A Convenient Preparation of Benzo[*k*]fluoranthene

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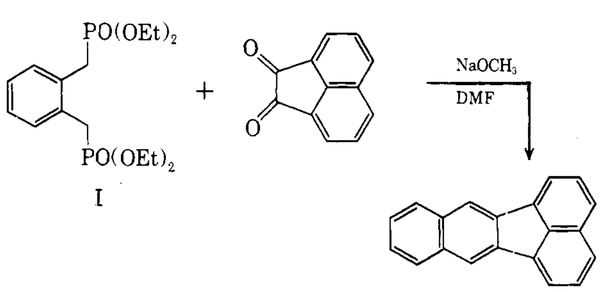
A useful modification of the Wittig reaction is that employing alkylphosphonate carbanions[1-4] in place of alkylidinetriphenylphosphoranes. In the presence of sodium methoxide, acenaphthenequinone and phosphonate I[5] condense smoothly to afford a moderate yield of benzo[*k*]fluoranthene.



The yield in this condensation, 20-27%, is relatively insensitive to the order of addition of the reagents, the nature of the metal alkoxide ($LiOCH_3$ or $NaOCH_3$), or the presence of methanol in the reaction mixture,[3] but drops to less than 1% when the reaction is conducted at 105°.

Experimental

A solution of 2.0 g. (37 mequiv.) of sodium methoxide in 20 ml. of anhydrous methanol was added over a period of 0.5 hr. to a slurry of 1.82 g. (10 mmoles) of acenaphthenequinone and 4.0 g. (10.5 mmoles) of tetraethyl *o*-xylylenediphosphonate in 25 ml. of dry DMF which was stirred at 0° under a nitrogen atmosphere. On completion of addition of the sodium methoxide solution the dark reaction mixture was allowed to stir at 0° for 1 hr. and at 25° for 2 hr. and then poured into 150 ml. of water. The aqueous layer was extracted with five 50-ml. portions of chloroform and the combined chloroform extracts were evaporated. The dark residue was taken up in 150 ml. benzene and the benzene solution was washed with 10-ml. portions of water until the aqueous extracts were colorless followed by saturated salt solution, dried over anhydrous sodium sulfate, and evaporated. The dark residue was chromatographed on 100 g. of alumina (Fisher Scientific Co.). Elution with 5% benzene in hexane afforded, after recrystallization from benzene, 554 mg. (22% yield) of benzo[*k*]fluoranthene as faintly yellow flakes, m.p. 215–216° (lit.[6] m.p. 217°), whose ultraviolet spectrum agreed with the published spectrum.[7].

Anal. Calcd. for $C_{20}H_{12}$: C, 95.21; H, 4.79. Found: C, 95.18; H, 4.78.

Large-scale reactions using nonchromatographic work-ups were not attempted.

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[2] E. J. Seus and C. V. Wilson, *J. Org. Chem.*, **26**, 5243 (1961).

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Reactions of Cyclooctanone Oxime Tosylate with Organolithium Reagents[1a]

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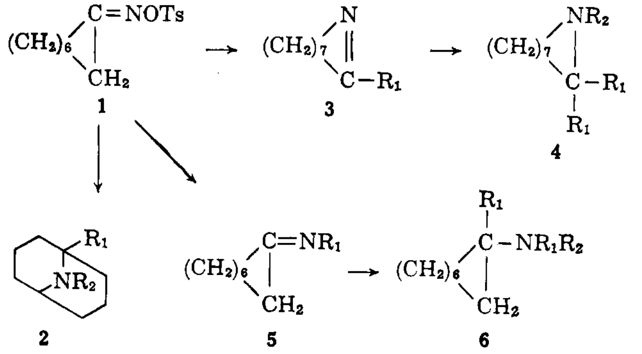
The recent disclosure by Pelosi and Lyle[2] on the reactions of oxime tosylates with Grignard reagents has prompted the reporting of a similar investigation involving cyclooctanone oxime tosylate **1** and organolithium reagents. The purpose of these experiments was to determine whether an electron-deficient nitrogen could be produced by the attack of an organolithium reagent on the C=N bond of an oxime tosylate with concomitant loss of the tosyl group.



a, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = C_6H_5$; $R_2 = H$
c, $R_1 = CH_3$; $R_2 = C_6H_5SO_2-$
d, $R_1 = C_6H_5$; $R_2 = C_6H_5SO_2-$

In view of the ease with which cyclooctane systems undergo transannular reactions, it seemed plausible that, if an electron-deficient nitrogen were generated, a transannular insertion reaction might produce an 9-azabicyclo[3.3.1]nonane derivative **2**. Since it was recognized that a Stieglitz rearrangement[3] could occur rather than, or in addition to, the desired reaction, the possibility that the resultant crude product would be a mixture of **2**, **3**, **4**, **5**, and **6** was considered. To facilitate the separation of these possible products, the material obtained from the reaction mixtures was treated with aqueous acid in order to hydrolyze any Schiff's bases **3** and **5**. After extraction with ether the acidic solution was made alkaline, and the resulting basic fraction was treated with benzenesulfonyl chloride in aqueous sodium hydroxide.

The reaction of methyllithium with **1** at $-30°$ was highly exothermic and yielded only one isolable product **4a** (71% as the benzenesulfonamide **4c**). The infrared spectra of the crude and purified material were essentially the same. The structural assignment was based primarily on spectral evidence. The presence of a *gem*-dimethyl group was clearly indicated by infrared absorptions at 1385 and 1370 cm.$^{-1}$. The n.m.r. spec-

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[1] (a) Abstracted from part of the Ph.D. Dissertation of N. W. Gabel, Dec., 1961; (b) Biological Research Laboratories, Department of Psychiatry, College of Medicine, University of Illinois, Chicago, Ill.

[2] S. S. Pelosi, Jr., and R. E. Lyle, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, p. 47N.

[3] (a) J. Stieglitz and P. N. Leech, Jr., *J. Am. Chem. Soc.*, **36**, 272 (1914); (b) M. L. Cohn, Ph.D. Dissertation, University of Chicago, 1929.