the general polyphosphoric acid cyclization directions.[9] Procedure described in Experimental was typical and appeared to be general for this type of cyclization.

In view of elimination of the two extra steps of tosylation and detosylation and the simplicity of the experimental procedure, this new method offers clear advantages over those previously reported and provides a convenient synthetic route for the preparation of quinoline derivatives.

This study is currently being extended to isoquinolones, oxindoles and 5-ketotetrahydrobenzazepines. Additional findings will be reported later.

Experimental

4-Keto-6-chloro-1,2,3,4-tetrahydroquinoline (I).—A mixture of 6 g. of 2-(*p*-chloroanilino)propionic acid[10] and 100 g. of polyphosphoric acid in a 150-ml. beaker was heated on a hot plate with hand stirring until the temperature reached 120° (around 20 min.,) and was then kept between 120–125° for 20 min. After cooling to 80° the cherry-red reaction mixture was poured into 300 ml. of ice–water with stirring. After a few hours, the yellow precipitate was filtered and washed with water to provide 2.1 g. of pure chloroquinolone (I), m.p. 124–126°. The filtrate was saturated with sodium chloride and extracted with ether, from which another 1.5 g. of material was isolated, m.p. 116–120°. The combined yield of nearly pure product was 3.6 g. (66%). Recrystallization from benzene–petroleum ether gave canary yellow crystals, m.p. 124–126° (reported m.p. 112°[5] and 125–126°[11]).

Similarly, after 10 min. at 130°, II was obtained in 60% yield without the necessity of extraction of the aqueous solution. It seems of interest to point out that I and II did not form phosphoric acid salts. However, compound III was sufficiently basic to necessitate neutralization in order to isolate the yellow product in 55% yield. I, II, and III all gave positive dinitrophenylhydrazine tests and exhibited a strong carbonyl absorption band in the infrared spectrum at 1650 cm.$^{-1}$.

(9) J. Koo, *J. Am. Chem. Soc.*, **75**, 1891 (1953).
(10) C. D. Hurd and S. Hayao, *ibid.*, **74**, 5889 (1952).
(11) C. D. Hurd and S. Hayao, *ibid.*, **76**, 5056 (1954).

A Simple Preparation of Nipecotic Acid

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A straightforward catalytic reduction of nicotinic acid uncomplicated by decarboxylation has never been reported. While successful hydrogenation of the isomeric 2- and 4-acids in neutral solution has been carried out with ruthenium dioxide,[1] with 5% rhodium on carbon,[2] and more recently with platinum oxide,[3] the same conditions cannot be applied to the 3-acid. Extensive decarboxylation occurred in each attempt. Some success was achieved with rhodium on carbon[2] but extensive decarboxylation did occur. A 44% yield of nipecotic acid was obtained but the result was not reproducible.

Decarboxylation can be prevented by hydrogenation of the hydrochloride salt according to the general method of Hamilton and Adams[4] for the reduction of pyridines, or by conversion in the form of the sodium salt.[5] However, isolation of the free acid in each instance leaves much to be desired. Decarboxylation has been observed by Sorm[6] even under acidic conditions. He reported that when nicotinic acid was hydrogenated in acetic acid solution, 50% of piperidine was obtained while reduction in dilute hydrochloric acid gave about 10% of piperidine as a result of decarboxylation.

It occurred to us that the resultant piperidine nitrogen should be basic enough to displace ammonia if a solution of ammonium nicotinate would be hydrogenated and that free nipecotic acid should be obtained. We were led to anticipate success by some work, still incomplete, on the reduction of some pyridylalkanoic acids.

Actual work-up, after hydrogenation, proved to be very simple. It was only necessary to concentrate the solution, after removal of catalyst, to obtain nipecotic acid in very good yield.

Experimental

Nipecotic Acid.—A suspension of 6.15 g. (0.05 mole) of nicotinic acid in 50 cc. of water was treated with 5–6 cc. of concentrated aqueous ammonia and hydrogenated in the presence of 2.4 g. of 5% rhodium on alumina at room temperature and 2 atm. Uptake of hydrogen was complete in 4 hr. or less. The solution was filtered and concentrated to dryness under reduced pressure. To ensure complete removal of water the residue was treated with pure anhydrous benzol and reconcentrated. The yield of product melting at 260–261° was 5.7 g. (88.5%). Infrared examination[7] shows that it is identical to a known standard. A mixed melting point with an authentic sample showed no depression. For further proof, the product was submitted for analysis.

