authors to conclude that this hydride was present as an impurity. In our hands **7** is obtained virtually pure, its structure being confirmed by the virtual identity of the high field pmr spectrum to that of $[(Et_3P)_3PtH]^+$ [9] and the identity of the ^{19}F spectrum and Si–F modes in the infrared region to those of other SiF_5^- salts. Although refluxing **7** in tetrahydrofuran with excess triphenylphosphine resulted in disappearance of the hydride, as previously reported,[2] the SiF_5^- spectrum remained unchanged. The compound **5** was unaffected by the latter treatment. Although the dehydrofluorination of **7** by tetrahydrofuran to yield **4** cannot presently be ruled out, the physical evidence would seem to point equally strongly to the conclusion that the purported silicon tetrafluoride adduct is a pentafluorosilicate.

The high field pmr spectrum of **5** is essentially that expected, but certain anomalies in line shapes suggest some effects due to a less than perfect equivalence of P3 and P5; see Figure 4a. The spectrum of **7** was simpler and more easily resolved (Figure 4b). It suggests that the ideal square planar structure does not exist in solution for this compound and that the two phosphorus atoms cis to the proton are not exactly equivalent. Several possible causes of this inequivalence, such as the diastereotopic packing of triphenylphosphine ligands, referred to above, or unsymmetrical association of ion pairs, are presently being explored.

In addition to the reactions described above, it has also been shown that BF_3 reacts with **2** and **3** to give the tetrafluoroborate analogs of **5** and **7**. Evidently, great care must be taken when interpreting the results of reactions of covalent fluorides with basic metal complexes when the reactions are carried out in glass apparatus.

Acknowledgment. Financial support for this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Research Council of Canada is gratefully acknowledged.

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P. Bird*
Department of Chemistry, Sir George Williams University
Montreal, Quebec, Canada

J. F. Harrod,* Khin Aye Than
Department of Chemistry, McGill University
Montreal, Quebec, Canada

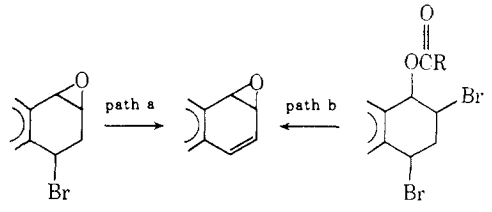
Received September 20, 1973

A Facile Synthesis of Arene Oxides at the K Regions of Polycyclic Hydrocarbons

Sir:

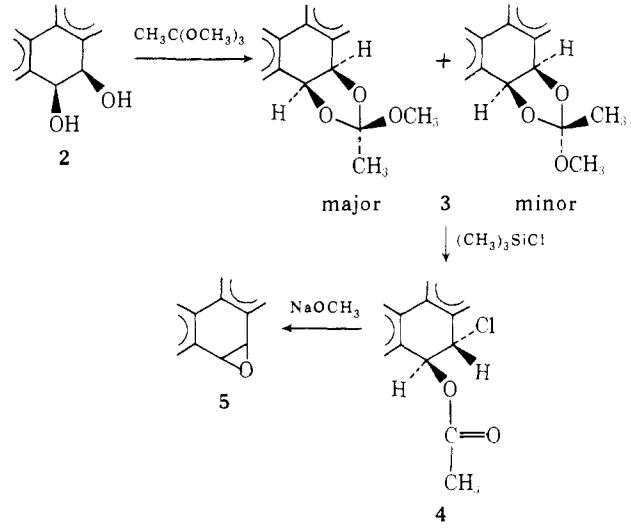
The establishment of arene oxides as primary intermediates in oxidative metabolism of aromatic substrates[1] has generated substantial interest in their pharmacology and biochemistry. To date, arene oxides have been implicated as causative agents in the carcinogenic, toxic, and mutagenic activity[2] displayed by many aromatic hydrocarbons. The broad interest in the biological effects of these compounds has prompted development of versatile and convenient entries into this class of unstable oxiranes.[3] K-Region arene oxides have been accessible through closure of the corresponding dialdehydes with tris(dimethylamino)phosphine[4] and, more recently, by dehydration of trans dihydrodiols with the dimethyl acetal of dimethylformamide.[5] Non-K-region arene oxides have been prepared by dehydrohalogenation of tetrahydrobromo epoxide precursors[6,7] (Scheme I, path a). A related but improved procedure employs halohydrin esters as precursors[8] (Scheme I, path b). The use of halohydrin esters has now been extended to the preparation of K-region arene oxides and provides facile access in high yield. This approach has been exemplified by the synthesis of K-region oxides of the six hydrocarbons (**1a–f**) listed in Table I.[9]

