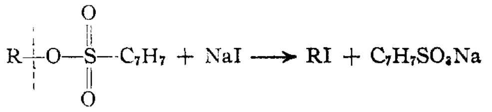
[CONTRIBUTION FROM THE IODINE EDUCATIONAL BUREAU'S INDUSTRIAL FELLOWSHIP, AND THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

The Action of Sodium Iodide on Some Aryl *p*-Toluenesulfonates

BY R. STUART TIPSON AND PAUL BLOCK, JR.

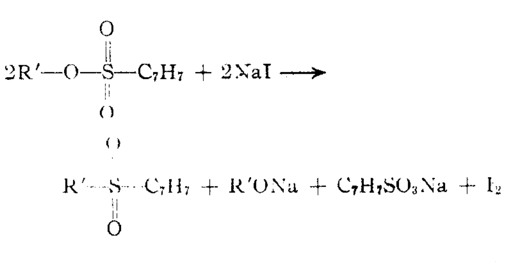
The action of sodium iodide, in water or acetone, upon *p*-toluene-sulfonyl ("tosyl") esters of primary aliphatic alcohols (including that grouping in sugars) has been rather extensively studied[1] and found to proceed as an alkyl-oxygen fission[2] in accordance with equation (1).



$$R\vdots O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_7H_7 + NaI \longrightarrow RI + C_7H_7SO_3Na \quad (1)$$

On the other hand, very little attention appears to have been paid to the action of this reagent upon aryl *p*-toluenesulfonates. Rodionov[1] mentions that a hot, concentrated aqueous or alcoholic solution of sodium iodide is devoid of action on phenyl or naphthyl *p*-toluenesulfonates at atmospheric pressure or in an autoclave. We now find that phenyl *p*-toluenesulfonate and monotosyl apocupreine are unaffected by treatment with sodium iodide in acetone, in a sealed tube at 100° during two hours.

Now it is well known that, compared with other aryl tosylates, negatively substituted aryl tosylates display enhanced lability and reactivity. We have therefore examined the behavior of 2,4-dinitrophenyl *p*-toluenesulfonate toward sodium iodide in acetone, under the above conditions, and find that a reaction takes place; but the reaction is not in conformity with equation (1), which would only give rise to 2,4-dinitroiodobenzene and sodium *p*-toluenesulfonate. Instead, the products include *p*-tolyl 2,4-dinitrophenyl sulfone, sodium 2,4-dinitrophenate, sodium *p*-toluenesulfonate, and free iodine, presumably formed in accordance with the following over-all equation (2), where R′ = 2,4-dinitrophenyl.



$$2R'-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_7H_7 + 2NaI \longrightarrow R'-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_7H_7 + R'ONa + C_7H_7SO_3Na + I_2 \quad (2)$$

The identity of the sulfone was established by elementary analysis and by its melting point. The latter was unchanged on admixture of a sample with authentic specimens prepared by either of two recognized methods.[3,4]

It seemed probable that the reaction with sodium iodide involves intermediate reduction to the *sulfinate*, the nitro groups remaining unaffected. In contrast, acid reduction gave 2,4-diaminophenyl *p*-toluenesulfonate; and reduction of the sulfone with stannous chloride gave *p*-tolyl 2,4-diaminophenyl sulfone.

Experimental

Action of Sodium Iodide on (a) Phenyl *p*-Toluenesulfonate and Monotosyl Apocupreine.[5]—A weighed amount of dry ester was treated with one hundred per cent. excess of a 10% solution of anhydrous sodium iodide in acetone, in a sealed tube at 100° during two hours. In each case the clear, colorless solution remained clear and colorless, and no crystals separated out on cooling to room temperature.

(b) **2,4-Dinitrophenyl *p*-Toluenesulfonate.**—The dry, recrystallized ester[5,6,7] (0.564 g.; m. p., 121–122°) was treated with sodium iodide in acetone as described above. The yield of sodium *p*-toluenesulfonate (insoluble in acetone, completely soluble in water) was 0.1467 g. (45.3% of the theoretical according to equation (1), or 90.6% according to equation (2)). Much free iodine was liberated.

