(-O-CH₃); infrared 1743, 1170, 1260, and 1370 cm⁻¹. The infrared, n.m.r., and gas-liquid chromatogram agreed with those of its authentic sample.

Fraction c was distilled to give a mixture of various dibasic acids but their complete separation was unsuccessful; b.p. 165 °C at 4 Torr, molecular weight 230 (calcd. for $C_{12}H_{18}O_4$; 226). The dimethyl ester was prepared similarly, and had the following properties, b.p. 160-165 °C at 3 Torr, infrared 1745 and 1160 cm⁻¹ (carb-oxylic acid), 785 cm⁻¹ (a trisubstituted double bond), saponification value 403 (calcd. for $C_{14}H_{22}O_4$, 444).

Anal. Calcd. for C14H22O4: C, 66.10; H, 8.72. Found: C, 67.10; H, 8.85.

From the ether solution a, 2 g of 2 was obtained by fractional distillation.

Infrared Absorption Spectra

These (liquid film) were measured on a Koken IRS spectrophotometer.

Nuclear Magnetic Resonance Spectra

These were determined on a Japan Electron Optics

Lab. instrument (60 Mc/s) with carbon tetrachloride solutions and with tetramethylsilane as an internal standard.

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- L. I. ZAKHARKIN and G. C. ZHIGAREVA. Izv. Akad. Nauk SSSR, Ser. Khim. (1), 168 (1964).
 A. MISONO, Y. UCHIDA, M. HIDAI, and Y. OHSAWA. Bull. Chem. Soc. Japan, 39, 2425 (1966).
 K. SUGA, S. WATANABE, and K. KAMMA. Can. J. Chem. 45, 933 (1967).
 K. SUGA and S. WATANABE. Bull. Chem. Soc. Japan, 40, 1557 (1057).
- 40, 1257 (1967).

The synthesis and saponification kinetics of some 4'-substituted 4-phenoxyphenyl acetates

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Phenoxyphenyl acetate and several 4'-substituted derivatives were synthesized and their rates of saponification determined. The nature of the 4'-substituent was correlated with the rate of saponification by means of the Hammett equation.

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The syntheses and saponification kinetics of esters represent subjects which have been subjected to a great deal of study (1). In the course of these studies both the acyl and alcohol moieties have been extensively varied; however, the syntheses and saponification kinetics of 2'-, 3'-, and 4'-substituted 4-phenoxyphenyl esters (1) have been neglected.



Ikawa's synthesis of 4-hydroxy-4'-nitrodiphenyl ether (2), Ungnade's synthesis of 4-carboxy-2'-methyldiphenyl ether (3), and Walker's synthesis of 4-carboxy-4'-hydroxydiphenyl ether (4) suggested that the following route should furnish the desired 4'-substituted 4-phenoxyphenyl acetates.

The substituted 4-phenoxyphenyl acetates synthesized by this route are found in Table I. The acetates were characterized by their ultraviolet and infrared spectra and by elemental analyses.

Precedent exists for assuming that substitution at the 4'-position might affect the rate of saponification of phenoxyphenyl acetates. Since Litvinenko, Tsukerman, Cheshko, and Kolesnikova (5) have shown that the acylation of 4-aminodiphenyl oxide occurs 12 times as fast as the acylation of 4-amino-4'-nitrodiphenyl oxide, similar effects might be expected for the saponification of esters derived from 1-hydroxydiphenyl oxide reported in Table I.

The saponifications were carried out in 25% ethanol/water (v/v), "pH" 10.3, employing phosphate as the buffer species, at 25 °C ± 0.01 , (ester) = $10^{-4} - 10^{-5} M$. The course of the reaction was conveniently followed by measur-

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1156

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 TABLE I

 Synthesis of 4'-substituted 4-phenoxyphenyl acetates*

| R | R′ | R'' | Yield % | Melting point (°C) | Boiling point (°C) |
|----------------------------|--|--|----------------------|--------------------------|--|
| OCH₃ Br OCH₃ | CH ₃ OCH ₃ NO ₂ | H† CH ₃ Br NO ₂ | 80 49 14 36 | 62-64 | 181 (15 mm) 153 (3.2 mm) 94 (2.2 mm) |
| $\langle \bigcirc \rangle$ | OCH3 | $\langle \bigcirc \rangle$ | 9 | 119–121 | |
| -0{\(\circ\)} | OCH3 | -0- | 42 | 69-71 | |
| *R- | + R'- | \rightarrow Br \rightarrow R'' | | 4c. | |



0

ing the optical density change of the reaction mixture as a function of time at the wavelength where the product phenolate strongly absorbs ($280m\mu - 300m\mu$). First order rate constants were calculated from plots of log (O.D. - O.D._{∞}) as a function of time by the procedure of Bruice (6) and are tabulated in Table II. Good first order plots were obtained which were reproducible within 2-3%.

