to di-*n*-butyltin oxide and ethylene glycol, which was characterized as its dibenzoate ester. No diethylene glycol was found in the products of hydrolysis.

EXPERIMENTAL[6]

The reaction of di-n-butyltin oxide with ethylene glycol. A mixture of di-*n*-butyltin oxide (25.0 g., 0.10 mole, dried at 110° for 2 hr.), freshly distilled ethylene glycol (6.0 g., 0.097 mole), and 250 ml. of dry benzene was heated under reflux for 1.5 hr. in an apparatus fitted with a Dean-Stark water separator. At the end of this time a clear solution was obtained and 0.1 mole of water was collected. The crystals which deposited from the solution on standing at room temperature overnight were removed by filtration and washed with petroleum ether. Recrystallization from benzene gave III as matted, white needles, 24.0 g. (85%), m.p. 223–229° with decomposition.

Anal. Calcd. for $C_{20}H_{44}O_4Sn_2$: C, 40.99; H, 7.57; Sn, 40.52; mol. wt., 586. Found: C, 41.2; H, 7.5; Sn, 40.79, 40.81, 40.87; mol. wt., 606 (Rast, camphor), 611 (ebullioscopic, benzene), 638 (isothermal distillation, chloroform).

Refluxing of di-*n*-butyltin oxide with a three-fold excess of ethylene glycol in the absence of benzene afforded the same product. The material was identical with that prepared from di-*n*-butyltin dichloride and the glycol by the method of Ramsden and Banks,[2] m.p. 223–226°, mixed m.p. not depressed.

Hydrolysis of III was readily effected by adding as light excess of water to a stirred, boiling solution of the compound in ethanol. Di-*n*-butyltin oxide precipitated immediately. After stirring and refluxing for an additional 10 min., the mixture was cooled to room temperature and filtered to remove the oxide. The filtrate was concentrated by heating gently under reduced pressure in order to remove the ethanol. The residue was dissolved in a small quantity of water, made alkaline with aqueous 10% sodium hydroxide, and shaken with benzoyl chloride. Crystallization of the product from petroleum ether gave the dibenzoate of ethylene glycol as felted needles m.p. 72.5–73.0°, which was found to be identical to an authentic sample[7] by means of m.p., mixed m.p., and comparison of the infrared spectrum.

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[6] Melting points are corrected. Infrared measurements were made using a Baird double beam recording spectrophotometer equipped with a sodium chloride prism. Analyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass., and Dr. S. M. Nagy, Microanalytical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

[7] E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds, Order I*, John Wiley and Sons, Inc., New York, 1941, p. 469.

Use of Tetracyanoethylene as a Color-Forming Reagent in Paper Chromatography of Aromatic Compounds[1]

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In earlier publications,[2a] we have reported on a system for paper chromatography of polycyclic aromatic compounds, which has proved useful in separation and identification of benzyprene derivatives and other polycyclic compounds.[2b–4] In this scheme, the position of spots on the paper was determined by observation of the fluorescence of the spots under ultraviolet light. A spray reagent which would indicate the position of spots of aromatic compounds which were not fluorescent would be of obvious advantage in this procedure.[5]

The observation[6] that tetracyanoethylene[7] forms colored complexes with many aromatic compounds, including simple ones, suggested an examination of this reagent in paper chromatography of aromatic compounds. It is the purpose of the present note to indicate that it does have promise in this connection.

EXPERIMENTAL

The pyrene derivatives were prepared by published procedures,[8] with some modifications, or were commercial samples purified by chromatography on alumina with petroleum ether as the eluant. The hydrocarbons were used as benzene solutions having concentration of 1 mg. per ml. About 10 γ of the material was applied as a spot on the paper.

The dry developed paper chromatogram, prepared by the published procedure,[2] was laid on paper towels in the hood. The freshly prepared tetracyanoethylene (TCNE) solution in distilled acetone[9] (*ca.* 0.01*M*) was sprayed gently and evenly over the surface. The acetone was dried rapidly by playing a stream of air over the surface, or by waving the sheet in the air if it was not too wet. As the solvent evaporated, the temporary dark gray complex of TCNE-acetone-paper disappeared and a permanent yellow color was left on the paper. If a spot was not visible, even when the paper was scrutinized against the light, the spraying was repeated. Often three or four applications were necessary.

In the Table are given the R_f values in hexane saturated with dimethylformamide, the color with TCNE, and for comparison, the color of the spots developed by spraying with picric acid in ethanol and with trinitrofluorenone[10] in acetone solution. As can be seen, the TCNE colors cover a much wider range than those produced with picric acid or

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[1] Aided by Grant C-2654 from the National Institutes of Health.

[2] (a) D. S. Tarbell, E. G. Brooker, A. Vanterpool, W. Conway, C. J. Claus, and T. J. Hall, *J. Am. Chem. Soc.*, **77**, 767 (1955); (b) W. Conway and D. S. Tarbell, *J. Am. Chem. Soc.*, **78**, 2228 (1956).

[3] D. S. Tarbell, E. G. Brooker, P. Seifert, A. Vanderpool, C. J. Claus, and W. Conway, *Cancer Research*, **16**, 1 (1956).

[4] B. L. Van Duuren, *J. Nat. Cancer Inst.*, **21**, 1 (1958).

[5] Tetrachlorophthalic anhydride forms complexes with a variety of aromatic compounds: P. Pfeiffer, *Ber.*, **55**, 413 (1922); Ng. Ph. Buu-Hoï and P. Jacquignon, *Compt. rend.*, **234**, 1056 (1952).

[6] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[7] T. L. Cairns *et al.*, *J. Am. Chem. Soc.*, **79**, 2340 (1957); **80**, 2775 (1958).