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.79; H, 8.58; N, 10.84; O, 24.77. Found: C, 55.64; H, 8.54; N, 10.91; O, 24.88.[8]

(5) M. S. Raasch, *J. Org. Chem.*, **27**, 1406 (1962).
(6) F. Sorm, *Collection Czech. Chem. Commun.*, **13**, 57 (1948).
(7) Infrared examination carried out by A. Kammer and W. Washburn of this laboratory.
(8) Microanalyses carried out by E. F. Shelberg and O. Kolsto and their associates of this laboratory. Oxygen analysis carried out by a modification of the Unterzaucher method described by V. A. Aluise, R. T. Hall, F. C. Staats, and W. W. Becker, *Anal. Chem.*, **19**, 347 (1947).

Quinoxaline Studies. XI. Unequivocal Syntheses of *cis*- and *trans-dl*-Decahydroquinoxalines. Resolution of *trans-dl*-Decahydroquinoxalines[1–3]

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In 1952, Beck, Hamlin, and Weston[4] reported the preparation of *trans*-decahydroquinoxaline (m.p. 150–151°) by the cyclization of 2-(β-aminoethylamino)-cyclohexanol. Four years later Christie, Rohde, and Schultz[5] reported that the reduction of an ethanolic

(1) Abstracted in part from the Ph.D. thesis at the University of Miami, June, 1962, of Earl Brill, who thanks the National Science Foundation and the University of Miami for research assistantships during the summer, 1961, and during the academic year, 1961–1962, respectively.
(2) Presented before the Division of Organic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 12, 1962.
(3) Paper X of this series: W. Blackburn, M. Danzig, H. Hubinger D. Soisson, and H. P. Schultz, *J. Org. Chem.*, **26**, 2805 (1961).
(4) K. M. Beck, *et al.*, *J. Am. Chem. Soc.*, **74**, 607 (1952).
(5) W. Christie, *et al.*, *J. Org. Chem.*, **21**, 243 (1956).

(1) M. Freifelder and G. R. Stone, *J. Org. Chem.*, **26**, 3805 (1961).
(2) M. Freifelder, R. M. Robinson, and G. R. Stone, *ibid.*, **27**, 284 (1962).
(3) M. Freifelder, *ibid.*, **28**, 602 (1963).
(4) T. S. Hamilton and R. Adams, *J. Am. Chem. Soc.*, **50**, 2260 (1928).

hydrogen chloride solution of 1,2,3,4-tetrahydroquinoxaline over platinum oxide catalyst at 60° and 50–80 p.s.i. gave the same decahydroquinoxaline. In 1960, Broadbent, *et al.*,[6] reported the reduction of quinoxaline over rhodium–alumina catalyst at 100° and 2000 p.s.i. to *cis*-decahydroquinoxaline (m.p. 56–58°) and presented evidence concerning the structures of *cis*- and *trans*-decahydroquinoxalines.

The purpose of this paper is to report additional proof of the structures of the two geometrical isomers of the decahydroquinoxalines. The problem was so organized as to elucidate at the same time the relationships between the geometries of the *cis*- and *trans*-decahydroquinoxalones-2 and the *cis*- and *trans*-decahydroquinoxalinediones-2,3.

The unequivocal syntheses of *cis*- and *trans*-decahydroquinoxalines utilized the known *cis*-1,2- and *trans*-1,2-cyclohexanediamines. Each was condensed with α-chloroacetic acid to give the corresponding *cis*- and *trans*-decahydroquinoxalone-2, stable products possessing no structural possibility of introduction of unsaturation onto the bridge carbon atoms of the fused rings. The *cis*-decahydroquinoxalone-2 was reduced with lithium aluminum hydride to *cis*-decahydroquinoxaline (m.p. 56°), identical with the product reported by Broadbent, *et al.*, as being obtained by the high temperature and pressure reduction of quinoxaline over rhodium–alumina catalyst.

trans-Decahydroquinoxalone-2 was similarly reduced to *trans*-decahydroquinoxaline, identical with the product reported by Beck, *et al.*, and by Schultz, *et al*, as well, as identical with the product obtained by Broadbent, *et al.*, *via* the *trans*-hexahydroquinoxaline.