Scheme I. Synthesis of Non-K-Region Arene Oxides *via* Dehydrohalogenation Routes



The general synthetic route (Scheme II) consists of (i) formation of a 2-alkoxy-1,3-dioxolane (**3**) from the cis dihydrodiol (**2**) at the K region,[10] (ii) transformation into a

Scheme II. Synthesis of K-Region Arene Oxides *via* Dehydrohalogenation of Chlorohydrin Acetates



(1) Plants, animals, and certain microorganisms employ this pathway with the eventual secondary formation of phenols, cysteine conjugates, dihydrodiols, and catechols. For a review, see J. W. Daly, D. M. Jerina, and B. Witkop, *Experientia*, **28**, 1129 (1972).

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(9) The best overall yields were obtained for the oxides of hydrocarbons **1c** and **1f** which have been considered the two most difficult types of K-region oxides to synthesize.[5]

(10) While most of the cis dihydrodiols were prepared through the action of OsO_4 on the hydrocarbon in benzene solvent with a 2 molar equiv of pyridine as described by J. W. Cook and R. Schoental, *J. Chem. Soc.*, 170 (1948), diols **2e** and **2f** were obtainable in much higher yield and purity when the reaction with OsO_4 was run for 5 days in pyridine followed by destruction of the osmate ester with aqueous $NaHSO_3$ as described by J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).

Table I. Synthesis of K-Region Arene Oxide

Hydrocarbon	Dioxolane (3)[a] % yield	Dioxolane (3)[a] Ratio of isomers	Chlorohydrin acetate (4) ratio,[b] 4:phenol acetate	Overall % yield (2 → 5)[c]
Phenanthrene (**1a**)	>95	(30:70)	80:20	51
Benzo[*a*]anthracene (**1b**)	>95	(25:75)	80:20	43
7,12-Dimethylbenzo[*a*]anthracene (**1c**)	85	(37:63)	84:26	52
3-Methylcholanthrene (**1d**)	>95	(30:70)	69:31	45
Pyrene (**1e**)	>95	(32:68)	77:23	45
Benzo[*a*]pyrene (**1f**)	95	(~30:70)	80:20	56

[a] The yields are based on the weight of the sample and the pmr spectrum. Detectable impurities consisted of phenol acetates (significant for **3c**) arising *via* dehydration and occasionally small amounts of *o*-quinones arising *via* autoxidation of **2**. The major dioxolane isomer always shows the ring hydrogens (H_4 and H_5) and the $-OCH_3$ at higher field and the $-CH_3$ at lower field ($H_{4,5}$ δ ~5.6, $-OCH_3$ ~2.6, $-CH_3$ ~1.8) compared to the minor isomer ($H_{4,5}$ δ ~5.7, $-OCH_3$ ~3.5, $-CH_3$ ~1.3). Only for **3b–d** were H_4 and H_5 magnetically nonequivalent. Considerations of shielding by the aromatic ring and deshielding by the oxygen of the $-OCH_3$ argue for the major isomer as that with the aromatic nucleus and the $-OCH_3$ group in closest proximity as shown (Scheme II). [b] Variable but minor amounts of diol monoacetate arising by hydrolysis of **3** contaminate the sample at this point. Only a single isomer of the chlorohydrin acetate ($-CHCl-$ δ ~5.5, $-CHOAc-$ ~6.5, CH_3CO_2- ~1.85; $J_{K-region}$ = 3–3.5 Hz) and the phenol acetate (CH_3CO_2- δ ~2.5) could be detected by pmr ($CDCl_3$) except for **4b** and **4f** which show two isomers for both in a ratio of ~2:1. [c] Readily obtained yields for pure oxides (**5**) based on starting diols (**2**) are presented. The yields of **5e**, for example, rises from 45 to 61% when pure diol is used, the amount of water is carefully limited, and yields for the individual steps are employed in the calculation. Physical and spectral properties are identical with reported values.[3b] The pmr spectrum of **5d** (oxirane H at δ 4.41 and 4.62 with $J_{11,12}$ = 4 Hz, CH_3 at 2.35, $-(CH_2CH_2)-$ at 3.15–3.75, aromatic H at 7.20–8.30 in $CDCl_3$) has not been reported. Pyrene 4,5-oxide (**5d**) has not been reported (mp 180°; *m/e* 218; ir, 8.1, 9.6, 12.1 μ; pmr, oxirane H at δ 4.80 and aromatic H at 7.8 in $CDCl_3$). However, these data are in good agreement with material prepared by an alternate route. We are grateful to B. L. Van Duuren, G. Witz, and S. C. Agarval, *J. Org. Chem.* (submitted), for preliminary disclosure of their data.

