nearly quantitative yield of 6-methyl-2-piperidone, m.p. 89–90°. Kuhn and Jerchel[8] prepared this compound using a platinum oxide catalyst and report m.p. 84–85°.

1-Ethyl-6-methyl-2-piperidone.—Three grams (0.022 mole) of 1-ethyl-6-methyl-5,6-dihydro-2(1)-pyridone (II, R = C_2H_5) was hydrogenated as above in 15 min. The crude product (2.6 g., 85%) was fractionated on the Podbielniak column to give pure 1-ethyl-6-methyl-2-piperidone (Table I).

This compound was also prepared accidentally in an attempt to N-alkylate 6-methyl-5,6-dihydro-2(1)-pyridone (II, R = H). In this experiment metallic sodium was powdered in the usual manner in toluene. After cooling, an equimolar portion of the lactam (II, R = H) was added; an immediate reaction took place and all of the sodium was used up. Ethyl iodide was added; the mixture was refluxed for 7 hr. and distilled to give a 39% yield of the alkylated and reduced product, 1-ethyl-6-methyl-2-piperidone, as indicated by an identical infrared spectrum, index of refraction, and boiling point.

1-Ethyl-6-methyl-5,6-dihydro-2(1)-pyridone.—Sodamide was prepared in the usual manner using 300 ml. of liquid ammonia, a crystal of ferric nitrate, and 1.3 g. (0.056 g.-atom) of sodium. After addition of 5.6 g. (0.050 mole) of 6-methyl-5,6-dihydro-2(1)-pyridone with stirring the ammonia was allowed to evaporate. Fifty milliliters of dry benzene and 11 g. (0.070 mole) of ethyl iodide were added, and the mixture was refluxed for 3 hr. Distillation yielded 3.4 g. (50%) of a product whose infrared spectrum and boiling point were identical with those of 1-ethyl-6-methyl-5,6-dihydro-2(1)-pyridone which had the correct elementary composition (Table I).

N,N-Diethylvinylacetamide.—In a reaction flask with reflux condenser and gas absorption attachment were placed 25.8 g. (0.30 mole) of vinylacetic acid[13,14] and 41.7 g. (0.35 mole) of thionyl chloride. The reaction started immediately and was allowed to continue overnight. The mixture was refluxed for 0.5 hr. and a solution of 58 g. (0.80 mole) of diethylamine in 100 ml. of dry ether was added slowly with stirring. The precipitate was filtered; the solution was dried over magnesium sulfate and distilled. The crude N,N-diethylvinylacetamide was fractionated through the Podbielniak column to yield 22.7 g. (54%) of high purity material (Table I).

Acknowledgment.—Grateful acknowledgement is given to Dr. Barbara K. Campbell of the Mead Johnson Research Center for her many fruitful suggestions during the course of this work and to Dr. Ernest L. Eliel for generously reading and commenting upon the original manuscript.

[13] A. E. Vogel, "A Textbook of Practical Organic Chemistry," 2nd Ed., Longmans, Green and Co., New York, N. Y., 1951, p. 451.

[14] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 724 (1945).

