Table II

Purification from Melt Containing 5% α-*l* Impurity

| Crystal fragment | Labeled impurity, % |
|---|---|
| Interior sections washed with hexane | 0.21 |
|  | 0.23 |
|  | 0.27 |
| Interior section obtained by cleavage only | 0.18 |
| Fragment including exterior surface | 0.17 |
| Av impurity, % | 0.2 |
| Concn of impurity in melt, % | ~5 |
| Purification factor | 25 |

in flowing hexane. Results for the first two masses grown are shown in Table I. The data demonstrate excellent reductions in impurity levels, or factors of purification of 10–70, from relatively impure starting material. It will be noted that the optically clear region of the crystal showed the highest purity.

Another clear crystal was prepared after about half of the α-*d*-propoxyphene in the original 3% radioactive melt had been allowed to solidify or had been withdrawn by crystal growth. Relevant data for sections of this crystal and its surface shavings are found in Table II.

As an approach to ultrapurity, the purification obtained with starting material of 99+% purity was then studied, using a synthetic starting material containing 0.15% α-*l*, radioactively labeled. Two single crystals were prepared; data for these appear in Table III. The experiments show that purification factors increase with (1) increasing purity of starting material and (2) physical clarity of the crystal. They demonstrate that single-crystal growth may find application in the preparation of compounds which are chemically, including enantiomerically, ultrapure.

Table III

Purification from Melt Containing 0.15% α-*l* Impurity

|  | Purification factor | Impurity content, ppm | Final purity, % |
|---|---|---|---|
| Crystal 1 |  |  |  |
| Center section | 35 | 40 | 99.996 |
| Crystal 2 |  |  |  |
| Center section | 35 | 40 | 99.996 |
| Center section | 32 | 43 | 99.996 |
| Exterior shavings | 30 | 50 | 99.995 |

**(2*R*:3*S*)-4-Dimethylamino-1,2-diphenyl-3-methyl-2-(propionoxy-1-$^{14}$C)butane Hydrochloride.**—The radioactive α-*l*-hydrochloride was prepared by the acylation of the α-*l*-carbinol with mixed propionic-1-$^{14}$C–trifluoroacetic anhydride. Recrystallization from methanol-ethyl acetate, adding ether, gave product melting at 162–164°. Thin layer chromatography was carried out on a silica gel GF (E. Merck) plate using an ethyl acetate–ethanol (1:1) system. The single fluorescent spot was shown to be radiochemically pure by liquid scintillation counting of 1-cm sections of the plate.

**Registry No.**—(2*R*:3*S*-4-Dimethylamino-1,2-diphenyl-3-methyl-2-(propionoxy-1-$^{14}$C)butane hydrochloride, 13133-76-1; (2*R*:3*S*)-4-dimethylamino-1,2-diphenyl-3-methyl-2-propionoxybutane hydrochloride, 13133-77-2.

# A Novel, Facile Preparation of 1,1′-Bipyrene

Alexander J. Fatiadi

*Organic Chemistry Section, Division of Analytical Chemistry, Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234*

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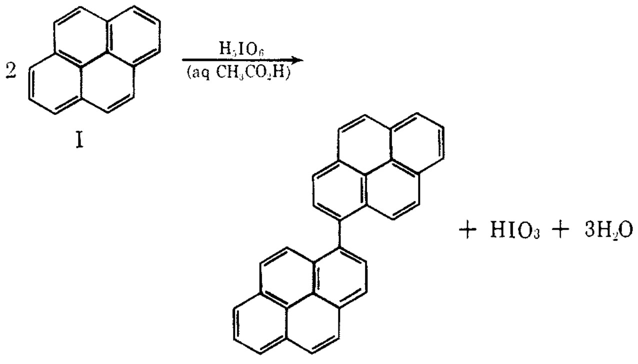
Previously, 1,1′-bipyrene (II) has been prepared in low yield (20–30%) by Ullman coupling, from iodopyrene and magnesium,[1] or bromopyrene and copper powder.[2,3] It has also been prepared[4] by shaking a mixture of pyrene (I), *p*-iodosotoluene, aqueous hydrofluoric acid, and chloroform for 3 days at 50°. The present method is the first report of a simple, one-step preparation of bipyrene by the use of a unique property of periodic acid; other important properties of this oxidant have been well reported.[5]



I

II

It has been found that treatment of a solution of pyrene (1 mole) in glacial acetic acid with an aqueous solution of periodic acid (1 mole) at 50° produces 1,1′-bipyrene in a yield of over 70%. The success of the reaction is dependent on (1) selectivity of the solvent (acetic acid) and (2) specificity of the oxidant (periodic acid). Acetic acid apparently participates in formation of solvated radicals and practically no coupling reaction is observed in *p*-dioxane, N,N-dimethylformamide, or ethanol. On the other hand, there is no coupling of pyrene when sodium periodate is used as the oxidant instead of periodic acid. This fact is consistent with the basicity of pyrene[6] and the assumption that the steps in the coupling of two pyrene molecules to give bipyrene include association with periodic acid, hydrogen abstraction, and recombination of radicals. The coupling reaction described may be specific for pyrene. Coupling products have not been obtained with 12 other polycyclic aromatic hydrocarbons examined.

