characterizing these nitropropanediols which often have poor melting or decomposition points. The various compounds prepared are listed in Table I.

EXPERIMENTAL[8,9]

METHODS

A. Reflux in benzene with external removal of water. Example: Preparation of 2,2,5-trimethyl-5-nitro-1,3-dioxane. A one-liter three-necked flask, fitted with a 55-mm. diameter Soxhlet extractor containing 250 g. of 8 mesh Drierite, was charged with 135 g. (1 mole) of 2-nitro-2-methyl-1,3-propanediol, 550 ml. of benzene, 100 ml. (1.4 mole) of acetone, and 0.5 g. of *p*-toluenesulfonic acid monohydrate. The mixture was refluxed for 44 hours. The drying agent was changed after 4 hours and after 20 hours with a 50:50 mixture of calcium chloride-Drierite. The reaction was followed by testing the amount of material remaining insoluble upon dilution of 1 ml. of the reaction mixture with 5 ml. of hexane and heating to boiling. After 44 hours, only traces of insoluble material remained.

At atmospheric pressure, 400 ml. of solvent was distilled. Hexane, 450 ml., was added and 450 ml. of solvent was distilled off again. The residue was diluted with 500 ml. of hexane at the boiling point and the solution was filtered through glass wool from a small amount of insoluble material. The filtrate, filled with crystals, was left in a deep freeze cabinet overnight and then was filtered. The product, dried *in vacuo*, weighed 157 g., m.p. 65–95°. It was not completely soluble in hot hexane indicating the presence of starting material. This material was dissolved in 150 ml. of hot acetone and was poured slowly with stirring into 600 ml. of water containing 2 ml. of conc'd ammonium hydroxide. The product crystallized instantly. Ice was added and after thorough cooling the mixture was filtered and the product was dried *in vacuo*. The yield was 132 g. (75%), m.p. 83–84°.

B. Using a molecular quantity of boron trifluoride-etherate and excess carbonyl reagent as solvent. Example: Preparation of 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane. A one-liter flask was charged with 151 g. (1 mole) of tris-hydroxymethyl nitromethane and 220 ml. (3 moles) of acetone. The mixture was heated on a steam-bath until all the tris-hydroxymethyl nitromethane had dissolved and then was cooled to 15–20°. The trimethylol compound crystallized in fine needles. Boron trifluoride-etherate (130 ml., 1 mole) was added with stirring. The temperature rose to 55° and crystals of product began to separate. After five minutes the mixture was poured as rapidly as possible into a stirred mixture of 1100 ml. of saturated sodium bicarbonate solution and excess ice. After stirring for 15 minutes the product was collected by filtration, washed with cold water, and dried *in vacuo*. The yield was 137 g. (72%). It was cream-colored and smelled slightly of mesityl oxide.

C. Using a molecular quantity of boron trifluoride-etherate and acetonitrile as solvent. Example: Preparation of 2-(3,3-dinitrobutyl)-5-hydroxymethyl-5-nitro-1,3-dioxane. Tris-hydroxymethyl nitromethane, 9 g. (0.06 mole), and 4,4-dinitropentanal, 8 g. (0.05 mole) were dissolved with slight warming in 24 ml. of acetonitrile. After addition of 7 ml. (0.05 mole) of boron trifluoride-etherate, the darkened solution was boiled on a steam-bath for 5–10 minutes and then was poured with stirring into a mixture of 65 ml. of saturated sodium bicarbonate solution and excess ice. The product was recrystallized from methanol to yield 7.4 g. (48%) of m.p. 157–159°.

Investigation of the effect of time of reaction on yield for Method B. Boron trifluoride-etherate, 42.6 g. (0.3 mole) was added to a solution of 50 g. (0.3 mole) of 2,2-dinitro-1,3-propanediol (90%) in 66 ml. (0.9 mole) of acetone. After the appropriate time interval, an aliquot was removed and poured into excess sodium bicarbonate solution and ice. The product was washed well with water and dried *in vacuo*.

