TABLE I

DIALKYL TOLUENE-2,4-DICARBAMATES FROM CERTAIN MONOHYDRIC ALCOHOLS

Alcohol	Dicarbamate M.P. Lit., °C.	Dicarbamate M.P. Obsd., °C. (Uncorr.)	Formula	Nitrogen Calcd.	Nitrogen Found
Methyl	170–171[9]; 171[8]	170	$C_{11}H_{14}N_2O_4$	11.76	11.67
Ethyl	136.5[8]; 137[7]	135	$C_{13}H_{18}N_2O_4$	10.52	10.57[a]
n-Propyl		104	$C_{15}H_{22}N_2O_4$	9.52	9.66
Isopropyl	134[10]; 136[8]	134	$C_{15}H_{22}N_2O_4$	9.52	9.49
n-Butyl	80[9]	81	$C_{17}H_{26}N_2O_4$	8.69	8.66[a]
Isobutyl		120	$C_{17}H_{26}N_2O_4$	8.69	8.53
sec-Butyl	93[8]	89	$C_{17}H_{26}N_2O_4$	8.69	8.68
n-Amyl		89	$C_{19}H_{30}N_2O_4$	7.99	7.87
Isoamyl		76	$C_{19}H_{30}N_2O_4$	7.99	7.84
Neopentyl		132	$C_{19}H_{30}N_2O_4$	7.99	7.98[a]
n-Hexyl		83	$C_{21}H_{34}N_2O_4$	7.40	7.38
n-Heptyl		82	$C_{23}H_{38}N_2O_4$	6.89	7.03
n-Octyl	69[9]	69–70	$C_{25}H_{42}N_2O_4$	6.45	6.57[a]
n-Nonyl		72	$C_{27}H_{46}N_2O_4$	6.06	6.10
n-Decyl		72–73	$C_{29}H_{50}N_2O_4$	5.71	5.71[a]
n-Undecyl		61	$C_{31}H_{54}N_2O_4$	5.40	5.52[a]
n-Dodecyl	86[8]	87	$C_{33}H_{58}N_2O_4$	5.12	5.16
n-Tetradecyl		90	$C_{37}H_{66}N_2O_4$	4.65	4.67[a]
n-Hexadecyl	95–96[9]	93–94	$C_{41}H_{74}N_2O_4$	4.25	4.21[a]
n-Octadecyl		99.5–100	$C_{45}H_{82}N_2O_4$	3.92	3.89[a]
Cyclohexyl		158	$C_{33}H_{30}N_2O_4$	7.48	7.32
Benzyl		101–102	$C_{23}H_{22}N_2O_4$	7.18	7.11
β-Phenylethyl		129.5–130	$C_{25}H_{26}N_2O_4$	—	—

[a] Micro-Dumas by a commercial laboratory, others by macro-Kjeldahl.

bamates have been tested for carcinogenic activity,[11] as well as having been reported to show definite influence on experimental animal tumors,[12] six members of this series of carbamates (the dimethyl, diethyl, di-*n*-butyl, di-*sec*-butyl, di-*n*-decyl, and di-*n*-octadecyl) were submitted through the National Research Council (Chemical-Biological Coordination Center) to the National Cancer Institute for tumor chemotherapy against Sarcoma 37 in CAF1 mice. The results were negative. The herbicidal properties of certain carbamates[13–15] have attracted attention within recent years also. Certain members of the present series of dicarbamates are to be tested for herbicidal properties.

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A Synthesis of Aceanthrene

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Whilst the formation of 9,10-dihydrophenanthrene derivatives by the interaction of phenyllithium and 2,2′-dibromomethylbiphenyls has been fairly extensively studied,[1] the analogous formation of an ethane-bridge between the 1,8-positions of a naphthalene system has only been observed in one case, the synthesis of acenaphthene from 1,8-dibromomethylnaphthalene.[2] It seemed, therefore, worthwhile to add at least one more example.

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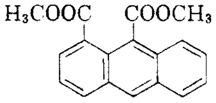
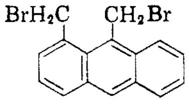
Dimethyl anthracene-1,9-dicarboxylate (I)[3] was reduced by lithium aluminium hydride to the corresponding diol and the latter converted into the dibromide (II). Treatment of II with phenyllithium gave aceanthrene (III) in 84% yield, the overall yield being 60%, calculated on the acid corresponding to I.

Aceanthrene (III) was identified by its m.p. and that of its picrate as well as by the absorption spectrum which was practically identical with that reported by Deno.[4]

For the preparation of anthracene-1,9-dicarboxylic acid, the oxidation of aceanthrenequinone (IV) by means of hydrogen peroxide was employed for the sake of convenience. This method has been used for the oxidation of acenaphthenequinone[5] and benzil.[6]



I



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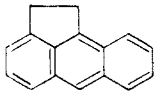
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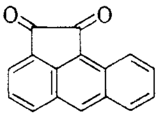

IV

EXPERIMENTAL

Aceanthrenequinone (IV) was prepared according to Liebermann and Zsuffa[7] from anthracene and oxalyl chloride in 58% yield. It was purified by sublimation and melted at 270°. The carbonyl absorption was observed at 1695 cm.$^{-1}$ (potassium bromide pellet).

