## A Convenient Preparation of Benzo[*k*]fluoranthene

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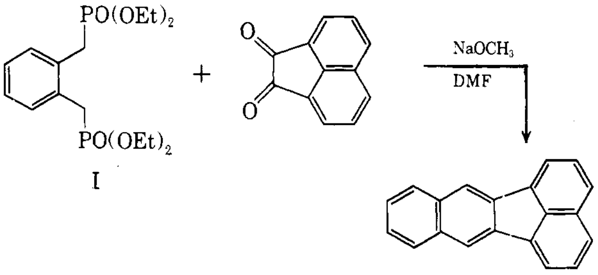
*Received March 27, 1964*

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.

**Acknowledgment.**—Partial support by the National Science Foundation is gratefully acknowledged.

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(1) W. S. Wadsworth, Jr., and W. P. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

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

(3) H. O. Huisman, *Chem. Weekblad*, **59**, 133 (1963).

(4) S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

(5) W. Stilz and H. Pommer, German patent 1,124,949 (1962); *Chem. Abstr.*, **57**, 3358c (1962).

(6) E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, 1952, p. 408.

(7) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum 543.

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

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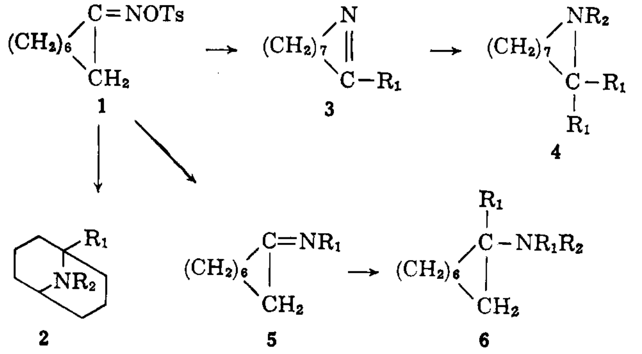
*Received May 28, 1964*

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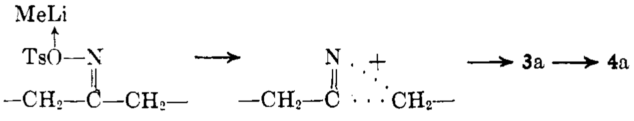
(1) (a) Abstracted from part of the Ph.D. Dissertation of N. W. Gabel, Dec., 1961; (b) Biological Research Laboratories, Department of Psychiatry, College of Medicine, University of Illinois, Chicago, Ill.

(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.

trum disclosed a multiplet with center at $\tau$ 2.41 (phenyl hydrogens), a small broad peak at 7.35 (hydrogens of methylene group adjacent to heterocyclic nitrogen), a sharp resonance peak at 8.30 (methyl hydrogens $\beta$ to sulfonamide nitrogen),[4] and a peak at 8.56 (methylene hydrogens). The ratio of aliphatic to aromatic hydrogens was 4.

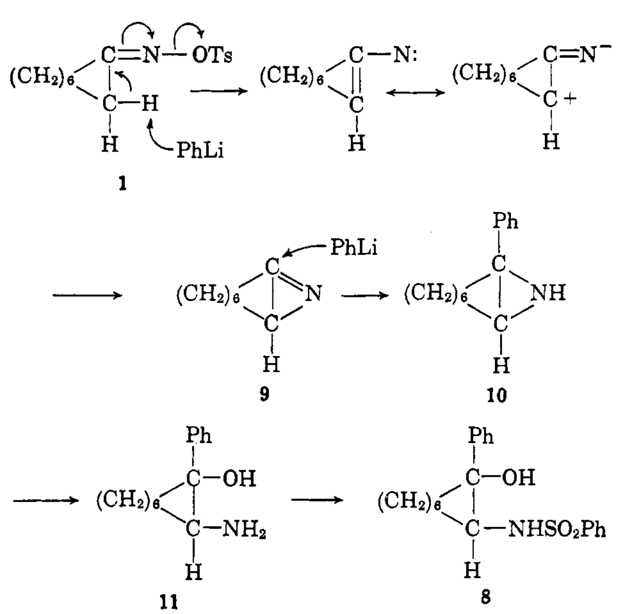
Although methyllithium appears to have added to the C=N double bond of **1** with concomitant loss of the tosyl group, the absence of an insertion product **2a** which might have resulted from the formation of an electron-deficient nitrogen intermediate suggests that loss of the tosyl group did not proceed concertedly with addition of a nucleophile. Futhermore, since there is probably little difference between the intrinsic migratory aptitudes of methylene and methyl groups, the absence of any product **6a** resulting from migration of the methyl group seems to indicate an intermediate similar to the one which is depicted for the Beckmann rearrangement. The tosyl group is removed *via* the electrophilic attack of the lithium from the methyllithium ion pair. The intermediate **7** then reacts with methyllithium to give **3a** and then finally **4a**.