Dinitrocarbazoles

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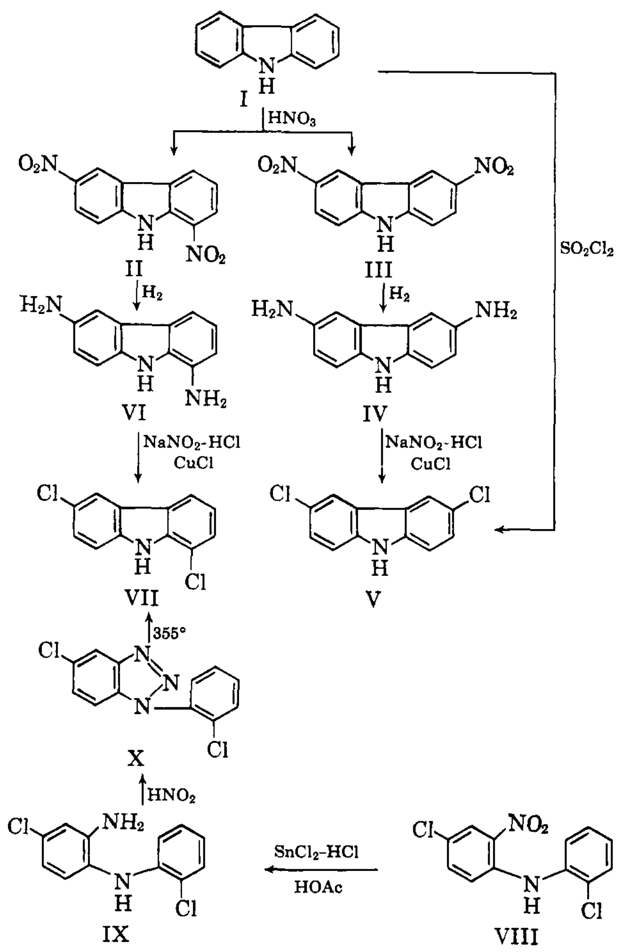
Although it has been recognized that attempts to dinitrate carbazole lead to mixed products,[1] only 3,6-dinitrocarbazole (III) appears to have been isolated from these mixtures. Its melting point has been variously reported as 365–367°,[1] about 360°,[2] 357°,[3] and even as low as 320°.[4] Its structure was assigned by Täuber[5] on the basis of the similarity of its reduction product (IV) with 3,6-diaminocarbazole unambiguously prepared from 2,2′,5,5′-tetraminodiphenyl. Crystal form, solubilities of its salts, and darkening temperatures of the two materials agreed. The isomeric 1,6-dinitrocarbazole (II) appears in the literature only as a speculative structure for a material charring between 300 and 360°.[6] We have found that both 1,6-dinitrocarbazole and 3,6-dinitrocarbazole are present in major amounts in the crude dinitrocarbazole mixture.



Carbazole (I) was nitrated in acetic acid at 75° with 3 equiv. of 70% nitric acid, and, alternatively, by treatment in acetic acid first with 1 equiv. of sodium nitrite and then with 2 equiv. of nitric acid at temperatures up to 100°. Extraction of the crude product from either nitration procedure with alcoholic potassium hydroxide produced two fractions: a red solid residue and a deep red solution. Acidification of the latter precipitated a yellow solid which recrystallized from nitrobenzene as fine yellow needles, m.p. 386–387°. Its reduction and conversion to the dichloride (V) by the Sandmeyer procedure provided a material identical with 3,6-dichlorocarbazole (m.p. 202–203°) prepared from carbazole and sulfuryl chloride,[7] the structure of which has been established by Plant.[8]

Digestion of the alcoholic alkali-insoluble residue with acid and recrystallization from nitrobenzene produced a dinitrocarbazole in glistening golden

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[1] H. Schotte and R. Ebert, U. S. Patent 2,392,067 (Jan. 1, 1946).

[2] R. K. Eikhman, V. O. Lukashevich, and E. A. Silaeva, *Org. Chem. Ind.* (*USSR*), **6**, 93 (1939); *Chem. Abstr.*, **33**, 7297[7] (1939).

[3] J. Amemiya, S. Fujii, and T. Horio, *Coal Tar* (Tokyo), **4**, 323 (1952); *Chem. Abstr.*, **48**, 2034*h* (1954).

[4] R. Oda, Z. Yoshida, and Y. Kato, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **55**, 239 (1952).

[5] E. Täuber, *Ber.*, **25**, 128 (1892).

[6] W. A. Schroeder, B. Keilin, and R. M. Lemmon, *Ind. Eng. Chem.*, **43**, 939 (1951).

[7] G. Mazzara and M. Lamberti-Zanardi, *Gazz. chim. ital.*, **26**, II, 236 (1896).