Time After Mixing, Mins.	Yield of 2,2-dimethyl-5,5-dinitro-1,3-dioxane, %	Color of Product
5	55	Almost colorless
15	53	Light cream
30	51	Cream
60	48	Yellow
150	42	Brown

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Synthesis of Alkylphenanthrenes

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Alkylphenanthrenes, particularly 1-methylphenanthrene (I) and 1-methyl-7-isopropylphenanthrene (retene) (II) are desirable for reference spectra and for use in studies of the chemistry of hydrocarbons typical of those present in petroleum. These compounds are generally prepared by rather involved syntheses[2–6] which do not lend themselves to the preparation of large quantities. A more practical route to these hydrocarbons was found involving the simultaneous dehydrogenation, decarboxylation, and dealkylation of abietic acid (III), a readily available, inexpensive starting material. This is accomplished by passing the acid over a Pt-alumina-halogen catalyst (Universal Oil Products Co. R-5 type platforming catalyst), followed by a preliminary distillation, chromatography, and finally a precise distillation into the desired components. Product analyses indicate

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[8] The analyses were carried out by Dr. A. Elek, Elek Microanalytical Laboratory, Los Angeles, Calif. All melting and boiling points are uncorrected.

[9] All of the nitro hydroxy compounds were obtained as technical grade materials from Commercial Solvents Corp. The 5,5-dinitro-2-hexanone and 4,4-dinitropentanal were made by the method of Shechter, *et al.*[10] Boron trifluoride etherate was purchased from the General Chemical Co.

[10] Schechter, Ley, and Zeldin, *J. Am. Chem. Soc.*, **74**, 3664 (1952).

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[2] Haworth, *J. Chem. Soc.*, 1125 (1932).

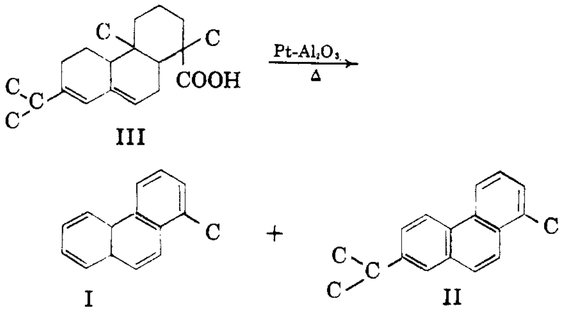
[3] Bardham and Sengupta, *J. Chem. Soc.*, 2520, 2798 (1932).

[4] Bogert, *Science*, **77**, 289 (1933).

[5] Cook and Hewett, *Chemistry & Industry*, **52**, 451 (1933).

[6] Vesterberg, *Ber.*, **36**, 4200 (1903).

that the following reactions occur during the process:



+ C_4–C_5 alkylphenanthrenes, CO_2, H_2, CH_4, C_2H_6, and C_3H_8 + partial degradation products

1-Methylphenanthrene and 1-methyl-7-isopropylphenanthrene were obtained in pure form. Hydrocarbons consisting of C_4 and C_5 alkylphenanthrenes were also isolated from the reaction mixture.

EXPERIMENTAL[7]

1-Methyl-7-isopropylphenanthrene. A 66% solution of abietic acid (Mathieson, Coleman and Bell, tech. grade) in benzene was prepared by dissolving 1260 g. of the acid in 735 ml. of the hydrocarbon solvent. The solution then was passed over a Pt-alumina catalyst in a fixed-bed continuous-flow unit. Operating conditions were as follows: Temperature = 480°, Hydrogen pressure = 50 p.s.i.g., Liquid hourly space velocity (vol. oil/vol. catalyst/hr.) = 0.8, H_2/oil mole ratio = 4/1. Gaseous products were analyzed by mass spectrometry. The total liquid product yielded 810 g. after the benzene solvent had been removed. A preliminary separation was made by means of a vacuum Engler distillation. The 315–400° cut (69%) containing the alkylphenanthrenes was chromatographed over alumina. The polyaromatic fraction from this operation (66%) then was distilled in a 30-plate 1-inch Oldershaw column at 24/1 reflux ratio. The fraction which had a b.p. 245–248°/22 mm. proved to be 1-methyl-7-isopropylphenanthrene and gave an over-all yield of 16.2%. Recrystallization of this fraction from aqueous ethanol afforded a product of m.p. 98–99°, similar to that in the literature.[8] The *picrate* melted at 124–125°.[8] Mass spectrometric analysis indicated the compound to be 99% methylisopropylphenanthrene.

