mole) of 3,5-dimethylbenzaldehyde[14,15] was added to the yellow solution. After standing for 5 days a white precipitate was observed. The solution was refluxed for 5 hr and the ethanol was concentrated to 5 ml on a rotary evaporator. The precipitate was dissolved in ether and the solution was extracted successively with dilute HCl and 15% Na_2CO_3 solution. The ether solution was concentrated and addition of 9.75 g of 2,4,7-trinitro-9-fluorenone (TNF) in 30 ml of ethanol gave a red, crystalline material, mp 199–200°.[16] Removal of the TNF by chromatography on neutral Al_2O_3 (Woelm) gave 182.2 mg of a white, crystalline material, mp 139–141°. Recrystallization from absolute ethanol gave the stilbene derivative as needle-like crystals, mp 140–141°.

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found:[17] C, 91.46; H, 8.58.

trans-**1,2-Di-α-naphthylethylene.**—This material was a gift from Dr. R. C. Sangster of the Massachusetts Institute of Technology.

Diphenyl Diselenide.—Diphenyl diselenide was obtained from Metallomer Laboratories. Its ultraviolet absorption spectrum showed a broad band at 238 mμ (log ε 4.42) tailing off with essentially no absorbance beyond 300 mμ.

Irradiation Apparatus.—A Hanovia 200-w Type S Hg lamp, without filter, inserted in a water-cooled Vycor jacket immersed in a water bath was used as an external light source. The irradiation vessel was a quartz tube 51 cm long and 2 cm in diameter fitted with an adapter for attachment to a high-vacuum line when necessary. Degassing was carried out in a manner similar to that recently described.[18] In all cases eight freeze–thaw cycles at pressures less than 5×10^{-5} mm were used.

Photoconversion of Stilbenes to Phenanthrene Derivatives. A. Photocyclization of *trans*-Stilbene.—Solutions (100 ml) of *trans*-stilbene in cyclohexane (10^{-3} *M*) were irradiated for the times indicated in Table I. Where Ph_2Se_2 was used as the sole oxidant, it was dissolved in a degassed cyclohexane solution and added to the degassed cyclohexane solution of *trans*-stilbene. The addition was performed under vacuum by the use of a special twisting adapter equipped with an addition tube. Before spectrophotometric analysis of the irradiated solutions was undertaken, selenium compounds were removed by chromatography on neutral Al_2O_3. The results are given in Table I.

B. Photocyclization of 3,3′,5,5′-Tetramethyl-*trans*-stilbene.—A stoichiometric amount of diphenyl diselenide was added to the stilbene solution and the resulting yellow solution was degassed prior to irradiation. After irradiation for 64.5 hr, quantitative spectral analysis revealed 51% 2,4,5,7-tetramethylphenanthrene. An authentic sample of 2,4,5,7-tetramethylphenanthrene was used for calibration and its complex with 1,3,5-trinitrobenzene proved identical with that obtained from the irradiated solution after removal of Se compounds by chromatography on neutral Al_2O_3.

C. Photocyclization of *trans*-1,2-Di-α-naphthylethylene.—A 10^{-4} *M* solution (50 ml) of *trans*-1,2-di-α-naphthylethylene in spectral grade cyclohexane was irradiated at room temperatures while a stream of compressed air was bubbled through the solution at a constant rate of 24 bubbles/min. On irradiation, the original fluorescence of the olefin disappeared and a crystalline substance precipitated. This material was filtered and identified as picene by its ultraviolet spectrum and the preparation of a complex with 2,4,7-trinitro-9-fluorenone which was identical with an authentic sample (melting point and mixture melting point). In a second experiment, the entire cyclohexane solution was evaporated to dryness. The residue was taken up in benzene and the ultraviolet spectrum showed an essentially quantitative conversion of *trans*-1,2-di-α-naphthylethylene to picene.

Acknowledgment.—We thank the National Science Foundation for their support of this work under grant GP-3356. We also thank Professor M. S. Newman for an authentic sample of 2,4,5,7-tetramethylphenanthrene.

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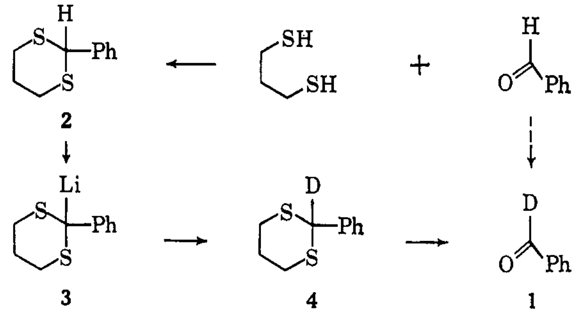
Synthesis of 1-Deuterioaldehydes. Benzaldehyde-1-*d*

D. SEEBACH,[1a] BRUCE W. ERICKSON,[1b] AND GURBAKHSH SINGH[1c]

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received August 1, 1966

The 1,3-dithiane ring is quantitatively metalated at C-2 with *n*-butyllithium in tetrahydrofuran at low temperatures.[2] This novel reaction provides a procedure of quite general applicability for replacing the hydrogen of an aldehyde by deuterium. An example of this procedure is the three-step conversion of benzaldehyde to benzaldehyde-1-*d* (1) in 82% over-all yield.