[8] S. G. P. Plant and J. F. Powell, *J. Chem. Soc.*, 937 (1947).

leaflets, m.p. 344–346°. Through reduction, diazotization, and treatment with cuprous chloride, the corresponding dichlorocarbazole was obtained, m.p. 122.5–124°. 1,6-Dichlorocarbazole (VII), hitherto unreported, was prepared by condensation of 2,5-dichloronitrobenzene with 2-chloroaniline,[9] reduction of the 2′,4-dichloro-2-nitrodiphenylamine (VIII) thus formed to 2-amino-2′,4-dichlorodiphenylamine (IX),[10] diazotization to produce 5-chloro-1-(2-chlorophenyl)benzotriazole (X), and thermal decomposition in the familiar Graebe–Ullmann procedure.[11] This dichlorocarbazole proved identical with the material prepared from the lower melting dinitrocarbazole and thus establishes the structure of the latter compound as the 1,6-dinitro isomer.

It is of interest that roughly the same proportion of the two dinitrocarbazoles was obtained from both nitration procedures, 50–60% of the 3,6- and 30–35% of the 1,6-isomer, though the use of sodium nitrite leads to a higher melting, more readily purified mixture.

Experimental[12]

Nitration of Carbazole.—A slurry of 83.6 g. (0.5 mole) of carbazole in 640 g. of glacial acetic acid, stirred at 30–40°, was treated during 1.5 hr. with 35.3 g. (0.5 mole) of sodium nitrite. After 2 hr. of agitation, most of the solid had dissolved (as 9-nitrosocarbazole), but the addition of an additional 5 g. of sodium nitrite failed to achieve complete solution. During 1.3 hr., 74 g. of 90% nitric acid (1.05 mole) diluted with an equal weight of acetic acid was added with intermittent cooling at 30–40°, and the slurry was stirred at that temperature for an additional 3.5 hr. The mixture was then held at 55° for 1.5 hr., at 65° for 1.5 hr., and at 95° for 2 hr., cooled to 65°, and filtered; the solid was washed with 350 ml. of cold acetic acid and finally with water. The 86 g. of crude product obtained in this way began to soften at 312° and was melted at 354°.

Separation of Isomeric Dinitrocarbazoles.—A 45.5-g. sample of crude dinitrocarbazole was divided into two portions and each was stirred at 50° with 1.5 l. of alcoholic potassium hydroxide (60 g./l.) and filtered. The insoluble red solid residues were combined, digested on a steam bath with dilute hydrochloric acid (whereupon the color changed to yellow), filtered, washed with water, and dried to give 14.4 g. (32%) of 1,6-dinitrocarbazole (II) which recrystallized from nitrobenzene as glistening golden leaflets, m.p. 344–346° (cor.).

Anal. Calcd. for $C_{12}H_7N_3O_4$: C, 56.0; H, 2.7; N, 16.3. Found: C, 55.9; H, 2.7; N, 16.3.

The red alkaline alcoholic solutions were acidified with concentrated hydrochloric acid and the solid yellow precipitates thus formed were combined and washed thoroughly with warm water to remove potassium chloride. The residue of 26.5 g. (58%) was recrystallized from boiling nitrobenzene to give 3,6-dinitrocarbazole (III) as fine yellow needles, m.p. 386–387° (cor.).

Anal. Found: N, 16.4.

3,6-Diaminocarbazole (IV).—Thirty grams of 3,6-dinitrocarbazole (III) in 150 ml. of ethanol containing 3 g. (weight wet with ethanol) of Raney nickel catalyst was reduced under 1000-p.s.i.g. pressure at 100 ± 5° for 6 hr. in a stirred autoclave. The reaction mixture was diluted with water and the solid residue was recrystallized twice from boiling aniline (boneblack) to give 18.3 g. (80%) of IV as tan platelets which softened at 316° and melted at 320–322°. Its dibenzoyl derivative melted at 275–277°. Ziersch, starting from a dinitrocarbazole reported as melting "above 320°," obtained dibenzamidocarbazole of m.p. 270°,[13] while Eikhman[2] obtained m.p. 281° starting from dinitrocarbazole of m.p. "about 360°."

Anal. Calcd. for $C_{12}H_{11}N_3$: C, 73.1; H, 5.6; N, 21.3. Found: C, 72.9; H, 5.4; N, 21.0.

