cence. DL-Glyceraldehyde and L-ascorbic acid did not give fluorescence. Nevertheless, these compounds could be detected by the color reaction.

The present method was also applicable to the determination of sugars on thin-layer plates utilizing a scanning fluorophotometer. The standard plot for glucose showed a linear relationship in the range of 0.1 to 0.5 nmol/spot and passed through the origin. The relative fluorescence intensities of 0.5 nmol each of glucose, galactose, mannose, maltose, maltotriose measured by this assay procedure were 100, 56, 73, 96 and 77, respectively.

Acknowledgements The authors would like to express their gratitude to Miss Motoko Ejima for her skilful assistance. They also wish to thank Wako Pure Chemical Co. for generous gifts of maltotriose, maltotetraose and maltopentaose.

Chem. Pharm. Bull.
27(5)1271—1273(1979)

UDC 547.672.04 : 547.438.1.04

Anodic Phosphonylation of Anthracene

HIDENOBU OHMORI, SHIRO NAKAI, and MASAICHIRO MASUI

Faculty of Pharmaceutical Sciences, Osaka University[1]

(Received December 14, 1978)

Controlled potential electrolysis of anthracene at a glassy carbon anode in acetonitrile containing an excess of triethylphosphite and subsequent treatment of the product with sodium iodide resulted in the formation of 9,10-bis(diethylphosphonyl)-9,10-dihydroanthracene. Anodic phosphonylation was also performed on 4′-methoxybenzanilide to give 2′-diethylphosphonyl-4′-methoxybenzanilide.

Keywords——anodic oxidation; controlled potential electrolysis; anodic phosphonylation; anthracene; triethylphosphonium ion; 4′-methoxybenzanilide

Previously we have reported the anodic arylation of trialkylphosphites,[2] in which nucleophilic attack of alkylbenzene on an anodically generated trialkylphosphite cation radical results in the formation of a trialkoxy arylphoshponium ion (eq. 1): the latter was converted to the corresponding dialkyl arylphosphonate on treatment with sodium iodide.

$$(RO)_3P + ArH \xrightarrow[\text{MeCN, NaClO}_4\text{, K}_2\text{CO}_3]{\text{glassy carbon anode}} (RO)_3\overset{+}{P}\text{-Ar} + 2e \tag{1}$$

Since the oxidation of trialkylphosphite takes place at fairly high positive potentials ($>$1.5 V *vs* S.C.E. in MeCN), the aromatic compounds available were limited. If nucleophilic attack of trialkylphosphites on a cation radical, a cation, or a dication derived from aromatic cmpounds can be achieved, the applicability of this process will be enhanced. Anodic phosphonylation would be a new addition to the list of anodic substitution reactions.[3] We selected anthracene and triethylphosphite as typical substrates and examined the possibility of such a reaction. Phosphonylation was also examined in the case of 4′-methoxybenzanilide for which anodic pyridination has been reported.[4]

---

1) Location: *133-1 Yamadakami, Suita, Osaka.*
2) H. Ohmori, S. Nakai, and M. Masui, *J. Chem. Soc. Perkin I*, accepted.
3) L. Eberson and K. Nyberg, *Tetrahebron*, **32**, 2185 (1976).
4) S. Ikenoya, M. Masui, H. Ohmori, and H. Sayo, *J. Chem. Soc. Perkin II*, **1974**, 571.

Results and Discussion

Electrolysis of anthracene in acetonitrile containing an excess of triethylphosphite at 1.0 V *vs* S.C.E. gave a coulometric *n*-value of *ca.* 2, and a yellow oil was obtained. Treatment of the oil with sodium iodide in dry acetone gave 9,10-bis(diethylphosphonyl)-9,10-dihydroanthracene (I) (*ca.* 50%), indicating that the immediate product of electrolysis is the 9,10-dihydroanthranyl-9,10-bis(triethylphosphonium) ion (II). Since a phosphonium ion having at least one alkoxy group is usually unstable, no attempt was made to characterize (II) by further purification. In acetonitrile containing excess pyridine, anthracene is oxidized at around 1.0 V by a two-electron process,[5,6] and 9,10-dihydroanthranylpyridinium diperchlorate has been obtained.[5] Although the exact sequence of the anodic pyridination is not completely clear,[7] the overall process of the phosphonylation may be represented as in Chart 1 by analogy with pyridination.