(Parenthetically, it was observed that the condensation of ethylene bromide or ethylene chloride with either the *cis*-1,2- or *trans*-1,2-cyclohexanediamine gave no decahydroquinoxaline, only tars, under a variety of experimental circumstances.)

Having prepared both the *cis*- and *trans*-1,2-cyclohexanediamines as starting materials, these substances were also utilized for the preparation of the corresponding decahydroquinoxalinedione-2,3 by condensing ethyl oxalate with each of the diamines. The *cis*-1,2-cyclohexanediamine reacted with ethyl oxalate to give *cis*-decahydroquinoxalinedione-2,3 in good yield; this was in turn reduced with lithium aluminum hydride to give fair yields of *cis*-decahydroquinoxaline. However, condensation of *trans*-1,2-cyclohexanediamine with ethyl oxalate gave a mixture of products. By crystallization of the crude reaction product, a low yield of *trans*-decahydroquinoxalinedione-2,3 was obtained; there was also isolated a material tentatively identified as the condensation product of one mole of amine with two moles of diethyl oxalate. The reduction of *trans*-decahydroquinoxalinedione-2,3 with lithium aluminum hydride gave the corresponding *trans*-decahydroquinoxaline in low yield.

The ultimate proof of the configuration of *trans-dl*-decahydroquinoxaline lay in the resolution of this compound into its optical antipodes; the *cis*-decahydroquinoxaline is a *meso* compound and therefore incapable of resolution. After exhaustive experimentation, it was discovered that resolution of *trans-dl*-decahydroquinoxaline could be effected by means first of dibenzoyl-*d*-tartaric acid, then of dibenzoyl-*l*-tartaric acid. Average optical activities of resolved *trans-d*- and *-l*-decahydroquinoxalines were ±10.1°.

Although *cis*-decahydroquinoxaline, as also observed by Broadbent, is very hygroscopic and decomposes in the presence of many solvents, the *trans-dl*-decahydroquinoxaline, as well as its resolved components, is very stable. This stability, strong basicity, relative efficiency of resolution, and low equivalent weight indicate that the optically active *trans*-decahydroquinoxalines may, themselves, be of value as resolving agents.

(6) H. S. Broadbent, E. L. Allred, L. Pendleton, and C. W. Whittle, *J. Am. Chem. Soc.*, **82**, 189 (1960).

Experimental

The infrared spectra were determined on a Baird Atomic Model KM I spectrophotometer at concentrations of 30 mg./ml. of chloroform, except that, for solubility reasons, the curves for the *cis*- and *trans*-decahydroquinoxalinediones-2,3 were determined in pyridine.

***cis*-1,2-Cyclohexanediamine.**—This compound was prepared by the reaction between sodium azide and *cis*-1,2-cyclohexanedicarboxylic acid[7] using the procedure of Yashunskii,[8] except that instead of employing steam distillation to isolate the diamine, the alkaline, aqueous solution containing the product was extracted with 200 ml. of benzene for 4 days in a liquid–liquid extractor. The benzene solution then was extracted with four 20-ml. portions of 10% hydrochloric acid solution; evaporation to dryness of the acid solution yielded 6.8 g. (28.8%) of *cis*-1,2-cyclohexanediamine dihydrochloride, m.p. 307–310°—an increase of 10% over the yield reported by Yashunskii (lit.,[8] m.p. 307–310°).