3,6-Dichlorocarbazole (V).—A 3.2-g. (0.016 mole) portion of 3,6-diaminocarbazole (IV) was slurried in 90 ml. of concentrated hydrochloric acid and tetrazotized at 5–10° by the addition of 2.2 g. (0.032 mole) of sodium nitrite dissolved in the minimum amount of water. The tetrazonium salt solution was filtered and added slowly to a boiling solution of cuprous chloride prepared by treating a hot solution of 15 g. of copper sulfate and 3.9 g. of sodium chloride in 48 ml. of water with 3.3 g. of sodium bisulfite and 2.1 g. of sodium hydroxide in 24 ml. of water, washing the solid with water, and dissolving the cuprous chloride in 40 ml. of concentrated hydrochloric acid. The solution was boiled until foaming from nitrogen evolution subsided, and the greenish yellow product (1.5 g., 39%) was filtered and recrystallized (boneblack) twice from petroleum ether (b.p. 60–110°). This 3,6-dichlorocarbazole, m.p. 200–202.5°, did not depress the melting point of authentic 3,6-dichlorocarbazole (m.p. 201–203°) prepared from carbazole and sulfuryl chloride.[7]

Initial attempts to conduct this Sandmeyer reaction by adding the tetrazonium salt solution to a cold cuprous chloride solution in hydrochloric acid followed by heating were unsuccessful, leading to tarry materials from which 3,6-dichlorocarbazole could not be extracted.

1,6-Diaminocarbazole (VI).—Hydrogenation of 10 g. of 1,6-dinitrocarbazole (II) in a manner similar to that used for 3,6-dinitrocarbazole gave, after recrystallization from xylene, 0.8 g. (10%) of VI as purple-gray needles which darkened at 235° and decomposed around 255°.

1,6-Dichlorocarbazole (VII) from 1,6-Diaminocarbazole.—A 1.6-g. (0.008 mole) portion of 1,6-diaminocarbazole (VI) in 45 ml. of concentrated hydrochloric acid and 20 ml. of water was tetrazotized by the addition at 5–10° of 1.1 g. (0.016 mole) of sodium nitrite dissolved in the minimum amount of water. The tetrazonium salt solution was added at 5–10° to a stirred cuprous chloride solution prepared as above from 5 g. of copper sulfate and dissolved in 8 ml. of concentrated hydrochloric acid. Nitrogen evolution began at once. The reaction mixture was allowed to warm to room temperature and finally heated on the steam bath for 1.5 hr. The dark gummy solid which adhered to the sides of the vessel was dissolved in ethanol, treated with boneblack, diluted with water until quite turbid, and extracted with petroleum ether (b.p. 60–110°). Evaporation of most of the petroleum ether and cooling the solution induced crystallization of VII which recrystallized from petroleum ether as white needles, m.p. 122.5–124°.

2-Amino-2′,4-dichlorodiphenylamine (**IX**).—One gram of 2′,4-dichloro-2-nitrodiphenylamine (VIII)[9] was dissolved in 50 ml. of acetic acid, the solution was filtered, and to it was added 2 g. of stannous chloride dihydrate and 3 ml. of hydrochloric acid. The solution was heated to boiling and additional increments of stannous chloride totaling 5 g. and hydrochloric acid totaling 7 ml. were added at intervals until, after about 10 min. of boiling, the orange color had disappeared and the solution became greenish yellow. The solution was made strongly alkaline with aqueous sodium hydroxide, and cooled; the solid product was removed by filtration and recrystallized from ethanol to give 0.6 g. (67%) of white needles of IX, m.p. 107–108.5°, lit.[10] m.p. 103°.

Attempted use of Borodkin's sodium sulfide procedure[10] and the use of stannous chloride–hydrochloric acid solution alone[14] were not successful in our hands. In each case unreduced VIII was recovered.

5-Chloro-1-(2-chlorophenyl)benzotriazole (**X**).—To a slurry of 2.5 g. (0.01 mole) of 2-amino-2′,4-dichlorodiphenylamine (IX) in 35 ml. of hydrochloric acid and 45 ml. of water cooled to 10° was added 0.7 g. (0.01 mole) of sodium nitrite in 25 ml. of water. The slurry turned purple and was stirred for 1 hr. after addition of nitrite was complete while the temperature was raised to 45°. The solid product was separated, dissolved in ethanol, treated with boneblack, filtered, and diluted with water while hot. On cooling, 1.3 g. (50%) of glistening white needles of X, m.p. 116–118°, were deposited.

