Pergamon

*Tetrahedron Letters*, Vol. 38, No. 13, pp. 2333-2334, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00307-9

# Epoxidation of Polyaromatics Using $HOF{\bullet}CH_3CN$

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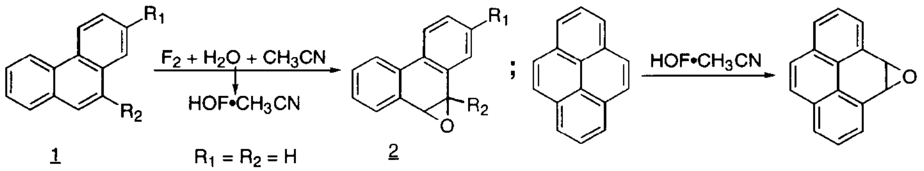
***Abstract:*** The reaction of the $HOF{\bullet}CH_3CN$ complex, made directly by passing fluorine through aqueous acetonitrile, with some phenanthrene and pyrene derivatives results in fast epoxidation.

Arene oxides have been identified as the primary metabolites of polycyclic aromatic compounds produced by mammalian cells and their biological importance has stimulated expending interest in their syntheses and chemistry.[1] Several preparation routes have been studied including direct oxidation of aromatic hydrocarbons in a two phase liquid system[2], under phase transfer conditions[3], utilizing hydrogen peroxide in the presence of dialkylcarbodiimide,[4] and applying dimethyldioxirane on the respective hydrocarbon.[5] Some arene oxides can be obtained only by one of these methods which might give unsatisfactory yields. In recent years the $HOF{\bullet}CH_3CN$ complex has proven to be an excellent oxygen transfer agent and was used for many oxidizing reactions including near quantitative epoxidation of many types of double bonds.[6] It is easily prepared in a matter of minutes in a glass vessel, by bubbling 10% $F_2$ in $N_2$, a mixture also commercially available, through 10% $H_2O$ in $CH_3CN$ solution at 0 °C. Concentrations of 0.25 to 0.5 molar are readily achieved and could be monitored by any iodometric titration method. No isolation, purification or other manipulation of the reagent is required. Its fast reactions, coupled with the very mild conditions required, prompted us to examine its interaction with some phenanthrene and pyrene derivatives.[7]

Thus, 1 g of phenanthrene (1) dissolved in 40 ml $CH_2Cl_2$ containing about 1-2 ml of $Et_3N$, was added to a twofold excess of a cold (-15 °C) solution of $HOF{\bullet}CH_3CN$. The cooling bath was immediately removed and after 10 seconds the reaction was quenched with bicarbonate solution forming the desired oxide 2,[8] mp 148 °C[4] in 97% yield although in 45% conversion. Prolonging the reaction time to 30 seconds pushed the conversion to 90% with yield reduction to 77%. Reacting 2-acetyl phenanthrene (3) for 60 seconds under similar conditions resulted in an 82% yield (90% conversion) of the corresponding epoxide 4, prepared previously in low yield only.[5] Pyrene (5) seems to be more reactive then the other derivatives and it took a 2.2 fold excess of HOF•CH3CN and only 5 seconds to be converted to the pyrene-4,5-oxide (6)[9] in 80% yield (65% conversion), considerably higher than most other published methods.[1] While the reactions took only a few seconds with the above compounds, the 9,10 π region of 9-acetyl phenanthrene (7) is much more electron depleted in comparison, and it took a sixfold excess of HOF•CH3CN and 25 minutes in order to form the corresponding oxide (8)[4] mp 88 °C, in 100% yield and 33% conversion. Increasing the oxidizer excess to sixteenfold resulted in a full conversion and 55% isolated yield.



1 $R_1 = R_2 = H$ 2
3 $R_1 = Ac$; $R_2 = H$ 4
7 $R_1 = H$; $R_2 = Ac$ 8

5

6

## *References and Notes*

1. Harvey, R. G. *Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity*, Cambridge University Press, 1991, Ch. 4 and 12.
2. For a comprehensive review see Shirwaiker, G. S.; Bhatt, M. V. *Advances in Heterocyclic Chemistry* **1984**, *37*, 67.
3. Ishikawa, K.; Charles, H. C.; Griffin, G. W. *Tetrahedron Lett.*, **1977**, 427.
4. Krishnan, S.; Kuhn, D. G.; Hamilton, G. A. *Tetrahedron Lett.*, **1977**, 1369.
5. Jeyaraman, R.; Murray, R. W. *J. Am. Chem. Soc.* **1984,** *106*, 2462.
6. Rozen, S. *Acc. Chem. Res.* **1996**, *29*, 243.
7. Under longer reaction times and larger excesses than applied here, HOF•CH3CN converts phenanthrene to phenanthrenequinone: Kol, M.; Rozen, S *J. Org. Chem.* **1993,** *58,* 1593.
8. All physical properties including $^1$H NMR, IR and MS are in excellent agreement with the ones published in the literature.
9. Lee, H. K.; Kim, K. S.; Kim, J. C. Kim, Y. H. *Chem. Lett.*, **1988**, 561.

***Acknowledgment:*** *This research was supported by the USA-Israel Binational Science Foundation (BSF) , Jerusalem, Israel.*

(*Received in UK* 13 *January* 1997; *accepted* 14 *February* 1997)