***cis*-Decahydroquinoxalone-2.**—One hundred milliliters of cold (0°), 1 *N* sodium hydroxide solution was added dropwise to a cold, stirred solution of 9.35 g. of *cis*-1,2-cyclohexanediamine dihydrochloride in 50 ml. of water. To this cold, stirred, basic solution was added dropwise a cold solution of 4.7 g. of chloroacetic acid in 50 ml. of water, followed by 5 ml. of cold, 28% ammonium hydroxide solution. After stirring the reaction solution for 24 hr. at 0°, it was then heated for 2 hr. at 90°. A dark, flocculent precipitate was filtered off and discarded. The solution was evaporated to dryness on a water bath; the dark brown, hygroscopic residue was transferred to the thimble of a Soxhlet extractor and extracted for 4 days with 75 ml. of benzene. The benzene solution of product was dried over anhydrous sodium sulfate, poured onto a 1 × 10 cm. column of neutral alumina (Woelm, activity grade 1), and eluted with a 1:1 benzene–alcohol-free chloroform solution. Twenty 10-ml. fractions were collected, all of which had the same material in solution; hence the fractions were combined and evaporated to dryness to yield 1.0 g. (13%) of white crystals, m.p. 131–134°. The product was recrystallized from benzene with charcoal treatment, to give 0.65 g. (8.4%) of product, m.p. 135–136°.

Anal. Calcd. for $C_8H_{14}N_2O$: C, 62.3; H, 9.16; N, 18.2; neut. equiv., 154.2. Found: C, 62.4; H, 9.09; N, 18.2; neut. equiv., 156.4. ν_{max} cm.$^{-1}$: 3450 (NH); 1660 [C(=O)-NH]; pK_a = 6.1.

N-Nitroso-*cis*-decahydroquinoxalone-2.—To a 0° solution of 1.54 g. of *cis*-decahydroquinoxalone-2, 15 ml. of water, and 5 ml. hydrochloric acid (sp. gr., 1.18) was added a cold solution of 0.69 g. of sodium nitrite in 5 ml. of water. After 2 hr. at 0°, a solid began to separate from the solution; after 4 hr. at 0°, the nitroso derivative was filtered to give 1.1 g. (60%) of cream-colored crystals, m.p. 162–165°. The product was recrystallized, with charcoal treatment, from 1:1 ethanol–water to give 0.8 g. (43%) of material, m.p. 165–167°.

Anal. Calcd. for $C_8H_{13}N_3O_2$: C, 52.4; H, 7.15; N, 22.9. Found: C, 52.4; H, 7.02; N, 22.9. ν_{max} cm.$^{-1}$: 1313, 1327, 1360 (NNO); 1680 [C(=O)NH].

***cis*-Decahydroquinoxalinedione-2,3.**—A solution of 5 g. of freshly distilled *cis*-1,2-cyclohexanediamine and 30 g. of ethyl oxalate was heated at 90° for 6 hr. Upon cooling, a white, crystalline material formed in the excess ethyl oxalate; the product was filtered, rinsed first with ethyl oxalate, and then with ethyl ether to give 4.6 g. (62.4%) of white crystals, m.p. 244–246.5°. The material was thrice recrystallized from 70-ml.

(7) E. F. Jenkins and E. J. Costello, *ibid.*, **68**, 2733 (1946).

(8) V. G. Yashunskii, *Zh. Obshch. Khim.*, **28**, 1364 (1958); *Chem. Abstr.*, **52**, 19979f (1958).

portions of isopropyl alcohol to give constant melting material weighing 1.85 g. (25%), m.p. 248–249°.

Anal. Calcd. for $C_8H_{12}N_2O_2$: C, 57.1; H, 7.18; N, 16.7. Found: C, 57.2; H, 7.15; N, 16.7. ν_{max} cm.$^{-1}$: 1670, 1690 [C(=O)NH].

cis-Decahydroquinoxaline. A. From *cis*-Decahydroquinoxalone-2.—Into a 1-l., three-neck, round-bottom flask equipped with stirrer and a reflux condenser carrying a drying tube were placed 500 ml. of anhydrous ethyl ether and 5 g. of lithium aluminum hydride. Ten grams of *cis*-decahydroquinoxalone-2 was slowly added in small portions, the addition being executed in a manner which prevented excessive refluxing. After addition of the amide was complete, the reaction mixture was maintained at a gentle reflux and stirred for 48 hr. Dropwise addition of 10 ml. of water hydrolyzed the reduction complex and destroyed the excess of lithium aluminum hydride, after which the reaction mixture was filtered with gentle suction, rinsing the gelatinous residue with four 20-ml. portions of ethyl ether. The ether solution was dried over sodium sulfate, filtered, treated with anhydrous hydrogen chloride until salt formation ceased, and evaporated *in vacuo* to yield 8.25 g. (59.7%) of *cis*-decahydroquinoxaline dihydrochloride, m.p. 298–301° (lit.,[6] m.p. 293–300°).

