Preparation of 2- and 5-Substituted-1,3-Dioxanes[1]

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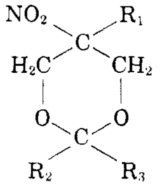
A new method for the preparation of cyclic ketals and acetals of variously substituted 2-nitro-1,3-propanediols has been developed. The usual procedure for the preparation of


I

such compounds is to reflux the diol and the carbonyl reagent in benzene with an acid catalyst and with the azeotropic removal of the water produced in the reaction.[2–6] However with a volatile ketone such as acetone ($R_2 = R_3 = CH_3$) the separation of water is difficult and the reaction proceeds reasonably well only when the distillate is passed over a drying agent before returning to the reaction vessel.[5] These reactions take from 2 to 50 hours for completion (Method A in Table I). We have found that addition of one mole of boron trifluoride-etherate to a solution of the diol in excess carbonyl reagent (Method B in Table I) or to a solution of one mole of diol and one mole of carbonyl reagent in acetonitrile (Method C in Table I) caused the rapid formation of the cyclic derivative, the reaction being complete in 5 to 10 minutes.

TABLE I

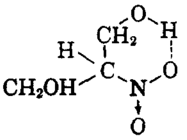
Substituted 5-Nitro-1,3-dioxanes of Formula I

R_1	R_2	R_3	M.P., °C.	Yield %	Method[a]	Calc'd C	Calc'd H	Calc'd N	Found C	Found H	Found N
CH_3	CH_3	CH_3	83–84[b]	75	A	47.99	7.48	8.00	48.18	7.24	8.60
				70	B						
CH_2OH	CH_3	CH_3	133–134[c]	72	B	43.97	6.85	7.33	44.49	6.57	6.95
NO_2	CH_3	CH_3	55.5–56[b]	70	A	34.95	4.89	13.59	35.54	5.00	13.62
				55	B						
C_2H_5	CH_3	C_2H_5	Liquid[d]	50	C	53.18	8.43	6.89	53.11	8.27	7.27
CH_3	H	H	70–71[e]	73	C	40.81	6.17	9.52	40.81	6.17	9.84
H	CH_3	CH_3	60–61[b]	37	B	44.71	6.88	8.69	45.32	6.78	8.52
C_2H_5	CH_3	CH_3	54–55[f]	53	B						
CH_2OH	H	$CH_3C(NO_2)_2CH_2CH_2$	157–159[g]	48	C	34.96	4.89	13.59	35.18	4.89	14.51
CH_2OH	CH_3	$CH_3C(NO_2)_2CH_2CH_2$	83–85[h]	34	C	37.15	5.30	13.00	37.77	5.50	12.43

[a] See experimental section. [b] From hexane. [c] From diisopropyl ether; previously reported by Senkus,[6] m.p. 130°, and Malinowski and Urbanski[7] m.p. 133–134°. [d] B.p. 65–70°/0.5 μ; previously reported by Senkus[6] b.p. 96°/2.5 mm. [e] From ethanol; previously reported by Senkus[2,4] m.p. 69°. [f] From methanol previously reported by Newman, *et al.*[3] m.p. 54–56°. [g] From methanol. [h] From chloroform.

Upon checking the effect of reaction time on yield it was found that the yield did not increase after five minutes, but on the contrary the yield dropped slowly after ten minutes. Replacement of the boron trifluoride-etherate with sulfuric acid or hydrochloric acid resulted in much lower yields of desired product and increased amounts of carbonyl reagent, self-condensation products.

Malinowski and Urbanski[7] recently reported that 2-nitro-1,3-propanediol did not react with ketones to form cyclic ketals, postulating a very stable cyclic structure with a hydrogen bond to account for this unusual behavior.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With the new method reported here, no difficulty was observed in transforming this diol to the cyclic acetone ketal.

With one exception, all the compounds prepared were readily hydrolyzed back to the starting materials with dilute aqueous mineral acid. The crystalline acetone derivatives of the diols investigated thus offer a ready means of purifying the technical products which are difficult to obtain free from small amounts of impurities of related structures. The acetone ketal of 2,2-dinitro-1,3-propanediol is much more stable to hydrolysis than the others. It can readily be purified by steam-distillation with little or no loss due to hydrolysis.

This new method serves as an excellent means of

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[1] This work was performed under a contract with the Office of Naval Research.

[2] Senkus, *J. Am. Chem. Soc.*, **63**, 2635 (1941).

[3] Newman, Magerlein, and Wheatley, *J. Am. Chem. Soc.*, **68**, 2112 (1946).

[4] Senkus, U. S. Patent 2,297,921.

[5] Salmi, *Ber.*, **71**, 1805 (1938).

[6] Senkus, U. S. Patent 2,368,071.

[7] Malinowski and Urbański, *Roczniki Chem.*, **25**, 183–212 (1951); *Chem. Abstr.*, **46**, 7993 (1952).

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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[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).

Synthesis of Alkylphenanthrenes

Albert Zlatkis[1]

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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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[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).