## Experimental Section[7]

**Preparation of 1,1′-Bipyrene (II).**—A solution of 12.0 g (0.053 mole) of periodic acid in 10 ml of water and 40 ml of glacial

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[1] H. Lund and A. Berg, *Kgl. Danske Videnskab. Selskab. Mat-Fys. Medd.*, **22**, No. 15, 1 (1946); *Chem. Abstr.*, **40**, 6072 (1946).

[2] L. Ammerer and A. Zinke, *Monatsh.*, **84**, 25 (1953).

[3] E. Clar and O. Kuhn, *Ann. Chem.*, **601**, 181 (1956).

[4] G. M. Badger and J. F. Stephens, *J. Chem. Soc.*, 3637 (1956).

[5] E. L. Jackson, *Org. Reactions*, **2**, 341 (1944); J. M. Bobbitt, *Advan. Carbohydrate Chem.*, **11**, 1 (1956).

[6] E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

[7] Infrared spectra were determined on a Perkin-Elmer Infracord 137 spectrophotometer calibrated with a polystyrene film. Melting points are uncorrected.

acetic acid at 50° is added to a solution of 10.1 g (0.05 mole) of pyrene in 300 ml of glacial acetic acid contained in a 500-ml erlenmeyer flask and preheated to 50°. The reaction mixture is stirred at 48–51° for 45 min; 30 ml of warm water is then added; and the mixture is stirred for an additional 15 min. The reaction mixture is cooled to about 15–20° and crude bipyrene is collected on a Büchner funnel and washed with two 10-ml portions of warm 90% aqueous acetic acid. The still-wet product is then suspended in a solution of 5 g of sodium bisulfite and 10 g of sodium hydrosulfite dihydrate in 200 ml of 50% aqueous ethanol and stirred at 65° for 30 min. The hot suspension is filtered and the product is washed successively with warm water (50 ml) and warm 95% ethanol (50 ml): yield of crude bipyrene, 6.4–6.8 g. Concentration at 40° of the original filtrate to about 120 ml yields an additional crop, which is collected on a Büchner funnel and stirred with 50 ml of the bisulfite solution previously described: total yield, 7–7.5 g (70–75%); mp 310–315°. A further dilution of the original filtrate with water yields 2.0–2.5 g of brown-red solid containing 1,6- and 1,8-pyrenediones, 1-iodopyrene, and other products; this mixture can be separated by column chromatography.[8]

The crude bipyrene is purified in the following manner. Crude material (2.5 g) is dissolved in 425 ml of hot toluene and the solution is decolorized with carbon (5 g) and rapidly filtered. The product crystallizes out, but is redissolved by heating, giving a deep blue fluorescent solution which is kept overnight at room temperature. Bipyrene crystallizes as light-green, lustrous plates, 1.5–1.6 g, mp 334–336° (uncor). Concentration of the filtrate and extraction of the filter paper and decolorizing carbon yields additional material. Total yield of recrystallized bipyrene is 1.7–1.8 g (68–72%).

A sample of bipyrene purified by sublimation at 275° (0.05 mm), followed by recrystallization from *p*-xylene, melted at 336–338°. A sample of bipyrene recrystallized three times from 1:1 (v/v) toluene-pyridine and dried at 110° (0.1 mm) for 2 hr melted at 335–337°; this material produced a homogeneous, blue fluorescent spot on a thin layer chromatogram (silica gel and 90:5:5 (v/v) heptane-toluene-acetic acid), $R_f$ 0.41 ± 0.01. The product was found to be identical with an authentic sample of 1,1′-bipyrene[3] by mixture melting point (332–334°) and ultraviolet spectrum.[3] The infrared spectrum of II showed a characteristic triplet at $\nu_{max}^{KCl}$ 853, 846, and 835 $cm^{-1}$, not exhibited by pyrene. The reported melting points for bipyrene are 319–320°,[1] 327–328°,[2,3] and 325–326°.[4] The approximate solubility of pure bipyrene at 22° (in grams per 100 ml of solvent) is *p*-xylene, 0.1; pyridine, 0.185; and glacial acetic acid, 0.007.