**7**

When phenyllithium and **1** were stirred together for 5 hr. at room temperature, treatment of the reaction mixture in the previously stated manner again yielded only one isolable product (62% as the benzenesulfonamide) having an empirical formula of $C_{20}H_{25}NO_3S$. This immediately excluded **2b**, **4b**, **5b**, and **6b** as products of the reaction. Although the benzenesulfonyl derivative of the amine resulting from hydrolysis of **3b** has the same empirical formula, the carbonyl region of the infrared spectrum was blank. The infrared spectrum of a dilute chloroform solution showed sharp absorption peaks at 3610 and 3385 cm.$^{-1}$ which can be attributed to nonbonded O–H stretching and N–H stretching of a monosubstituted benzenesulfonamide.[5]

The only structure which can be written to accomodate the foregoing evidence and can also be rationalized on the basis of the probable course of the reaction is **8**. What apparently occurs is a base-induced $\gamma$-elimination of the tosyl group followed by ring closure to an intermediate azirine **9** which is then attacked by a second mole of phenyllithium to give 1-phenyl-9-azabicyclo-[6.1.0]nonane **10**. Acid-catalyzed hydrolysis of the aziridine ring gave 1-phenyl-1-hydroxy-2-aminocyclooctane **11** which was isolated as its benzenesulfonamide **8**. Campbell, *et al.*,[6] have shown that acid-catalyzed hydrolysis of 2-arylaziridines only yields amino alcohols with hydroxy groups and aryl groups on the same carbon atom. It should be noted that reaction **1** → **9** is a Neber rearrangement[7] the mechanism of which has been previously proposed by Cram and Hatch.[7c]



**1** **9** **10** **11** **8**

As corroboration for the structural assignment of **8**, its n.m.r. spectrum in deuteriochloroform disclosed two sharp resonance peaks at $\tau$ 2.81 and 3.11 (phenyl hydrogens), a diffuse doublet with center at 5.00 (sulfonamide hydrogen), a diffuse peak with center at 6.25 (hydrogen $\alpha$- to amide nitrogen), a broad peak at 7.76 (hydroxyl hydrogen), and a broad peak with center at 8.64 (methylene hydrogen). After the deuteriochloroform solution was shaken with deuterium oxide, the peaks at $\tau$ 5.00 and 7.67 disappeared demonstrating that both were due to exchangeable protons.

Since there are two asymetric carbon atoms in **8**, there is a possibility of two pairs of enantiomorphs arising from this reaction sequence. However, during the SN1 acid-catalyzed hydrolysis of the aziridine **10**, the most thermodynamically stable isomer with both phenyl and amino groups in quasi-equitorial positions should be formed. This would result in the isolation of only one pair of enantiomorphs as the product.

An explanation for the difference between the reactions that **1** underwent with methyllithium and phenyllithium can be found in their differing behavior as electrophilic reagents. Alkyllithium compounds are known to act as electrophilic reagents owing to coordination of the lithium with centers of electron density in such reactions as metalations, halogen–metal interchange, and substitution of aromatic rings.[8] Phenyllithium, in contrast, is a very poor electrophile, evidenced by its greatly decreased reactivity compared with alkyllithiums in the aforementioned reactions.[8] Therefore, it did not bring about a Beckmann type of rearrangement but instead served as a base for the $\gamma$-elimination reaction.