Anal. Calcd. for $C_{12}H_7Cl_2N_3$: C, 54.6; H, 2.7. Found: C, 54.4; H, 2.6.

1,6-Dichlorocarbazole (VII) from 5-Chloro-1-(2-chlorophenyl)-benzotriazole.—A procedure used by Preston, *et al.*,[15] for the

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[9] V. F. Borodkin, *Zh. Prikl. Khim.*, **21**, 987 (1948).

[10] V. F. Borodkin, T. V. Malkova, and N. N. Nikolskaya, *ibid.*, **20**, 283 (1947).

[11] C. Graebe and F. Ullmann, *Ann.*, **291**, 16 (1896).

[12] Melting points are uncorrected except where indicated. Elemental analyses were performed by Mr. Frank E. Huber, Jr.

[13] P. Ziersch, *Ber.*, **42**, 3797 (1909).

[14] See J. S. Buck and W. S. Ide, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 130.

[15] R. W. G. Preston, S. H. Tucker, and J. M. L. Cameron, *J. Chem. Soc.*, 500 (1942).

preparation of other carbazoles was used. A 0.5-g. portion of 5-chloro-1-(2-chlorophenyl)benzotriazole (X) was heated in a small open tube for 10 min. at 355° and the residue was dissolved in ethanol and treated with boneblack. The product was precipitated from the ethanolic solution by addition of water and was twice recrystallized from petroleum ether (b.p. 60–110°) to give 0.1 g. (22%) of white crystalline 1,6-dichlorocarbazole, m.p. 123–124°.

Anal. Calcd. for $C_{12}H_7Cl_2N$: C, 61.0; H, 3.0; N, 5.9. Found: C, 60.8; H, 2.9; N, 5.8.

This material did not depress the melting point of the 1,6-dichlorocarbazole derived from 1,6-dinitrocarbazole, thus establishing the structure of the latter compound.

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The Preparation of *trans*-4-*t*-Butylcyclohexene Oxide

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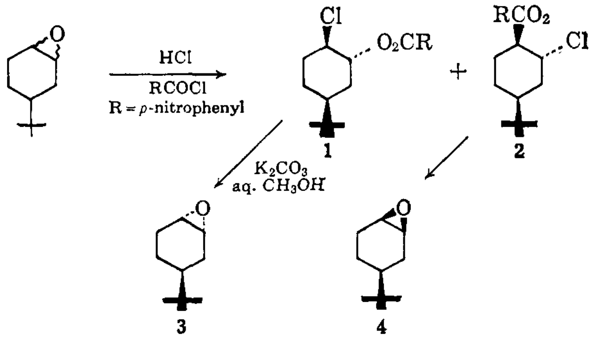
The preparation of isomerically pure liquid epoxides of substituted cycloalkenes has been a major problem in the study of the stereochemistry of oxide ring-opening reactions. Direct fractional distillation is often impossible; *e.g.*, a mixture of *cis* and *trans*-4-*t*-butylcyclohexene oxides on distillation through a 60-cm. spinning band column gives no evidence of fractionation.

Routes to the isomeric 4-*t*-butylcyclohexene oxides have been devised by two groups[1,2]; both sequences are multistep and involve either column chromatography or ion-exchange chromatography which limits their usefulness in large-scale preparations.