Anal. Calc'd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.63.

Anal. Calc'd for *picrate* $C_{24}H_{21}N_3O_7$: N, 9.07. Found: N, 9.18.

1-Methylphenanthrene. The fraction boiling at 217–219°/22 mm. during the final distillation above consisted of 1-methylphenanthrene. On recrystallization from aqueous ethanol the compound had m.p. 119–120°[9] and the *picrate* melted at 137–138°.[9] Mass spectrometric analysis indicated the product to be 99% methylphenanthrene. The yield was 5.4%.

Anal. Calc'd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.37; H, 6.30.

Anal. Calc'd for picrate $C_{21}H_{15}N_3O_7$: N, 9.97. Found: N, 9.93.

C_4 and C_5 Alkylphenanthrenes. A liquid product (1.2%) was obtained during the final distillation above which had b.p. 257–259°/22 mm. Mass spectrometric analysis indicated this sample to be >95% C_4 and C_5 alkylphenanthrenes, n_D^{20} 1.6450.

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[7] All melting points uncorrected.

[8] Haworth, Letsky, and Mavin, *J. Chem. Soc.*, 1784 (1932); 1-methyl-7-isopropylphenanthrene, m.p. 98–99°; *picrate*, m.p. 123–124°.

[9] Bachmann and Wilds, *J. Am. Chem. Soc.*, 60, 624 (1938); 1-methylphenanthrene, m.p. 120–121°; *picrate*, m.p. 136–136.5°.

The Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine with Lithium Aluminum Hydride

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Recently reported work from this laboratory has shown that the lithium aluminum hydride reductions of acylhydrazines containing the group —CONH— are slow and that the yields of alkylhydrazines are generally poor.[1,2] In this class are found such compounds as benzhydrazide, 1-benzoyl-2,2-dimethylhydrazine, and 1,2-diacetylhydrazine. When the hydrogen of the —CONH— is replaced by a methyl or a phenyl group, reduction to the corresponding alkylhydrazine is rapid and the yields are fairly good (40–60 per cent).[1,2] This group of acylhydrazines includes such substances as 1-benzoyl-1-methylhydrazine,[2] and 1,2-diacetyl-1,2-dimethylhydrazine.[1] As would be expected, when both types of groups are contained in the same molecule, the group which lacks the hydrogen undergoes preferential reduction.[3]

To explore further the scope of this correlation between structure and ease of reduction the reaction of a 1,1-diacyl-2,2-dimethylhydrazine with lithium aluminum hydride was examined. Since the —CONH— group is absent, rapid reduction would be expected. 1,1-Dibenzoyl-2,2-dimethylhydrazine (I) was selected because of its availability.[1] From the reduction, carried out with a 100% excess of lithium aluminum hydride in refluxing tetrahydrofuran for two hours, the following products were isolated: 1-benzyl-2,2-dimethylhydrazine (21% yield), 1-benzoyl-2,2-dimethylhydrazine (18%), and a mixture of benzyl alcohol and benzaldehyde in which the alcohol predominated. A basic gas, which was evolved during decomposition of the excess hydride, was identified as *unsym*-dimethylhydrazine. None of the starting material was recovered. These facts are summarized in equation (1).

$$(1)\ \underset{\text{I}}{(C_6H_5CO)_2NN(CH_3)_2} \longrightarrow C_6H_5CONHN(CH_3)_2 + C_6H_5CH_2NHN(CH_3)_2 + C_6H_5CH_2OH + C_6H_5CHO + (CH_3)_2NNH_2$$

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[1] R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

[2] R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 2463 (1956).

[3] R. Huisgen, F. Jakob, W. Siegel, and A. Cadus, *Ann.*, **590**, 1 (1954).