodium hydroxide (500 cm^3) was added and the mixture was extracted with dichloromethane (3×500 cm^3). The combined organic layers were dried with $MgSO_4$ and evaporated. Chromatography of the residue on silica gel (6% water) with dichloromethane gave a large yellow band which was collected. Removal of the solvent and recrystallization from dichloromethane afforded yellow crystals of 1,3-pyrenedicarbaldehyde (**3**) (2.3 g, 57% yield): yellow needles from dichloromethane, mp 245—246 °C (sealed capillary tube, sublimes at around 200 °C); IR (KBr) 1650, 2700 cm^{-1}; UV/VIS (in CH_2Cl_2) λ_{max} (ε) 244 (17200), 285 (25200), 292 (28000), 396 (29900), 400 (sh, 31500), 403 (32000), 407 (sh, 29900) nm; MS, (70 eV) *m*/*z* (rel intensity) 258 (M^+, 33%), 229 (M^+—CHO, 25%), 202 (30%), 201 (65%), 200 (M^+—2CHO, 100%), 199 (34%), 198 (30%); ^{1}H NMR ($CDCl_3$), δ= 10.78 (s, 2H, 1-CHO, 3-CHO), 9.49 (d, 2H, J= 9.15 Hz, H-4 and -10), 8.83 (s, 1H, H-2), 8.46 (d, 2H, J= 9.15 Hz, H-5 and -9), 8.43 (d, 2H, J= 7.63 Hz, H-6 and -8), 8.19 (t, 1H J= 7.63 Hz, H-7); ^{13}C NMR ($CDCl_3$), δ= 192.06, 137.34, 134.63, 133.98, 130.51, 129.04, 127.37, 127.14, 125.24, 123.81, 123.17. Found: C, 83.69; H, 3.90%. Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%.

A Vilsmeier reaction of the isomeric 3,4-dihydro-1*H*-cyclopenta[*cd*]phenalene gave comparable results. The treatment of **1** with two equivalents of *N*,*N*-dimethylformamide/phosphoryl chloride likewise leads to **3** and a recovery of the starting hydrocarbon **1**, while hydroxyfulvene **2** was not observed.

1,3-Pyrenedicarbaldehyde-d_3 (3-d_3). This compound was obtained from the Vilsmeier reaction of **1** with *N*,*N*-dimethylformamide-d_7 and phosphoryl chloride.

Exact mass, Found: *m*/*z* 261.0850; Calcd for $C_{18}H_7O_2D_3$; M, 261.0869. ^{1}H NMR signals at δ= 10.78 and 8.83 in **3** were completely disappeared.

The present study was partially supported by a Grant-in-Aid for Special Project Research No. 60129030 from the Ministry of Education, Science and Culture.

References

1) E. Clar "Polycyclic Hydrocarbons," Vol. II, Academic Press, New York (1964).

2) R.G. Harvey, J. Pataki, and H. Lee, *Org. Prep. Proced. Int.*, **16**, 144 (1984).

3) M. de Clercq and R.H. Martin, *Bull. Soc. Chim. Belg.*, **64**, 367 (1955).

4) I. Murata, T. Nakazawa, and K. Shima, *Chem. Lett.*, **1972**, 669.

5) For example, K. Nakasuji, K. Yoshida, and I. Murata, *J. Am. Chem. Soc.*, **105**, 5136 (1983).

6) I. Murata, K. Nakasuji, K. Yamamoto, T. Nakazawa, Y. Kayane, A. Kimura, and O. Hara, *Angew. Chem.*, **87**, 170 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 170 (1975).

7) R.N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

8) K. Hafner, K.H. Vopel, G. Ploss, and C. Konig, *Justus Liebigs Ann. Chem.*, **661**, 52 (1963); see also: Houben-Weyl, Methoden der Organischen Chemie, Vol. 5/2c, Carbocyclische π-Elektronen-Systeme, Georg Thieme Verlag, Stut-

tgart, New York, 1985, pp. 553—557.
9) T. Umemoto, T. Kawashima, Y. Sakata, and S. Misumi, *Chem. Lett.*, **1975**, 837.
10) O. Hara, K. Tanaka, K. Yamamoto, T. Nakazawa, and I. Murata, *Tetrahedron Lett.*, **1977**, 2435.
11) R.G. Harvey and P.P. Fu, "Polycyclic Hydrocarbons and Cancer," Vol. 1, ed by H.V. Gelboin and P.O.P. Ts'o by Academic Press, New York (1978), Chap. 6.