We wish to report a simple, rapid method of separating pure *trans*-4-*t*-butylcyclohexene oxide from a mixture with its geometric isomer. Treatment with anhydrous hydrochloric acid in the presence of *p*-nitrobenzoyl chloride in chloroform solution gave a mixture of chloroesters from which **1** was readily isolated by recrystallization. The identity of **1** follows from C and H analysis, infrared and n.m.r. spectra, expectation of *trans* diaxial opening[3] in formation, and from the observation that *trans*-4-*t*-butylcyclohexene oxide is regenerated from it in high yield. While a number of other isomers could conceivably be formed in the initial ring-opening reaction, **1** and **2** must be by far the major products, as the mixed epoxide is recovered in good yield on facile basic hydrolysis of the crude chloro ester mixture.[4]



Recrystallization from methanol of the combined second crops rapidly gave sharp-melting material which appeared to be isomer **2**. However, the reformed epoxide from this material (high yield) was composed of approximately 80% *cis*- (**4**) and 20% *trans*-4-*t*-butylcyclohexene oxide (**3**). Exhaustive recrystallization from aqueous acetic acid gave a poor yield of the chloro ester **2** of approximately 95% purity. This product was used for analysis and n.m.r. spectrum determination.

The procedure described here promises to be of general utility in the separation of epoxides and, with the methods already available[1a] for stereospecific interconversion of these isomers, offers a straightforward pathway to both *trans* and *cis* forms.

Experimental

4-*t*-Butylcyclohexanol.—A 1-l. high-pressure hydrogenation bomb was charged with 342 g. (2.20 mole) of 4-*t*-butylphenol (recrystallized from aqueous methanol), 300 ml. of glacial acetic acid, and 2.5 g. of 5% rhodium-on-alumina catalyst. At ambient temperature and an average hydrogen pressure of 1800 p.s.i., reduction was complete in approximately 2.5 hr. The product, obtained in essentially quantitative yield, was composed of 60% *cis*- and 40% *trans*-4-*t*-butylcyclohexanol.

4-*t*-Butylcyclohexene was prepared in high yield by the method of Sicher,[2] b.p. 70–72° (20 mm.).

***cis*- and *trans*-4-*t*-Butylcyclohexene Oxide.**—The olefin, 105 g. (0.76 mole), was taken up in 1.5 l. of anhydrous ether, and 160 g. of commercial *m*-chloroperbenzoic acid[5] was added in portions over a period of about 2 hr. Occasional cooling was required. The mixture was allowed to stand 24 hr., washed with 10% sodium sulfite solution and dilute base, and dried over anhydrous magnesium sulfate; the solvent was evaporated. Distillation of the residue gave 107 g. (92%) of the epoxide mixture, b.p. 68–69° (4 mm.).

This mixture, which was identical with that formed by the action of either perbenzoic or monoperphthalic acid on the olefin, was comprised of 60% *cis* and 40% *trans* epoxide.[6]

***trans*-2-Chloro-*trans*-5-*t*-Butylcyclohexyl *p*-Nitrobenzoate.**—The epoxide mixture, 97 g. (0.63 mole) was dissolved in 500 ml. of chloroform, and 140 g. (0.75 mole) of *p*-nitrobenzoyl chloride (recrystallized from petroleum ether, b.p. 90–110°) was added. With magnetic stirring, a slow stream of anhydrous hydrochloric acid was passed into the solution over a period of 6 hr.; the reaction was very slightly exothermic. The chloroform solution was washed with water to remove excess acid and evaporated to give a residue which was taken up in pyridine. A few chips of ice were added to decompose the excess acid chloride, after which the mixture was taken up in ether, washed extensively with 5% hydrochloric acid, then with dilute bicarbonate and water. After drying, evaporation of the ether gave 215 g. of solid material (essentially quantitative crude yield).

Recrystallization was effected from methanol solution, with rapid purification rather than high recovery being stressed. Five recrystallizations gave 24 g. (28%), m.p. 124.5–126°.

Anal. Calcd. for $C_{17}H_{22}ClNO_4$: C, 60.1; H, 6.5. Found: C, 60.4; H, 6.8.

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[1] (a) N. A. LeBel and R. F. Czaja, *J. Org. Chem.*, **26**, 4768 (1961); (b) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

[2] J. Sicher, F. Šipoš, and M. Tichý, *Collection Czech. Chem. Commun.*, **26**, 847 (1961).

[3] For a review of the stereochemistry of epoxide-opening reactions, see R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

[4] D. Y. Curtin and R. J. Harder, *J. Am. Chem. Soc.*, **82**, 2357 (1960).

[5] FMC Corporation, 85% minimum assay material was used.

[6] Analysis was by vapor phase chromatography.