The salt was converted to the free amine by dissolving 10 g. of the salt in 50 ml. of 20% sodium hydroxide solution, and extracting with four 25-ml. portions of ethyl ether. After drying the ether solution with sodium sulfate, the ether was removed by distillation and the amine distilled to give 4.6 g. (70%) of *cis*-decahydroquinoxaline, b.p. 85–87° (1 mm.); m.p. 56–57° [lit.,[6] b.p. 85–87° (0.25 mm.); m.p. 56–58°]. The infrared spectrum has been reported.[6]

Anal. Calcd. for $C_8H_{16}N_2$: neut. equiv., 70.1. Found: neut. equiv., 70.1.

The picrate precipitated from ethanol and was recrystallized from ethanol–acetone, m.p. 274–275° dec., (lit.,[6] m.p. 275° dec.).

B. From *cis*-decahydroquinoxalinedione-2,3.—A solution of 2 g. of *cis*-decahydroquinoxalinedione-2,3 and 1.79 g. of lithium aluminum hydride in 50 ml. of anhydrous ethyl ether was stirred and refluxed for 56 hr. The complex was hydrolyzed and the excess lithium aluminum hydride destroyed by cautious, dropwise addition of 3 ml. of water. The dihydrochloride salt of *cis*-decahydroquinoxaline was obtained in 0.8 g. (31.4%) yield, m.p. 297–300° (lit.,[6] m.p. 293–300°) by method A described above for the preparation of *cis*-decahydroquinoxaline. The melting point of a mixture of this material with the material produced as described in method A, above, was 298–301°.

The N,N′-dinitroso-*cis*-decahydroquinoxaline was prepared and recrystallized from 1:1 ethanol–water, m.p. 86–88° (lit.,[6] m.p. 86–88°).

***trans*-1,2-Cyclohexanediamine.**—This material was prepared as the dihydrochloride salt, m.p. 322–325°, (lit.,[9] m.p. 322–325°) in 39% yields, exactly according to the procedure of Yashunskii and Shchukina,[9] by the sodium–ethanol reduction of cyclohexanedione-1,2-dioxime.[10]

***trans*-Decahydroquinoxalone-2.**—This material was prepared from the condensation of 0.05 mole chloroacetic acid with 0.05 mole *trans*-1,2-cyclohexanediamine by exactly the same procedure outlined above for the preparation of *cis*-decahydroquinoxalone-2. However, after evaporating the reaction solution to dryness, the residue was not extracted with benzene, but was taken up in 200 ml. of hot, absolute ethanol, decolorized with charcoal, and again evaporated to dryness on a water bath to give 3.25 g. (42%) of tan crystals, m.p. 180–200°. The crude product was recrystallized twice from benzene, with charcoal treatment, to a constant melting point to give 2.96 g. (38.4%), m.p. 199–199.5°.

Anal. Calcd. for $C_8H_{14}N_2O$: C, 62.3; H, 9.15; N, 18.2; neut. equiv., 154.2. Found: C, 62.6; H, 9.11; N, 18.2; neut. equiv., 154.2. ν_{max} cm.$^{-1}$: 3450 (NH), 1660 [C(=O)NH]; $pK_a = 6.5$.

N-Nitroso-*trans*-decahydroquinoxalone-2.—This material was prepared in 73.8% crude yield, m.p. 189–193°, by exactly the same procedure outlined above for the preparation of N-nitroso-*cis*-decahydroquinoxalone-2. The crude product was recrystallized four times from 95% ethanol, with charcoal treatment, to give a 54.5% yield of colorless product, m.p. 194–195°.

Anal. Calcd. for $C_8H_{13}N_3O_2$: C, 52.4; H, 7.15; N, 22.9. Found: C, 52.2; H, 7.04; N, 22.9. ν_{max} cm.$^{-1}$: 1330, 1320, 1350 (NNO); 1670 [C(=O)NH].