halohydrin ester (**4**), and (iii) direct cyclization to the desired arene oxide (**5**) with base. Several recent publications describe the facile conversion of 1,3-dioxolanes to halohydrin esters.[11]

Diols (**3**) were converted into 2-methyl-2-methoxy-1,3-dioxolanes (**3**) in high yield (Table I) by heating with trimethyl orthoacetate in benzene containing a trace of benzoic acid as catalyst. Evaporation to dryness provided crystalline mixtures of stereoisomers at C-2, the ratio of which was not significantly affected by the use of triethyl orthoacetate or triethyl orthopropionate. The reagent of choice for conversion of the dioxolanes (**3**) into trans chlorohydrin acetates (**4**) is trimethylsilyl chloride,[11d] since excess reagent and by-products from the reaction are volatile. The reaction is much more facile than those previously reported[11] and is complete within a short time at 0° in CH_2Cl_2 containing a trace of triethylamine. When water is rigorously excluded, the reaction does not occur. While positional isomers are possible for the trans chlorohydrin acetates (**4**) of asymmetric hydrocarbons, they were only observed with benzanthracene (**4b**) and benzpyrene (**4f**). The proximate alkyl substitution in dimethylbenzanthracene (**4c**) and methylcholanthrene (**4d**) apparently determined the mode of opening of the dioxolanes. A significant by-product is the acetate of the K-region phenol which again consists of a mixture of isomers only for the reactions of **3b** and **3f**. The amount of undesired phenol acetate increases when triethylamine is omitted, while an excess of this base inhibits halohydrin formation. Excess pyridine may be employed; however, the amount of phenol acetate is somewhat higher. After evaporation of solvent, the crude residues were treated in THF with an excess of dry $NaOCH_3$ at 4° for several hours. Salts, including phenoxides, were precipitated by the addition of dry ether. The resulting solutions contain the desired oxide (**5**) and occasionally some of the starting diol (**2**) arising by hydrolysis of **3**. Overall yields for the three steps, based on starting diols (**2**), were in the range of 43–56%. Details of a typical procedure are presented.[12]

Reaction conditions are simple and there is only one purification step, *viz.*, crystallization of the final product. It is clear from Table I that the yield in the last step (exclusive of losses in crystallization) is not quantitative. Presumably some elimination of HCl from **4** occurs to form phenol acetates. Finally, the approach may be limited to K-region arene oxides, since, under the conditions employed here, treatment of the dioxolane from *cis*-1,2-dihydroxy-1,2-dihydronaphthalene[13] with trimethylsilyl chloride led primarily to 1- and 2-acetoxynaphthalene instead of the desired halohydrin acetate.

Acknowledgment. We are particularly grateful to Professor Melvin S. Newman at The Ohio State University for several fruitful discussions and for suggesting the use of trimethylsilyl chloride in forming the halohydrin acetates.

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(12) For the synthesis of benzo[*a*]pyrene 4,5-oxide (**5f**), a suspension of 180 mg of diol (**2f**) in 6 ml of dry benzene containing 0.25 ml of trimethyl orthoacetate and 8 mg of benzoic acid was distilled at the rate of 1 ml/hr for 3 hr under nitrogen. After cooling to room temperature, 50 mg of solid Na_2CO_3 was added to the solution which was then filtered and concentrated to dryness. The crystalline residue (**3f**) was dissolved in 4 ml of CH_2Cl_2, added at 0° to 2 ml of CH_2Cl_2 containing 0.2 ml of trimethylsilyl chloride and 0.02 ml of triethylamine, and stored at 4° for 3 hr. After evaporation at the solvent, the residue (**4f** and phenol acetates) was dissolved in 16 ml of THF, added slowly under nitrogen to 500 mg of dry $NaOCH_3$ in 10 ml of THF at −78°, and stirred for 18 hr at 4°. Salts were precipitated by addition of 100 ml of dry ether and the resulting solution was filtered, washed with cold water, dried ($MgSO_4$), and concentrated to dryness. Recrystallization of the residue from THF–ether provided 89 mg (56% overall) of pure **5f** which is identical in all respects with the known substance.[5]

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(14) Guest Worker at the NIH supported by CNRS of France and NATO postdoctoral fellowships.

Patrick Dansette,[14] Donald M. Jerina*

The National Institute of Arthritis, Metabolism, and Digestive Diseases
The National Institutes of Health
Bethesda, Maryland 20014

Received November 28, 1973