Photocyclization–Aromatization of Stilbenes Using Selenium Radicals. A Synthesis of 2,4,5,7-Tetramethylphenanthrene[1]

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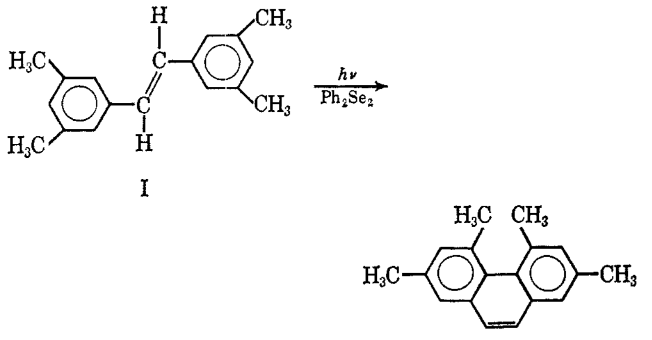
Previous work in this laboratory[2,3] has shown that selenium aromatization of hydroaromatic compounds can be achieved to a substantial degree without the concomitant formation of H_2Se. The selenium in such cases functions as a hydrogen-transfer agent and aromatization proceeds by disproportionation and the simultaneous production of compounds more highly hydrogenated than the original hydroaromatic. The reactive selenium species is unquestionably a selenium radical, RSe, and because such radicals may be generated at low temperatures by irradiation of appropriate precursors,[4] attention was focused on room-temperature irradiation processes.

It has been shown elsewhere[5] that irradiation of *trans*-stilbene in the presence of air, or air and iodine, gives phenanthrene *via* *trans*-4a,4b-dihydrophenanthrene as an intermediate. We repeated this work except that air was rigidly excluded and have confirmed that although isomerization occurs under these conditions, no phenanthrene is produced. However, when diphenyl diselenide is present in the air-free system, phenanthrene is obtained in 21% yield. A mixture of dissolved air and diphenyl diselenide gave phenanthrene in 86% yield. These experiments demonstrate that selenium radicals can abstract hydrogen atoms and cause aromatization.

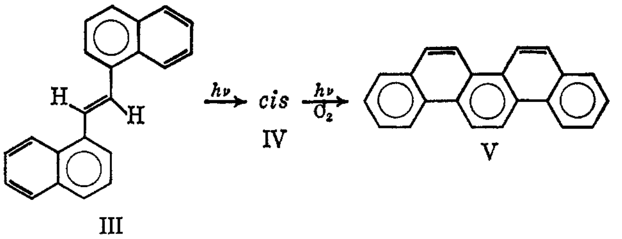
The photoconversion reaction was then extended to the synthesis of highly hindered phenanthrene derivatives. The irradiation of 3,3′,5,5′-tetramethyl-*trans*-stilbene (I) in the presence of diphenyl diselenide gave the known[6] hindered 2,4,5,7-tetramethylphenanthrene (II). It is of interest to note that photocyclization of 3,3′-dimethoxy-*trans*-stilbene is reported[7] to give only 2,5- and 2,7-dimethoxyphenanthrenes; no 4,5-dimethoxyphenanthrene was found.



I

II

In a further extension of this reaction we have found that irradiation of *trans*-1,2-di-α-naphthylethylene (III) at room temperature in air, which was previously reported[8] to yield irreversible unidentified photoreaction products, actually yields picene (V). Picene was identified by its ultraviolet spectrum[9] and by its charge-transfer complex with 2,4,7-trinitro-9-fluorenone.[10] Very likely the cyclization proceeds *via* the *cis* intermediate (IV) which, however, was not isolated.



III

Table I summarizes the results of our photocyclizations. Yields were determined spectrophotometrically[11,12] on a Cary Model 11 recording spectrophotometer.

TABLE I

PHOTOCONVERSION OF STILBENES TO PHENANTHRENE DERIVATIVES[a]

Stilbene	Concn, M, in cyclohexane	Irrad time, hr	Oxidant, concn (M)	Yield of aromatic compd, %
trans-Stilbene	10^{-2}	4.5	$(C_6H_5)_2Se_2$, 10^{-2}	Phenanthrene, 21
trans-Stilbene	10^{-2}	47	$(C_6H_5)_2Se_2$ + O_2, 10^{-2}	Phenanthrene, 86
5,3′,5,5′-Tetramethyl-*trans*-stilbene	10^{-2}	64.5	$(C_6H_5)_2Se_2$, 10^{-2}	2,4,5,7-Tetramethylphenanthrene, 51
trans-1,2-Di-α-naphthylethylene	10^{-4}	3	O_2	Picene, 100

[a] No attempt was made to optimize efficiency or yields.

Experimental Section

***trans*-Stilbene.**—Scintillation grade *trans*-stilbene obtained from Matheson Coleman and Bell was used without further purification. Its absorption spectrum was identical with that reported in the literature.[12]

3,3′,5,5′-Tetramethyl-*trans*-stilbene.—3,5-Dimethylbenzylphosphonium bromide (0.6 g, 0.024 mole) was prepared by refluxing 4.6 g (0.025 mole) of 3,5-dimethylbenzyl bromide[13] with 6.55 g (0.025 mole) of triphenylphosphine in 50 ml of tetrahydrofuran for 24 hr. The precipitate was filtered and dissolved in 100 ml of absolute ethanol. After addition of 1.3 g (0.024 mole) of sodium methoxide in 30 ml of absolute ethanol, 3.52 g (0.024

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[1] Taken in part from the Ph.D. Dissertation of Elliott J. Levi, University of Cincinnati, 1966.

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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^{-2} *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.

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

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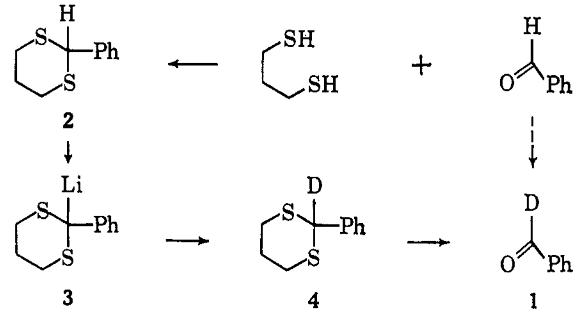
The 1,3-dithiane ring is quantitatively metalated at C-2 with *n*-butyllithium in tetrahydrofuran at low temperatures.[2] This novel reaction provides a procedure of quite general applicability for replacing the hydrogen of an aldehyde by deuterium. An example of this procedure is the three-step conversion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