Crystalline 2-phenyl-1,3-dithiane (2) was isolated in 94.5% yield after treating an equimolar solution of 1,3-propanedithiol and benzaldehyde with hydrogen chloride.[3] Reaction of dithiane 2 with *n*-butyllithium in tetrahydrofuran below −50° generated a solution of lithium compound 3, which is synthetically equivalent to the conjugate base of benzaldehyde.[2] Addition of deuterium oxide gave deuteriodithiane 4 in 94.5% isolated yield. The extent of deuteration at C-2 was 99.9 ± 0.1% by nmr and mass spectral analysis. Pure benzaldehyde-1-*d* was obtained in 92% yield on hydrolysis of 4 with mercuric chloride–mercuric oxide.[4]

Previously benzaldehyde-1-*d* has been prepared by three methods of general use for the synthesis of 1-deuterioaldehydes: (1) by Rosenmund reduction of benzoyl chloride (66% over-all yield, 70–83% deuterium incorporation);[5] (2) by lithium aluminum deuteride reduction of methyl benzoate to benzyl alcohol-α,α-d_2 and Sommelet oxidation of the corresponding chloride (36%, 98%);[6] and (3) by α-deuteration of benzyltriphenylphosphonium chloride and hydrolysis of the N-benzalaniline-α-*d* formed on reaction with nitrosobenzene (64%, >92%).[7] These methods and

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[1] (a) Institut für Organische Chemie, Technische Hochschule Karlsruhe, 75-Karlsruhe, West Germany. (b) To whom inquiries should be sent; National Science Foundation Graduate Fellow, 1965–1967. (c) Foreign Scholar, U. S. Government Grant-in-Aid under the Fulbright-Hayes Program, 1965–1966, on leave from Banaras Hindu University, Varanasi, 5 India.

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seven less general routes[8] to **1** suffer from low over-all synthetic yield, low deuterium incorporation, or the use of costly lithium aluminum deuteride.

In contrast, the dithiane method incorporates deuterium derived from inexpensive deuterium oxide quantitatively and specifically at the aldehyde carbon in high over-all yield. This standard procedure is applicable to the rapid, large-scale preparation of a wide variety of 1-deuterioaldehydes.

In addition, 1-deuterioaldehyde precursors of type **4**, Ph = R, are readily and quite generally available from 1,3-dithiane by consecutive alkylation and deuteration.[2,3] Both operations may be carried out efficiently and conveniently in the same flask. Thus successive treatment of 1,3-dithiane with *n*-butyllithium, 2-iodopropane, *n*-butyllithium, and deuterium oxide provided 2-isopropyl-1,3-dithiane-2-*d* in 95% over-all yield.

Experimental Section

Melting points are corrected. Infrared spectra were observed in carbon tetrachloride on a Perkin-Elmer 237 grating spectrophotometer. Nmr spectra were observed in carbon tetrachloride on a Varian A-60 spectrometer; peaks are reported as parts per million downfield from internal tetramethylsilane reference. Mass spectra were taken on an AEI MS-9 double-focusing spectrometer at 11 and 70 ev; samples were introduced by sublimation at room temperature.

2-Phenyl-1,3-dithiane (**2**).—Dry hydrogen chloride was bubbled rapidly into a solution of 1,3-propanedithiol (40.0 ml, 0.395 mole) and benzaldehyde (40.0 ml, 0.393 mole) in chloroform (300 ml) until the mixture was saturated (5 min). The exothermic reaction was moderated by brief external cooling with ice–water. After standing 0.5 hr the mixture was washed with two 100-ml portions of water, three 100-ml portions of 10% potassium hydroxide solution, and two 100-ml portions of water; then it was filtered through anhydrous sodium sulfate and evaporated on a rotary evaporator. The residue was treated with charcoal and crystallized from 200 ml of methanol to furnish white needles (72.7 g, 94.5%), mp 69.0–69.8° (lit.[9] mp 70–71°), in three crops.