**Registry No.**—II, 5101-26-8.

**Acknowledgments.**—The author thanks Drs. Robert Schaffer, Horace S. Isbell, and R. Stuart Tipson for their interest and the U. S. Department of Health, Education, and Welfare (Division of Air Pollution) for partial support of this research.

(8) A. J. Fatiadi, *J. Chromatog.*, **20**, 319 (1965).

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## Formation of 2-Methyl-2,4-pentanediol during a Meerwein-Ponndorf-Verley Reduction

CARL H. SNYDER

*Department of Chemistry, The University of Miami, Coral Gables, Florida 33124*

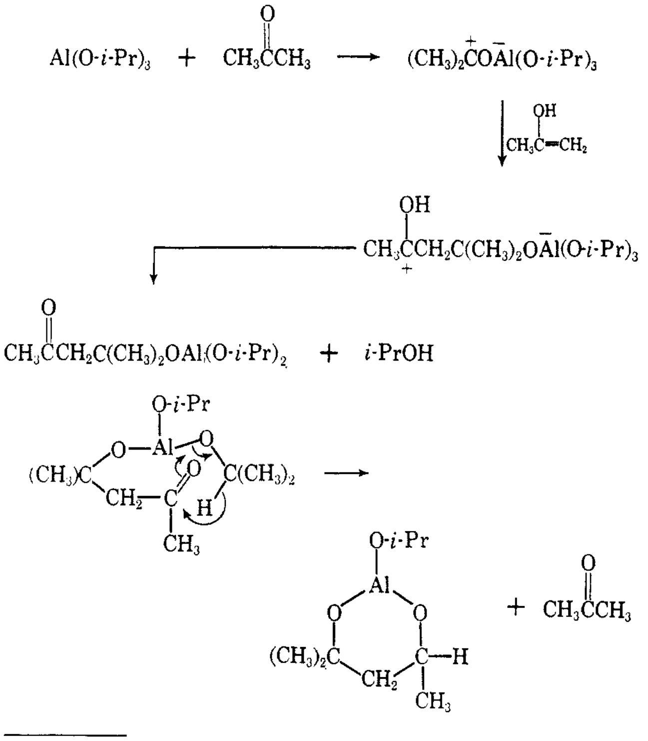
*Received February 27, 1967*

During gas chromatographic analysis of reaction products obtained on Meerwein-Ponndorf-Verley (MPV) reduction of 1,2-cyclohexanedione with aluminum isopropoxide,(1) a large, unexpected peak was observed. With the quantity of reagent dione held constant, the size of this unusual peak varied directly with aluminum isopropoxide stoichiometry. Reductions were carried out normally in toluene and under total reflux; the peak was not observed in chromatograms of either distillate or residue (after normal isolation) of one reduction from which acetone was distilled as it formed. The peak was observed, however, as a product on refluxing acetone and aluminum isopropoxide in toluene. On condensation of its corresponding effluent, the product proved to be 2-methyl-2,4-pentanediol (diacetone glycol).

Although catalysis of aldol additions by aluminum isopropoxide in the MPV reduction is well recognized,[2,3] this appears to be the first example of both a *reductive* aldol addition during an MPV reduction[4] and an MPV side reaction which must act to increase yields of desired alcohol by removing acetone from the MPV-Oppenauer equilibrium.

Although the mechanism of formation of this glycol has not been investigated, it presumably includes an aluminum isopropoxide promoted aldol dimerization of acetone to an aluminate of diacetone alcohol and an MPV reduction of this derivative to the aluminate of diacetone glycol. The process probably resembles that suggested for the acid-catalyzed aldol condensation of benzaldehyde and acetophenone.[5] One of several plausible routes may involve coordination of the aluminum with an acetone molecule, addition of the generated cationic moiety to acetone enol, and synchronous or stepwise exchange and MPV reduction. Aluminum isopropoxide, a Lewis acid, should be capable of catalyzing the keto-enol tautomerism of acetone. (See Scheme I.)

SCHEME I



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(1) C. H. Snyder, *J. Org. Chem.*, **31**, 4220 (1966).

(2) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 2646 (1949).

(3) A. L. Wilds, *Org. Reactions*, **2**, 178 (1944).

(4) Diacetone glycol was observed as one of the products of reaction of acetone and magnesium amalgam by L. Bouveault and R. Locquin (*Ann. Chim. Phys.*, **21**, 407; *Chem. Abstr.*, **6**, 472 (1911)).

(5) J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265, and references cited therein.