***trans*-Decahydroquinoxalinedione-2,3.**—Ethyl oxalate and *trans*-1,2-cyclohexanediamine were condensed with one another in exactly the same quantities and by the same procedure as outlined above for the preparation of *cis*-decahydroquinoxalinedione-2,3 to give 4.8 g. of crude material, m.p. 240–285°. The material was first crystallized from 150 ml. of hot water, with hot filtration. The hot water insoluble residue weighing 1 g., m.p. 151–154°, was not identified, nor studied further. The cooled filtrates precipitated 1 g. (13.6%) of fine, white crystalline material, m.p. 301–303°. Filtrates were evaporated to one-half original volume to precipitate 1.2 g. of material, m.p. 175–176°.

The infrared spectra of all three products were obtained and compared with the infrared spectrum of *cis*-decahydroquinoxalinedione-2,3. The product, m.p. 301–303°, had a spectrum that indicated it was the *trans*-decahydroquinoxalinedione-2,3. The material was, therefore, recrystallized twice more from water, with charcoal treatment, to yield 0.65 g. (9%), m.p. 301–303°.

Anal. Calcd. for $C_8H_{12}N_2O_2$: C, 57.1; H, 7.18; N, 16.7. Found: C, 57.2; H, 6.99; N, 16.8. ν_{max} cm.$^{-1}$: 1680, 1700 [C(=O)NH].

The material melting at 175–176° is believed to be the somewhat impure condensation product of one mole of diamine with two moles of diethyl oxalate, *trans*-N,N′-bis(ethoxyoxaloyl)-1,2-cyclohexanediamine. The elemental analyses and infrared spectrum support this view.

Anal. Calcd. for $C_{14}H_{22}N_2O_6$: C, 53.5; H, 7.06; N, 8.9. Found: C, 53.4; H, 7.07; N, 9.6. ν_{max} cm.$^{-1}$: 1680 [C(=O)-NH]; 1725, 1745 ($COOCH_2CH_3$).

***trans*-Decahydroquinoxaline. A. From *trans*-Decahydroquinoxalone-2.**—This material was prepared by the reduction of 1.54 g. of *trans*-decahydroquinoxalone-2 with 0.76 g. of lithium aluminum hydride in 300 ml. of anhydrous ethyl ether; the same procedure was employed as was utilized for the preparation of *cis*-decahydroquinoxaline by method A, described above. The yield of crude *trans*-decahydroquinoxaline that remained after removing the ether from the final solution of product was 1.4 g. (100%), m.p. 147–149°. This material was recrystallized once from ligroin (b.p. 66–75°) to give 1.1 g. (78%) of white crystals, m.p. 150–152° (lit.,[4] m.p. 150–151°; lit.,[5] 152.5–153°; lit.,[6] 146–148°). The infrared spectrum has been reported.[6]

Anal. Calcd. for $C_8H_{16}N_2$: neut. equiv., 70.1. Found: neut. equiv., 70.1.

The N,N′-dinitroso-*trans*-decahydroquinoxaline was prepared and recrystallized from 1:1 ethanol–water, m.p. 108–110° (lit.,[5] m.p. 110–111°).

B. From *trans*-Decahydroquinoxalinedione-2,3.—A solution of 0.5 g. of lithium aluminum hydride, 0.6 g. of *trans*-decahydroquinoxalinedione-2,3, and 25 ml. of anhydrous ethyl ether was reduced and worked up exactly as described for the preparation of *cis*-decahydroquinoxaline by method B, above. The yield of product was so little upon evaporating the ether from the final solution, that the dipicrate of the residue was forthwith prepared; 10 mg. of product, m.p. 297–300° dec., (lit.,[5] m.p. 301–303° dec.). A mixture melting point of this product with a sample of the picrate prepared by Schultz[5] had m.p. 298–301° dec.

Resolution of *trans-dl*-Decahydroquinoxaline.—To 4.2 g. *trans-dl*-decahydroquinoxaline in 800 ml. of water at 60° was added 12.4 g. dibenzoyl-*d*-tartaric acid hydrate[11] in 800 ml. 95% ethanol. After 24 hr. at 32°, 7.6 g. (47.5%) of small, white prisms, m.p. 199–200° dec., was obtained. (The filtrates were evaporated to dryness to give 9.3 g. of soapy, feathery crystals, m.p. 163–170°, *vide infra*). The insoluble salt was recrystallized twice to a constant melting point from 1:1 water–95% ethanol (100 ml./g.), with charcoal treatment, to give 4.2 g. (26%) of prisms, about 5 mm. × 1 mm., m.p. 208–209° dec., of *trans-l*-decahydroquinoxaline dibenzoyl-*d*-tartrate dihydrate.