Acetone was added to the clear, dark brown filtrate until the volume was 35 cc., and then 75 cc. of water was added. After standing overnight at room temperature, the colorless crystals which had deposited were filtered off and dried in the vacuum desiccator. This material proved to be slightly impure sulfone; it weighed 0.2330 g. (86.8% of the theoretical required by equation 2) and had m. p., 170°. It was recrystallized from 20 cc. of boiling, absolute ethanol, and then had m. p. 187–188°, and the following composition.

Anal. Calcd. for $C_{13}H_{10}O_6N_2S$: C, 48.42; H, 3.13; N, 8.70; S, 9.95. Found: C, 48.24; H, 3.22; N, 8.77; S, 9.66.

On admixture of a sample with authentic *p*-tolyl 2,4-dinitrophenyl sulfone having m. p. 187° (prepared either by the method of Bost, *et al.*,[3] or by that of Loudon[4]) the melting point was unchanged.

The colorless, aqueous acetone filtrate was now evaporated to dryness and the crystalline product stirred with 10 cc. of water. The mixture was filtered, the crystals washed with a further 10 cc. of water and then dried in a vacuum desiccator. This material weighed 0.1650 g., contained traces of sulfur and iodine, and had a composition indicating that it was slightly impure dinitrophenol.

Anal. Calcd. for $C_6H_4O_5N_2$: C, 39.12; H, 2.19; N, 15.22; Na, 0.00. Found: C, 39.98; H, 2.35; N, 14.11; Na, 0.00.

In order to estimate the amount of free iodine liberated, a separate sample of ester was treated with sodium iodide in acetone as described. After completion of the reaction the tube was immediately cooled in solid carbon dioxide–chloroform, opened, and the iodine rapidly estimated by titration with standardized sodium thiosulfate solution with starch indicator. Iodine found: 0.18 g. (85% of the theoretical required by equation 2).

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[1] Peacock and Menon, *Quart. J. Indian Chem. Soc.*, **2**, 240 (1925); Rodionov, *Bull. soc. chim.*, **39**, 305 (1926); Freudenberg and Raschig, *Ber.*, **60**, 1633 (1927); Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

[2] Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941); Balfe, Kenyon and Tárnoky, *J. Chem. Soc.*, 446 (1943).

[3] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

[4] Loudon, *J. Chem. Soc.*, 537 (1935).

[5] Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[6] Freudenberg and Hess, *Ann.*, **448**, 121 (1926).

[7] Ullmann and Nádai, *Ber.*, **41**, 1870 (1908).

Reduction of 2,4-Dinitrophenyl *p*-Toluenesulfonate.—Hydriodic acid (const. boiling, 1.5 cc.) was added to a solution of 2,4-dinitrophenyl *p*-toluenesulfonate (0.5 g.) in 7.5 cc. of acetic acid containing 1 g. of red phosphorus, and the mixture heated under reflux during ninety minutes. The phosphorus was then filtered off and washed with a little hot acetic acid. A small volume of aqueous sodium bisulfite was added to the filtrate, followed by saturated sodium hydroxide until the solution was alkaline. The resulting precipitate was filtered off (0.3 g., m. p. 112–117°) and purified by dissolving in acid, reprecipitating with alkali, and recrystallizing from dilute ethyl alcohol. It then had m. p. 121–123°. On acetylation it gave a diacetate which, after recrystallizing from absolute ethanol, had m. p. 166°. (Ullmann and Nádai[7] gave m. p. 167°.)

Reduction of *p*-Tolyl 2,4-Dinitrophenyl Sulfone.—On adding a solution of 2.25 g. of stannous chloride in 3 cc. of absolute ethanol to the sulfone (0.5 g.) there was a violent reaction. Concentrated hydrochloric acid (3 cc.) was added, the solution evaporated to half its volume, made alkaline with sodium hydroxide solution, and the crude amine filtered off. It was purified by dissolving in acid, reprecipitating with alkali, and recrystallizing from alcohol. It had m. p. 187° (191°, cor.) and on admixture with starting material melted at 160°.

Anal. Calcd. for $C_{13}H_{14}O_2N_2S$: C, 59.50; H, 5.38. Found: C, 59.66; H, 5.54.

Summary

A solution of sodium iodide in acetone is devoid of action on phenyl *p*-toluenesulfonate or monotosyl apocupreine, in a sealed tube at 100° during two hours. Under the same conditions, 2,4-dinitrophenyl *p*-toluenesulfonate gives rise to an equimolecular mixture of *p*-tolyl 2,4-dinitrophenyl sulfone, sodium 2,4-dinitrophenate, sodium *p*-toluenesulfonate, and free iodine.

