Resolution of a Sterically Hindered Stilbene Derivative, 4-Amino-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene

By Michinori Ōki

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The author and Y. Urushibara(1) deduced the non-planar structures of α, α'-disubstituted stilbene derivatives from their ultraviolet absorption. If one of the rings is sterically hindered from rotating over the central substituted vinylene group and substituted unsymmetrically, then the stilbene derivative is expected to exist in optical enantiomorphs.

The author synthesized 4-amino-3′-bromo-α'-chloro-α, 2′, 4′, 6′-tetramethylstilbene, 4-$H_2NC_6H_4CMe{=}CClC_6HBrMe_3$-3′, 2′, 4′, 6′, and resolved it by means of *d*-camphorsulfonic acid. The benzoyl derivative of the resolved amine showed m. p. 159–160° and $[\alpha]_D^{20}$ $+56.1°$. The enantiomorph was not isolated. This is the first example of an optically active stilbene derivative containing no asymmetric carbon atom.

Experimental Part

4-Nitrobenzyl 3′-bromo-2′, 4′, 6′-trimethylphenyl ketone (I).—4-$O_2NC_6H_4CH_2COC_6HBrMe_3$-3′, 2′, 4′, 6′. Powdered anhydrous aluminum chloride (15 g.) was added gradually to a boiling solution of bromomesitylene(2) (20 g.) and *p*-nitrophenylacetyl chloride(3) (20 g.) in carbon bisulfide (150 cc.), and the mixture was heated for 30 minutes, and treated with ice and hydrochloric acid. After standing overnight the solid was recrystallized from alcohol with use of active charcoal. Nearly colorless needles melting at 121.5—123° (yield 15 g.). Found: N, 3.95. Calculated for $C_{17}H_{16}O_3NBr$: N, 3.87%.

α-(4-Nitrophenyl)ethyl 3′-bromo-2′, 4′, 6′-trimethylphenyl ketone (II).—4-$O_2NC_6H_4CHMeCO$ C_6HBrMe_3-3′, 2′, 4′, 6′. I (10 g.) and a solution of metallic sodium (0.7 g.) in absolute alcohol (20 cc.) were heated to a homogeneous solution, then with addition of methyl iodide (4.3 g.) to neutral reaction, and poured into water (100 cc.). Alcohol was evaporated under diminished pressure and the remainder was shaken with ether. The ether solution was washed with aqueous sodium thiosulfate, dried, and evaporated. The residue solidified and was recrystallized from alcohol-acetone. Pale yellow leaflets melting at 125—126° (yield 8 g.). Found: N, 3.72. Calculated for $C_{18}H_{18}O_3NBr$: N, 3.72%.

4-Nitro-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene (III).—4-$O_2NC_6H_4CMe{=}CClC_6HBr$ Me_3-3′, 2′, 4′, 6′. II (12 g.) was dissolved in phosphorus oxychloride (60 cc.), phosphorus pentachloride (30 g.) was added, and the mixture was heated on a waterbath for 2 hours. The cooled reaction mixture was treated with ice water and the formed viscous substance was recrystallized from alcohol-acetone. (The mother liquor gave a hardly solidifiable mass, presumably the cis-isomeride.) One more recrystallization from acetone gave pale yellow prisms melting at 92—93° (yield 6 g.). Found: N, 3.59. Calculated for $C_{18}H_{17}O_2NClBr$: N, 3.55%.

4-Amino-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene (IV).—4-$H_2NC_6H_4CMe{=}CClC_6HBr$ Me_3-3′, 2′, 4′, 6′. III (7 g.) was heated with tin (10 g.) and alcohol (50 cc.) on a waterbath, concentrated hydrochloric acid (10 cc.) diluted with alcohol (10 cc.) was added gradually, and the mixture was heated until no violet coloration occurred on adding one drop to alcoholic potash. Alcohol was evaporated under reduced pressure, the residue was decomposed with 5% aqueous caustic soda, and the separated oil was collected. The amine, being uncrystallizable, was benzoylated for characterization. Colorless fine crystals melting at 159—160°. Found: N, 3.11. Calculated for $C_{25}H_{23}ONClBr$: N, 2.99%.

Dextro-rotatory Benzoyl Derivative from the Amine (IV).—A solution prepared by dissolving the free amine (IV) (3 g.) in an aqueous acetone solution of *d*-camphorsulfonic acid (5 g.) gave an oily deposit on cooling which solidified in a time. Recrystallization from water-acetone containing a small amount of *d*-camphorsulfonic acid to a constant melting point or rotation (three recrystallizations usually) gave colorless plates melting at 140°. Found: N, 2.42. Calculated for $C_{26}H_{35}O_4SNClBr$: N, 2.35%. $[\alpha]_D^{20}+272.8°$(0.0247 g. in 6 cc. alcoholic solution, $\alpha_D^{20}+1.14°$).

The recrystallized *d*-camphorsulfonate was decomposed with 10% aqueous caustic soda. The uncrystallizable free amine was benzoylated with benzoyl chloride and pyridine, and the product was recrystallized from benzene-petroleum ether. Colorless fine crystals melting at 159—160°. Found: N, 2.96. Calculated for $C_{25}H_{23}ONClBr$: N, 2.99%. α_D^{20} of 0.0627 g. of the substance in

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(1) This Bulletin, **25**, 109 (1952); Also see M. Ōki, ibid., **25**, 112 (1952); **26**, 37 (1953).

(2) R. Adams and H. A. Stearns, "Organic Syntheses", Vol. XI, p. 24.

(3) E. Wedekind, *Ann.*, **378**, 289 (1911).

4 cc. alcoholic solution was found +0.88°. $[\alpha]_D^{20}$ +56.1°.

Department of Chemistry, Faculty of
Science, Tokyo Metropolitan
University, Meguro, Tokyo