Anal. Calcd. for $C_8H_{16}N_2 \cdot C_{18}H_{14}O_8 \cdot 2H_2O$: C, 58.4; H, 6.40; N, 5.23. Found: C, 58.5; H, 6.40; N, 5.31. Dried 1 hr./1 mm./100°.

Anal. Calcd. for $C_8H_{16}N_2 \cdot C_{18}H_{14}O_8 \cdot H_2O$: C, 60.4; H, 6.23; N, 5.42. Found: C, 60.8; H, 6.38; N, 5.22. Dried 3 hr./1 mm./100°.

Because of insolubility at room temperature in all the usual solvents, or mixed solvents, the optical activity of the salt was not determined.

(9) V. G. Yashunskii and M. N. Shchukina, *Zh. Obshh. Khim.*, **28**, 234 (1958); *Chem. Abstr.*, **52**, 12777a (1958).

(10) R. Belcher, W. Hoyle, and T. S. West, *J. Chem. Soc.*, 2743 (1958).

(11) C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, **55**, 2605 (1933); M. Semonsky, A. Cerny, and V. Zikan, *Chem. Listy*, **50**, 116; *Collection, Czech. Chem. Commun.*, **21**, 382 (1956); *Chem. Abstr.*, **50**, 13059a (1956).

The free base was liberated from the dibenzoyl-*d*-tartrate salt in 100 ml. of 20% sodium hydroxide solution, which was repeatedly extracted with chloroform. After drying with sodium sulfate, the chloroform was evaporated and the residue (1 g.) was recrystallized, with charcoal treatment, from petroleum ether, b.p. 66–75°, to give 0.85 g. (20%) of white platelets of *trans-l*-decahydroquinoxaline, m.p. 175–175.5°; $[\alpha]^{26}D$ −9.7° (*c*, 10.2, chloroform).

Anal. Calcd. for $C_8H_{16}N_2$: neut. equiv., 70.1. Found: neut. equiv., 70.1.

The residue of salt from the filtrates mentioned parenthetically above was quite soluble in water, and hence was not investigated further, but the base was liberated, recovered, and recrystallized from petroleum ether to give 2.0 g. partially resolved *trans-d*-decahydroquinoxaline, m.p. 160–171°, $[\alpha]^{26}D$ +6.4° (*c*, 10.4, chloroform). This product was transformed into its dibenzoyl-*l*-tartrate salt, purified, and liberated exactly as described above for its enantiomer to give 0.5 g. (12%) of *trans-d*-decahydroquinoxaline, m.p. 175–175.5°; $[\alpha]^{26}D$ +10.4° (*c*, 10, chloroform); same melting points, analyses of salt and base were observed.

The resolution was repeated exactly, except that the *trans-dl*-decahydroquinoxaline was *first* neutralized with dibenzoyl-*l*-tartaric acid, and the resolution of the more soluble salt eventually executed with dibenzoyl-*d*-tartaric acid. Again the same analyses, melting points, and approximate yields were observed. The observed values of the optical rotations of the resolved *trans*-decahydroquinoxalines were +10.3° and −10.1° at concentrations of 10 g./100 ml. of chloroform solutions; the infrared spectra were the same as for the racemic substance.

A Selenium Heterocyclic from the Reaction of Diphenylacetylene and Selenium Tetrachloride

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In the few cases studied, selenium tetrachloride has been shown to add to alkynes forming bis-2-chloroalkenylselenium dichlorides.[1,2] Our experiments show that diphenylacetylene reacts forming a substance of different selenium/alkyne ratio. The compound does not contain a Se–Cl linkage, as evidenced by the inactivity of the chlorine atom to water and even to Grignard reagents, and is very stable thermally and oxidatively, which suggests that it contains divalent selenium linked only to carbon. Several different methods (*vide infra*) have been used to characterize this material as 2-phenyl-3-chlorobenzoselenophene.