Reduction of the sulfone with stannous chloride yields *p*-tolyl 2,4-diaminophenyl sulfone.

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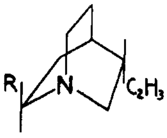
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The *cis*- and *trans*-Forms of *dl*-3,4-Diethylpiperidine[1]

BY C. F. KOELSCH AND CHARLES H. STRATTON

Twenty-two years ago, certain ingenious deductions led Kenner[2] to the conclusion that quinine and cinchonidine corresponded sterically to structure I, quinidine and cinchonine to structure II.



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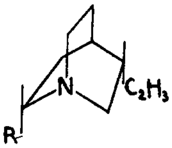
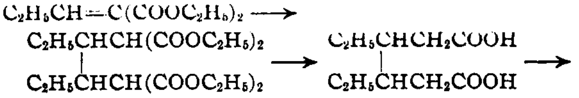
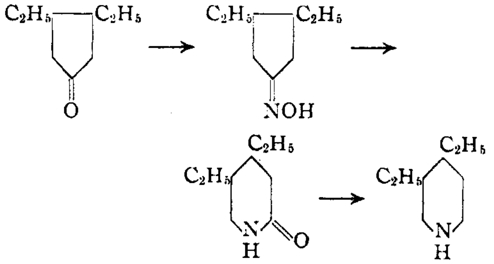


II

Some time ago it appeared desirable to establish these structures more directly, and some experiments were undertaken in this Laboratory with that end in view. However, the recent work of Prelog and Zalán[3] has amply confirmed Kenner's conclusion,, and our investigation has now been discontinued. One result of our investigation of some general interest is described in the present paper. The synthesis of the two forms of *dl*-3,4-diethylpiperidine has been carried out through the reactions outlined below, and it has been possible to identify the *cis* and the *trans* forms of the base by determining the respective *meso* or *dl* configuration of the intermediate β,γ-diethyladipic acid.



$$C_2H_5CH{=}C(COOC_2H_5)_2 \longrightarrow \begin{array}{l} C_2H_5CHCH(COOC_2H_5)_2 \\ \quad | \\ C_2H_5CHCH(COOC_2H_5)_2 \end{array} \longrightarrow \begin{array}{l} C_2H_5CHCH_2COOH \\ \quad | \\ C_2H_5CHCH_2COOH \end{array} \longrightarrow$$



Experimental

Reduction of ethyl propylidenemalonate with sodium amalgam according to the procedure used for the ethylidene analog[4] was unsatisfactory. Even though the reaction mixture was never allowed to become basic, large amounts of ketonic material were formed. Reduction with aluminum amalgam, the reagent used by Vogel[5] for a similar purpose, likewise gave a mixture containing ketonic material. But hydrolysis of this latter mixture under special conditions, followed by decarboxylation furnished the desired two forms of β,γ-diethyladipic acid. The following experiment is representative of eleven similar ones.

Ten grams of 0.001 in. aluminum foil was pressed into a 500 ml. flask and covered with 10% sodium hydroxide. When the evolution of hydrogen became brisk, the solution was decanted, and the metal was washed with water, alcohol, and ether. A mixture of 200 ml. of ether, 100 g. of ethyl propylidenemalonate and 3 g. of mercuric chloride was poured into the flask, and the whole was shaken vigorously until amalgamation appeared complete. Water (30 ml.) was then added and the flask was left under a reflux condenser for ten hours. Sodium sulfate was then added, the mixture was filtered, and the insoluble materials were washed well with ether. Distillation of the ether solution gave 34.5 g. of ethyl propyl- and propylidenemalonate, b. p. 105–115° at 12 mm., and 52 g. of dimeric reduction products, b. p. 184–188° at 3 mm. Redistillation of the latter at 6 mm. (b. p. 190°) led to no useful

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(1) From the Ph.D. Thesis of Charles H. Stratton, September, 1943.

(2) Kenner, *Ann. Rep. Chem. Soc.*, **19**, 156 (1922).

(3) Prelog and Zalán, *Helv. Chim. Acta*, **27**, 535 (1944).

(4) Higgenbotham and Lapworth, *J. Chem. Soc.*, **123**, 1618 (1923).

(5) Vogel, *ibid.*, 1985 (1927); 1013 (1928).