## Experimental

**Reaction of Cyclooctanone Oxime Tosylate with Methyllithium.**—To a solution of 10.0 g. (0.034 mole) of cyclooctanone oxime

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(4) The resonance peak due to the methyl hydrogens of the *t*-butyl group of N-*t*-butyl-*p*-toluenesulfonamide was found to occur at $\tau$ 8.82. It is possible that in **4c** the phenyl ring is allowed to exert a greater deshielding effect.

(5) J. N. Baxter, J. Cymerman-Craig, and J. B. Willis, *J. Chem. Soc.*, **1955**, 669.

(6) K. N. Campbell, B. K. Campbell, L. G. Hess, and I. J. Schaffner, *J. Org. Chem.*, **9**, 184 (1944).

(7) (a) P. W. Neber and A. von Friedolsheim, *Ann.*, **449**, 109 (1926); (b) P. W. Neber, A. Burgard, and W. Thier, *ibid.*, **526**, 277 (1936); (c) D. J. Cram and M. J. Hatch, *J. Am. Chem. Soc.*, **75**, 33 (1953); (d) M. J. Hatch and D. J. Cram, *ibid.*, **75**, 38 (1953); (e) H. O. House and W. F. Berkowitz, *J. Org. Chem.*, **28**, 307, 2271 (1963).

(8) H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

tosylate[9] in 300 ml. of dry 5:1 ether–benzene at −30° was added dropwise 70 ml. of 1.5 *M* methyllithium (0.1 mole) in ether. A vigorous, exothermic reaction took place while the addition was carried out. At the end of the addition period the reaction mixture was allowed to warm up to room temperature and was then poured into 250 ml. of ice–water. The organic layer was separated, dried over $Na_2SO_4$, and evaporated at reduced pressure to a dark oil which was then stirred with 25 ml. of 1 *N* HCl for 1 hr. The acidic solution was extracted with ether to remove neutral material and was then made strongly basic and reextracted with ether. No cyclooctanone was found in the first extract. The second extract was evaporated to a dark oil which was treated with benzenesulfonyl chloride in aqueous sodium hydroxide. The basic aqueous solution was separated from insoluble material and upon acidification gave only a small amount of benzenesulfonic acid. The insoluble material yielded, after recrystallization from ethanol, 7.2 grams (71%) of a benzenesulfonamide of a secondary amine, m.p. 84°.

*Anal.* Calcd. for $C_{16}H_{25}NO_2S$ (295.44): C, 65.04; H, 8.41; N, 4.74; S, 10.85. Found: C, 64.70; H, 7.79; N, 5.08; S, 10.69.

**Reaction of Cyclooctanone Oxime Tosylate with Phenyllithium.**—A solution of 5.0 g. (0.017 mole) of cyclooctanone oxime tosylate in 150 ml. of dry ether and 50 ml. of dry benzene was cooled to −30°. With stirring under nitrogen 35 ml. of 1.5 *M* phenyllithium (0.05 mole) in ether was added dropwise over 15 min. No evolution of heat occurred when the reagent was added. The mixture was very slowly warmed to room temperature and stirred for 5 hr. The crude product was processed in the same manner as in the preceeding experiment and yielded 3.7 g. (62%) of a benzenesulfonamide, m.p. 140° (ethanol).

*Anal.* Calcd. for $C_{20}H_{25}NO_3S$ (359.48): C, 66.82; H, 7.01; N, 3.90. Found: C, 66.85; H, 7.04; N, 4.00.

**Acknowledgment.**—The author would like to thank Professor G. L. Closs for suggesting this problem.

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[9] (a) P. W. Neber and G. Huh, *Ann.*, **515**, 283 (1935); (b) P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948); (c) W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5880 (1958).