Ξ

| TABLE I | ľ |
|---------|---|
|---------|---|

| Saponification* of R $ O$ $ O$ $ OC$ $ CH_3$ | | | | |
|--|---|--|--|--|
| R | $\overline{K_1 \times 10^2 \text{ (min}^{-1})}$ | | | |
| H | 2.39 | | | |
| CH_3 | 2.40 | | | |
| Br | 4.04 | | | |
| $\langle \bigcirc \rangle$ | 2.12 | | | |
| NO ₂ | 4.19 | | | |

*At "pH" 10.3.

5

The nature of the 4'-substituent may be related to the rate of saponification of the 4'-substituted 4-phenoxyphenyl acetates by use of the Hammett equation (7). A ρ of +0.289, r = 0.803, was calculated.

The transmission of electronic effects through the phenoxy bridge may be evaluated by comparison of the ρ obtained in these experiments with the ρ for the saponification of substituted phenyl acetates. Bruice (6) calculated a ρ of +1.15 for the saponification of phenyl acetates in 25% ethanol/water (v/v), "pH" 8.0, at 30°. The shielding effect of the phenoxy bridge is substantial. The ratio ρ/ρ_0 (ρ_0 for substituted phenyl acetates) is 0.25 and agrees with that calculated from transmission coefficients for the transmission of polar effects through oxygen and phenylene links, 0.16 (8).

 J. HINE. Physical organic chemistry. McGraw-Hill Book Company, Inc., New York. 1962. Chap. 12, and references cited therein.

<sup>and references cited therein.
2. K. IKAWA. Yakugaku Zasshi, 79, 1493 (1959);</sup> Chem. Abstr. 54, 19022h (1960).

CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968

- H. E. UNGNADE. J. Am. Chem. Soc. 63, 2091 (1941).
 C. R. HARINGTON and R. V. PITT RIVERS. J. Chem. Soc. 1101 (1940). J. WALKER. J. Chem. Soc. 347 (1942).
- L. M. LITVINENKO, S. V. TSUKERMAN, R. S. CHESHKO, and B. M. KOLESNIKOVA. Zh. Obshch. Khim. 27, 1663 (1957); Chem. Abstr. 52, 4546e (1958).
- T. C. BRUICE. J. Am. Chem. Soc. 79, 1663 (1957).
 A. A. FROST and R. G. PEARSON. Kinetics and mechanism. John Wiley and Sons, Inc., New York. 1940. p. 186. L. P. HAMMETT. Physical organic chemistry. McGraw-Hill Book Co., Inc., New York. 1940. p. 186 ff.
- 8. K. BOWDEN. Can. J. Chem. 41, 2781 (1963).

Organic and biological spectrochemical studies. XXVII. Electron spin resonance spectra of the pyrene monomer and dimer cation radicals¹

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The electron spin resonance spectra of pyrene, dissolved in sulfur dioxide – boron trifluoride, are investigated. Two different spectra can be obtained, depending on the experimental conditions, and are ascribed to the monomeric and dimeric hydrocarbon radical cations.

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Radical dimers of polynuclear hydrocarbons are of some biological interest because they may provide a mechanism whereby metastable free radicals are stabilized. For example, the cation radical dimer of 3,4-benzpyrene has been postulated as a reaction intermediate involved in biological activity (1, 2) and may thus, at least partly, be responsible for the biological activity of that compound. In the course of surveying a number of polynuclear hydrocarbon cation radicals for possible dimer formation, the electron spin resonance (e.s.r.) spectrum of pyrene was investigated in various acid media.

The e.s.r. spectrum of the cation radical of pyrene (1) has previously been reported by Lewis and Singer (3); it was obtained by oxidizing the hydrocarbon with antimony pentachloride using methylene dichloride as solvent. However, the spectrum was not well resolved (line-width ca. 150 mG).

For the liquid sulfur dioxide-boron trifluoride system (cf. deBoer and Praat (4)) hydrocarbon and boron trifluoride concentrations of ca. $5 \times 10^{-4} M$ were used. Samples were prepared in liquid nitrogen and allowed to melt in the spectrometer cavity at -50 °C when the spectrum shown in Fig. 1 was obtained.

This spectrum is better resolved (line width ca. 65 mG) and the main lines are well accounted for by a simulated spectrum, assuming the following proton splitting constants: $a_1 = 2.17$ G (four protons; $\rho = 0.098$); $a_3 = 5.39$ G (four protons; $\rho_3 = 0.178$); $a_4 = 1.20$ G (two protons; $\rho_4 = -0.054$) which are in good agreement with the previously reported values (3). The corresponding calculated spin densities, p, using the McLachlan molecular orbital - selfconsistent field theory (5) are given in parentheses. Generally, for most polynuclear hydrocarbons, which in sulfuric acid afford e.s.r. spectra, the SO₂-BF₃ system appears to give equally well or better resolved spectra.² In some cases, for example pyrene and dibenz-(a,c)triphenylene, a spectrum is obtained in this medium although none can be obtained in sulfuric acid.

Marked changes occur on altering the temperature. The previously blue solution

1158

¹For part XXVI in this series, see W. F. Forbes and P. D. Sullivan, Can. J. Chem. 46, 325 (1968).

²J. T. Cooper, Unpublished information.