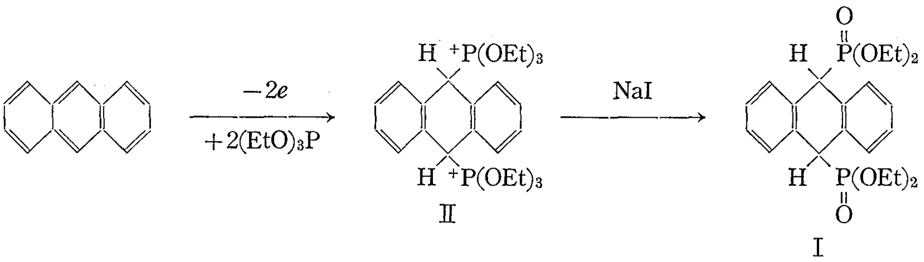

Chart 1

The PMR spectra (Fig. 1) of the phosphonate (I) suggest that I is a mixture of two isomers. Since dihydroanthracene is not planar, three isomers can be considered for I: two *cis* and one *trans* isomers. Molecular models suggest that one of the *cis* isomers in which both the phosphonyl groups are axial is sterically improbable. The doublet at $\delta=4.60$ and 5.06 ppm ($J_{\text{P-C-H}}=26.5$ Hz)[8] can be assigned to the axial protons in the other *cis* isomer, and the doublet of doublets at $\delta=4.86$ and 5.32 ppm ($J_{\text{P-C-H}}=27.5$, $J_{\text{P-C-C=C-C-H}}=\sim4.6$ Hz)[8] to the protons in the *trans* isomer. The latter isomer must consist of a mixture of rapidly interconverting conformers, because an entirely different spectrum would be expected if the isomer had fixed conformation.

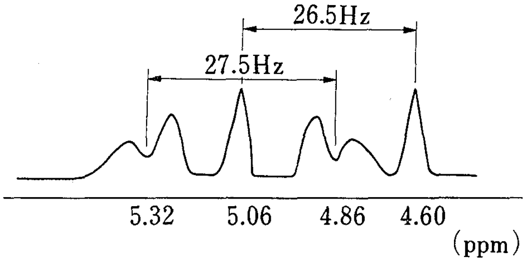

Fig. 1. Typical PMR Signals for Protons at the 9 and 10 Positions of (I)

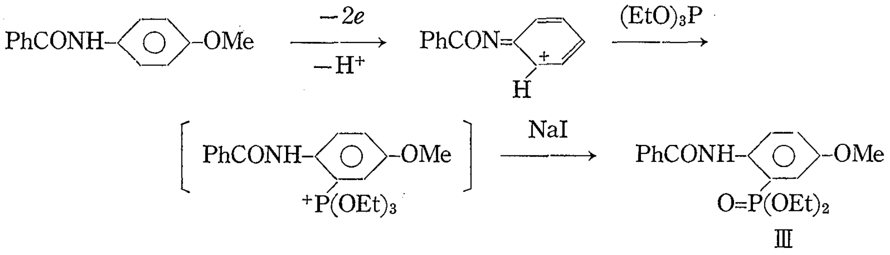

Chart 2

---

5) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

6) V.D. Parker and L. Eberson, *Acta Chem. Scand.*, **24**, 3542 (1970).

7) L. Marcoux, *J. Am. Chem. Soc.*, **93**, 537 (1971) and references therein.

8) The assignment was made by comparing the spectra obtained at 60 and 90 MHz.

The isomer ratio in the product seems to vary with slight changes in the chromatographic conditions employed for the isolation (see "Experimental"). In some cases only one isomer, either *cis* or *trans*, was obtained.

Electrolysis of 4′-methoxybenzanilide under similar conditions followed by similar work-up gave 2′-diethylphosphonyl-4′-methoxybenzanilide (III). The process shown in Chart 2 is suggested for its formation by analogy with the anodic pyridination of the carboxamide.[4)]

Experimental

Materials——Triethylphosphite was purified by distillation. Sodium iodide was dried in an oven at 120° for 8 hr. Sodium perchlorate[9)] and acetonitrile[10)] were purified as described previously. 4′-Methoxybenzanilide was prepared as described previously.[4)] Anthracene was obtained commercially and used without further purification.