Anthracene-1,9-dicarboxylic acid. When 6 ml. of 2*N* sodium hydroxide and 5 ml. of 30% hydrogen peroxide solution were added to a suspension of 1 g. of (IV) in 20 ml. of dioxane, an exothermic reaction set in which was kept under control by cooling with ice water. After 45 min., 50 ml. of water was added to the yellow solution and the acid precipitated by addition of dilute sulfuric acid. The yellow precipitate was filtered, washed with water, and dried. The yield was 1 g. (quantitative). The compound melted at 290° (this is probably the m.p. of the anhydride).[3]

Dimethyl anthracene-1,9-dicarboxylate (I). To a solution of 2.65 g. of the foregoing acid in 10 ml. of 2*N* sodium hydroxide, 2 ml. of dimethyl sulfate was added at 0° with stirring. After 1 hr., a yellow precipitate began to settle. With stirring, 1 ml. of dimethyl sulfate and 5 ml. of 2*N* sodium hydroxide and after a further hour, 0.5 ml. of dimethyl sulfate and 2.5 ml. of 2*N* sodium hydroxide were added, both at room temperature, and the stirring was continued for 1 further hour at room temperature and for 30 min. at 70°. The mass was cooled and the product filtered and recrystallized from isopropyl alcohol. The yellow needles of m.p. 149–150° were obtained in a yield of 2.5 g. (86%). The carbonyl absorption (potassium bromide pellet) was observed at 1700 cm.$^{-1}$

1,9-Dihydroxymethylanthracene. The solution of 2.2 g. of (I) in 50 ml. of benzene and 150 ml. of anhydrous ether was added to 1 g. of lithium aluminum hydride in 200 ml. of ether at 0°. Then the mixture was refluxed for 2 hr., cooled and decomposed with ice and dilute sulfuric acid. The organic layer was washed with water, sodium bicarbonate solution and water, dried and concentrated. After recrystallization from isopropyl alcohol, the product formed needles of m.p. 181–182°. The yield was 1.7 g. (95%).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 81.0; H, 5.7. IR spectrum (KBr pellet): 3200, 2900, 2800 cm^{-1}.

1,9-Dibromomethylanthracene (II). At 60°, 2.4 g. of phosphorus tribromide was added to the solution of 1.5 g. of the foregoing compound in 150 ml. of benzene, to which 3 drops of pyridine had been added. After 2 hr. at 55° (stirring), the mass was cooled, and water and ether was added. The organic layer was washed with sodium bicarbonate solution and water, dried and concentrated. The oily residue was triturated with petroleum ether and the solid product recrystallized from a mixture of benzene and petroleum ether. The yield was 2.1 g. (87%), the m.p. 138–139°.

Anal. Calcd. for $C_{16}H_{12}Br_2$: C, 52.8; H, 3.3. Found: C, 52.9; H, 3.5.

Aceanthrene (III). During 15 min., a solution of 1.8 g. of II in 20 ml. of dry benzene was added to a solution of phenyllithium, prepared from 0.033 g. of lithium and 0.8 g. of bromobenzene in 30 ml. of ether. The operation was carried out in an atmosphere of nitrogen. After 1 hr. at room temperature, 20 ml. of benzene was added and the mixture refluxed for 1 hr. The usual work-up yielded 0.8 g. (84%) of aceanthrene (III), which, after recrystallization from ethanol, formed yellow leaflets of m.p. 113–114°.[8,9]

Anal. Calcd. for $C_{16}H_{12}$: C, 94.1; H, 5.9. Found: C, 93.8; H, 5.6.

The *picrate*,[8,9] prepared in benzene solution and recrystallized from isopropanol, formed dark red needles of m.p. 120–121°.

Anal. Calcd. for $C_{22}H_{15}N_3O_7$: C, 61.0; H, 3.4. Found: C, 60.8; H, 3.4. Spectrum (in ethanol): 225 mμ (4.05); 256 mμ (4.14); 258 mμ (5.06); 355 mμ (3.50); 375 mμ (3.80); 395 mμ (3.56).

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Compounds Related to Podophyllotoxin. IX. 3,4-Methylenedioxyphenyllithium[1]

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The present communication is concerned with the preparation of 3,4-methylenedioxyphenyllithium, a reagent of interest in connection with work on the synthesis of picropodophyllin.

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(1) Previous papers of this series will be found in *J. Am. Chem. Soc.*, **72,** 3318 (1950); **73,** 5555 (1951); **74,** 2959 (1952); *J. Org. Chem.*, **18,** 9 (1953); *J. Am. Chem. Soc.*, **76,** 315, 5890 (1954); **77,** 3674 (1955); *J. Org. Chem.*, **21,** 261 (1956).