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# A New Bicyclic Thiete Sulfone[1]

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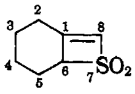
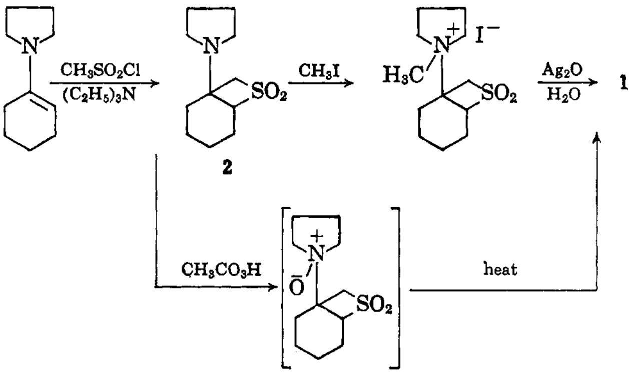
*Received May 12, 1964*

Only four reports of the synthesis of thiete sulfone (thiacyclobutene 1,1-dioxide) derivatives, all monocyclic, are found in the literature.[2-5] We were interested in the preparation of substituted thiete sulfones since these compounds might not undergo ring opening on reduction with lithium aluminum hydride as do several of the more simple derivatives.[4,6] Reports by Stork and Borowitz[7] and by Opitz and Adolf[8] of the synthesis of aminothietane sulfones by reaction of enamines with methanesulfonyl chloride in the presence of a base prompted us to apply this method to the synthesis of the bicyclic thiete sulfone, 7-thiabicyclo-[4.2.0]-1(8)-octene 7,7-dioxide (**1**).



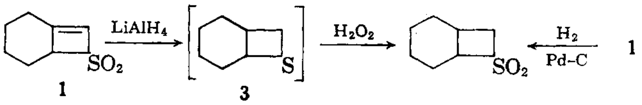
**1**

The reaction of methanesulfonyl chloride with cyclohexanone pyrrolidine enamine[9] in benzene in the presence of triethylamine gave an 80% yield of the cyclic sulfone **2**. Treatment of **2** with methyl iodide in methyl ethyl ketone gave the quaternary salt (30% yield) which was stirred overnight with freshly prepared silver oxide to yield, upon heating to 40–50°, the thiete sulfone **1**, in 35–40% yield. A better procedure is to convert the intermediate amine **2** to the amine oxide which on heating is converted to the unsaturated sulfone in 55–65% yield.



The structure of the bicyclic thiete sulfone **1** was supported by its infrared spectrum, proton magnetic resonance spectrum, elemental analysis, and molecular weight. Its infrared spectrum showed absorption at an olefinic C–H stretching frequency of 3003 cm.$^{-1}$ and at a C–C double bond stretching frequency of 1608 cm.$^{-1}$. The proton n.m.r. spectrum provides further proof that the double bond is *exo* to the six-membered ring. Absorption (at 60 Mc. relative to tetramethylsilane) occurs at $\delta$ 2.0 (relative area 8, protons of cyclohexane ring), 4.5 (relative area 1, 6-proton), and 6.2 (relative area 1, 8-proton). Had the double bond been between carbons 1 and 6, only two principal proton absorptions would have been observed in the ratio 8:2. The *exo* product is the one expected on the basis of a *trans* elimination of N-methylpyrrolidine.

Reduction of **1** with lithium aluminum hydride gives an oil (lacking infrared absorption for a sulfone or an olefin) which can be oxidized to a sulfone which is identical with the product obtained on catalytic reduction of the double bond of **1**. This result strongly suggests that the oil has structure **3**, and that this reduction of a thiete sulfone with lithium aluminum hydride is the first one which occurs without opening of the four-membered ring. The fused six-membered ring may hinder attack on the 6-position by hydride ion



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[1] This work was supported by Grant GP-726 of the National Science Foundation.

[2] D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

[3] W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Letters*, 1677 (1963).

[4] W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3236 (1963).

[5] R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963).

[6] D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

[7] G. Stork and I. J. Borowitz, *ibid.*, **84**, 313 (1962).

[8] G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 27 (1962).

[9] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).