Apparatus——Controlled potential electrolysis was carried out as described previously.[10)] IR and PMR spectra were obtained using Hitachi EPI-2 and R-20A spectrometers, respectively.

Controlled Potential Electrolysis——Typical examples of the procedure are described below. A glassy carbon anode was used throughout.

a) Anthracene (910 mg) was subjected to electrolysis at 1.0 V *vs* S.C.E. in deaerated acetonitrile (100 ml) containing 10 g of sodium perchlorate and 5 ml of triethylphosphite under an atmosphere of dry nitrogen until the current dropped to approximately the background value (580 min). Initially suspended anthracene dissolved gradually as the oxidation proceeded. From the curren-time curve 1068 C, which corresponded to $n=2.2$, was found to be consumed. Water (50 ml) was added to the anolyte and the mixture was extracted with chloroform (5×50 ml). Evaporation of the chloroform gave a yellow oil. The oil was dissolved in dry acetone (100 ml) containing dry sodium iodide (2.4 g), and the mixture was refluxed for 6 hr. After being cooled to room temperature, the acetone was removed under reduced pressure, and water (100 ml) was added to the residue. The resulting mixture was extracted with chloroform (3×50 ml). The organic layer, after being dried with anhydrous magnesium sulfate, was evaporated under reduced pressure in a nitrogenstream at room temperature. The residue was subjected to column chromatography first on silica gel with chloroform–methanol (20: 1) as an eluant, and then on neutral alumina with benzene–methanol (10: 1). I was obtained as a yellow oil (1530 mg, 49%). *Anal.* Calcd. for $C_{22}H_{30}O_6P_2$: C, 58.40; H, 6.68; P, 13.69. Found:[11)] C, 57.27; H, 6.47; P, 13.26. IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1250 (P=O), 1160 (P–OEt). PMR (CDCl$_3$) δ: 1.03—1.55 (12H, triplet-like multiplet, CH$_3$); 3.65—4.48 (8H, quintet-like multiplet, O–C$\underline{H}_2$–CH$_3$); 4.60 and 5.06 (singlet and singlet, $J=26.5$ Hz, *cis* –CH–), and 4.86 and 5.32 (doublet and doublet, $J=27.5$ and ~4.6 Hz, *trans* –CH–), (2H) (see Fig. 1); 7.20—7.98 (8H, multiplet, aromatic).

b) 4′-Methoxybenzanilide (680 mg) was electrolyzed similarly at 1.2 V in acetonitrile (40 ml) containing triethylphosphite (2 ml) and sodium perchlorate (2 g) (280 min). A coulometric n-value of 2.1 was obtained. Essentially the same treatment, including chromatographic procedure, of the anolyte as in a) gave (III) as colorless crystals (410 mg, 38%); mp 158°. *Anal.* Calcd. for $C_{18}H_{22}NO_5P$: C, 59.50; H, 6.10; N, 3.86; P, 8.52. Found: C, 59.25; H, 5.96; N, 3.92; P, 8.58. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3250 (NH), 1670 (C=O), 1260 (P=O), 1165 (P-OEt), 1040—1015 (P–O–C). PMR (CDCl$_3$) δ: 1.05—1.50 (6H, triplet, CH$_3$), 3.75—4.28 (4H, quintet, O–C$\underline{H}_2$–CH$_3$), 3.86 (3H, singlet, OCH$_3$), 6.72—8.50 (9H, multiplet, aromatic and NH).

Acknowledgement The authors are grateful to Dainippon Seiyaku Co. Ltd. for performing elemental analysis of the electrolysis products.

---

9) M. Masui and H. Ohmori, *J. Chem. Soc. Perkin II*, **1972**, 1882.

10) H. Ohmori, S. Nakai, and M. Masui, *J. Chem. Soc. Perkin I*, **1978**, 1333.

11) The analytical value for carbon was about 1% smaller than that expected. It has been reported, however, that in the elemental analysis of organophosphorus compounds the value for carbon is sometimes low: F.J.M. Daemen, G.H. de Hass, and L.L.M. van Deenen, *Rec. Trav. Chim. Pays-Bas*, **81**, 348 (1962).