Several related substances containing the same heterocyclic ring system (*e.g.*, benzoselenophene,[3–7] 2-$\alpha(\gamma)$-pyridylbenzoselenophene,[8] and 2-methylbenzoselenophene[9] have been reported previously but have been made in low yields, usually in a multistep syntheses. The one-step route to the 2-phenyl compound outlined represents a substantial improvement in both time and yield for the preparation of this ring system.

Experimental

2-Phenyl-3-chlorobenzoselenophene.—A 22.1-g. portion (0.1 mole) of selenium tetrachloride was treated with a Dry Ice-cooled solution containing 0.25 mole (36.0 g.) of diphenylacetylene dissolved in 100 ml. of ether. On warming to room temperature, a copious quantity of hydrogen chloride was evolved (in contrast to the other alkyne reactions). Partial evaporation and several days standing at −78° produced large yellow crystals which, on recrystallization from ether, yielded an 83% (based on $SeCl_4$) yield of off-white needles. Use of less than a 2:1 mole ratio led only to impure products from which only low yields of the desired compound were obtained.

Anal. Calcd. for $C_{14}H_9ClSe$ (291.1): C, 57.65; H, 3.11; Cl, 12.16; Se, 27.38. Found: C, 57.67; H, 3.26; Cl, 12.02; Se, 27.05; mol. wt. (Signer), 293.

Reduction with Raney Nickel.—A 2.9-g. portion (0.01 mole) of the compound was refluxed several hours with Raney Nickel under a hydrogen stream using the method of Gould and Wiseman.[10] Recovery and recrystallization of the product afforded a 61% yield of bibenzyl which was identified through its infrared spectrum and a mixture melting point determination with an authentic sample.

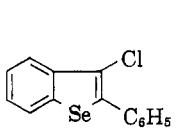
Spectral Work.—The ultraviolet spectrum (Cary Model 14) taken on 10^{-4} *M* solutions of the compound dissolved in spectral grade cyclohexane shows five peaks and shoulders: λ_{max} (log-ϵ); 212 (4.33), 244 (4.34); 253 (4.10 sh.), 283 (3.41 sh.), 298 (4.20).

The infrared spectrum of a Nujol mull of the material, taken on a Perkin–Elmer, Model 21, spectrophotometer, showed the following peaks (all weak) between 1660 and 2000 cm.$^{-1}$: 1660, 1690, 1708, 1755, 1785, 1803, 1872, 1905, 1945, and 1965 cm.$^{-1}$.

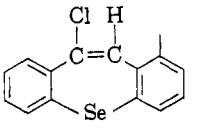
The n.m.r. spectrum (taken at 60 Mc.) of the compound dissolved in carbon tetrachloride shows a complex array of overlapping peaks spread over 60 c.p.s. and centered at 0.9 p.p.m. downfield from the T_1 peak (aromatic protons) of toluene used as an internal standard.

Discussion

The analytical and molecular weight data suggest either I or II below as a possible structure for the compound. Formation of bibenzyl by the compound



I



II

when reduced by Raney Nickel probably would not distinguish between the two structures, but Baufield, *et al.*,[11] have shown that 2-phenylbenzothiophene is similarly reduced.

Comparison of the ultraviolet spectrum of the compound with those of closely similar sulfur analogues of I and II, 2-phenylbenzothiophene[12] and dibenzo[*b,f*]-thiepin[13] shows the closest similarity exists between the spectrum of the compound and that of 2-phenylbenzothiophene. However, the spectra of the two sulfur compounds are similar and the influence of the 3-chlorine is unknown, so conclusions from the ultraviolet spectra should be cautiously drawn.

The infrared absorptions in the 1600–2000-cm.$^{-1}$ region of phenyl compounds are reported to be characteristic of the type of ring substitution.[14] Nine of the ten low intensity infrared absorptions appearing between 1660 and 2000 cm.$^{-1}$ form a pattern which is characteristic of the combination expected for a monosubstituted and a disubstituted (*ortho*) ring. This indicates structure I rather than II.

Using concentrated solutions and carefully searching the spectral region in which olefinic hydrogen resonances

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