The infrared spectrum of **2** included strong bands at 3.38, 3.44, 6.88, 7.03, 7.85, 8.55, 10.97, 11.35, 14.4, and 14.8 μ. A band at 10.98 ± 0.04 μ is highly characteristic of the 1,3-dithiane ring.[3]

2-Phenyl-1,3-dithiane-2-*d* (**4**).—A solution of dithiane **2** (138.7 g, 0.705 mole) in anhydrous tetrahydrofuran (1.3 l.) was treated under nitrogen at −60 to −75° during 1 hr with a solution of *n*-butyllithium in hexane (Foote Mineral Co.; 500 ml, 0.80 mole). After standing 6 hr below −50° the solution was treated with deuterium oxide (>99.9% *d;* 90 ml) and warmed to room temperature; 0.05 *M* hydrochloric acid was added to the organic phase and tetrahydrofuran was removed on a rotary evaporator. The residue was shaken with 1:1 (v/v) dichloromethane–pentane; the organic phase was washed with sodium bicarbonate solution, water, and saturated salt solution and then dried over potassium carbonate. The residue after evaporation of solvent was crystallized from methanol to provide white needles (131.4 g, 94.5%), mp 68.8–69.8°, in three crops.

The nmr singlet at 5.07 ppm due to the proton at C-2 was absent. Deuterium incorporation at C-2 was 99.9 ± 0.1% by low voltage mass spectral comparison with nondeuterated **2**. The infrared spectrum was similar to that of **2**, except that the 8.55-μ band was absent, new bands were seen at 4.58 and 4.69 μ (weak; C–D stretch) and 14.1 μ, and the bands at 10.97 (dithiane) and 11.35 μ were shifted to 11.02 and 11.31 μ, respectively.

Benzaldehyde-1-*d* (**1**).—Treatment of a warm solution of dithiane **4** (9.87 g, 50.0 mmoles) in 9:1 (v/v) methanol–water (250 ml) with solid mercuric oxide (9.8 g, 45 mmoles) and a solution of mercuric chloride (27.2 g, 100 mmoles) in the same solvent mixture (50 ml) gave a voluminous white precipitate. The mixture was refluxed for 4 hr under nitrogen and then cooled. After filtration to remove the white solid, solvent was removed from the filtrate by distillation through a 20-cm Vigreux column under nitrogen until about 100 ml remained. Dichloromethane–pentane (100 ml), 1:1 (v/v), was added and the mixture was shaken twice with 100 ml of half-saturated ammonium acetate solution and twice with 100 ml of saturated salt solution and then dried over sodium sulfate. Most of the solvent was removed as before to furnish a colorless liquid that consisted of dichloromethane (53 mole %) and deuterioaldehyde **1** (47 mole %, 4.9 g, 92%) by nmr analysis. Distillation afforded a colorless liquid (4.32 g, 81%), bp 77–78° (27 mm), that was pure benzaldehyde-1-*d* by nmr; no aldehyde proton absorption was seen at 9.95 ppm.

2-Isopropyl-1,3-dithiane-2-*d*.—A solution of 1,3-dithiane (0.252 g, 2.1 mmoles) in anhydrous tetrahydrofuran (10 ml) was stirred at −25° under nitrogen while *n*-butyllithium solution (2.3 mmoles) was added. After 1.5 hr the solution was warmed to 0° and treated with 2-iodopropane (0.42 g, 2.5 mmoles). After 14 hr at 0° the solution was cooled to −25° and treated with *n*-butyllithium solution (2.7 mmoles). After 1.5 hr deuterium oxide (>99.9%, 1 ml) was added. The isolation procedure described for **4**, but using pentane as extraction solvent, furnished a colorless liquid (0.326 g, 95%) which microdistilled at a bath temperature of 58° (0.15 mm). Deuterium incorporation at C-2 was greater than 98% by nmr analysis.

Acknowledgments.—This work was supported in part by the National Science Foundation and the National Institutes of Health.

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Nickel as an Alkylation Catalyst

William A. Bonner and Robert A. Grimm

Department of Chemistry, Stanford University,
Stanford, California 94305

Received June 2, 1966

This investigation was initiated in an attempt to learn more about the action on various substrates of "hydrogen-free Raney nickel" (RaNi-200°), prepared by degassing ordinary Raney nickel catalyst[1] at 200–250° under vacuum.[2,3] In particular, we wished to study the reactions of this catalyst with certain halogenated and oxygenated compounds of types not previously studied.

The usual reaction, if any, of ordinary Raney nickel with organic halides involves simple hydrogenolysis to the corresponding monomeric alkane derivative.[4–8] In a few instances,[7,8] however, especially when the catalyst/substrate ratio was low,[7] Raney nickel has been found to convert organic halides into dimeric coupling products—benzyl chloride, for example, yield-

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