[8] H. Vollman *et al.*, *Ann.*, **531**, 1 (1937); M. de Clercq and R. H. Martin, *Bull. soc. chim. Belg.*, **64**, 367 (1955).

[9] Chloroform proved to be an unsatisfactory solvent because TCNE is only slightly soluble (less than 2 mg./100 ml.), and also it does not evaporate fast enough; rapid evaporation is necessary to prevent the dissolving of the complex and consequent spreading of the spot.

[10] M. Orchin and W. O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

TABLE

				Color with	
Compound	Fluorescence	R_f	TCNE	Picric acid	Trinitrofluorenone
Pyrene	Blue	0.63	Brown-violet	Orange	Orange
3-Methylpyrene	Yellow-blue	0.69	Brown-violet	Red	Brown-red
3,5-Dimethylpyrene	Yellow	0.74	Red-brown	Orange	Brown
3,8-Dimethylpyrene	Green-yellow	0.78	Red-brown	Orange	Brown
3-Nitropyrene	Orange	0.38	Gold	Yellow	Orange
3-Bromopyrene	Blue	0.68	Green	Red-orange	Red-orange
3,8-Dibromopyrene	Blue	0.69	Green	Orange	Orange
3-Acetylpyrene	Bright yellow	0.37	Green	Yellow	Orange
3-Hydroxymethylpyrene	Green	0.05	Brown	Red-orange	Brown
3-Carboxypyrene	Yellow	0.01	Light green	Yellow	—
3-Formylpyrene	Gold	0.37	Yellow	Orange	Orange
3-Methyl-5-formylpyrene	Orange	0.46	Light green	Orange	Brown-orange
Anthracene	Violet	0.70	—	Orange	Brown-red
9,10-Dibromoanthracene	Yellow	0.77	Green	Orange	Orange
1,2-Benzanthracene[a]	Yellow	0.60	Blue	Orange	Red-orange
1:2,5:6-Dibenzanthracene[a]	Violet	0.47	Green	Light orange	Orange
Chrysene[a]	Dark blue	0.63	Light violet	Light orange	Orange
Fluoranthene	Blue	0.79	Violet	Yellow	Yellow
20-Methylcholanthrene[a]	Yellow	0.82	Gray-green	Brown	Gray-green
10-Ethylbenzpyrene[a]	Yellow	0.66	Brown	Brown	Gray
10-Acetylbenzpyrene[a]	Gold	0.18	Gray-brown	Light orange	Tan
5-Acetylbenzpyrene[a]	Blue	0.09	Light brown	Orange	Brown-gray
Phenanthrene	Violet	0.63	Violet	Yellow	Yellow
9-Bromophenanthrene	—	0.78	Violet	Yellow	Yellow
Naphthalene	Blue	0.89	Red-violet	Yellow	Yellow
1-Nitronaphthalene	—	0.50	Orange	Yellow	Yellow
2-Methylnaphthalene	Blue	0.92	Blue-gray	Yellow	Yellow
Di-m-xylylene[b]	—	0.66	Red	—	—
Di-(2-methyl-m-xylylene)[b]	—	0.66	Gold	—	—
Acepleiadiene[b]	Black-red	0.69	Gold	Dark gray	Brown
Acepleiadylene[b]	Orange-red	0.59	Brown	Red-brown	Red-brown
Tetrahydroacepleiadane[b]	Blue	0.06	Purple	Yellow	Yellow
Perinaphthanone[a]	Light blue-violet	0.51	Salmon	Yellow	Yellow
Benzpyrene[a]	Blue	0.60	Violet-pink	Brown	Gray-brown
Fluorene[a]	Light violet	0.65	Light brown	Yellow	Yellow
1-Phenyl-1-(α-naphthyl)-propene-1[a]	Blue	0.74	Purple	Yellow	Yellow

[a] Gift of Dr. S. C. Pakrashi of this Laboratory. [b] Gift of Dr. Leslie Humber of this Laboratory.

trinitrofluorenone. It is possible to detect the position of nonfluorescent compounds, such as the xylylenes and the substituted naphthalenes, by the TCNE spots. The method is sensitive to 1 gamma of pyrene, and 10 gamma of naphthalene; the equilibrium constants for the complex formation in methylene chloride solution for these two compounds[6] are 29.5 and 11.7.

A slight drawback to the method is the impermanence of the color, which fades in some cases in the course of 3 min. but generally is visible for over 1 hr. The rate of fading appears to depend on the stability and amount of the complex present.

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1-Phenyl-2,2-dimethylbutane

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When Francis[1] published his review on the properties of the alkylbenzenes in 1948, fifteen of the seventeen possible monoalkylbenzenes of the formula $C_{12}H_{18}$ had been described. One of the two remaining unknown isomers, 1-phenyl-3,3-dimethylbutane, has since been prepared.[2] The other, 1-phenyl-2,2-dimethylbutane (VI), was reportedly obtained by Tafel and Jurgens[3] from the electrolytic reduction of "methylbenzylacetoacetic ester." Later Tafel and Andre[4] decided that their hydrocarbon was probably 1-phenyl-3-methylpentane rather than VI. Francis[1] stated that VI "must be considered unknown." This paper reports the synthesis of VI by the following reaction sequence.

Prout *et al.*[5] have reported carrying out the first two steps above, leading to the acid (III). The latter was smoothly reduced to the alcohol (IV) by means

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(1) A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).

(2) E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **72**, 222 (1950).

(3) J. Tafel and W. Jurgens, *Ber.*, **42**, 2556 (1909).

(4) J. Tafel and F. Andre, *Ber.*, **45**, 437 (1912).

(5) F. S. Prout, E. P.-Y. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).