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(A contribution from the H. Fletcher Brown Laboratory
of the University of Delaware)

The Configuration of Some Dichlorocamphanes

Harold Kwart

Abstract

The dipole moments of the compounds previously known as bornyl dichloride and β chlorocamphane have been measured. The configurational relationships of the two chlorine atoms in each of these compounds is deduced from these data and other considerations. The mechanism of the reactions by which these substances are formed is clarified by knowledge of their respective configurations. Some general conclusions may be inferred concerning the steric course of and the transition states in the Wagner-Meerwein and Nametkin rearrangements. Evidence bearing on the relationship of the bornyl and isobornyl configurations has also been deduced from these data.

The structure of the principal dichlorination product of α pinene(I) described by Aschen and others¹ has been identified as

(1) O. Aschen, Ber. 61, 38 (1928)
O. Brus, Compt. Rend. 180, 1507 (1925)

2,6 dichlorocamphane on the basis of tricylene formation when this product is treated with zinc or sodium. Although referred to by

Simonsen and others² as bornyl dichloride the previously reported

(2) J. L. Simonsen, THE TERPENES, Oxford University Press, 1949,
Vol. II, p. 167
(See also reference (4))

evidence has not permitted a configurational assignment of the chlorine atoms; i.e. whether exo or endo. We report here a basis for distinction in the results of dipole moment measurements and a comparison of these results with the values calculated for all possible configurations. (See table I).

Table I

2,6 Dichlorocamphane (III)

Possible Configuration	μ^* Calculated	μ Observed
<u>exo-exo</u>	2.5 D	
<u>exo-endo</u>	2.5 D	
<u>endo-endo</u>	4.2 D	4.0 D

2,4 Dichlorocamphane (XI)

2- <u>exo</u>	2.5 D	2.5 D
2 <u>endo</u>	2.5 D	

*The dipole moments of bornyl and isobornyl chlorides were determined (see experimental section) and found to be identical. This value of the C-Cl bond moment (2.1 D) was used in calculating the moments of all possible configurations.

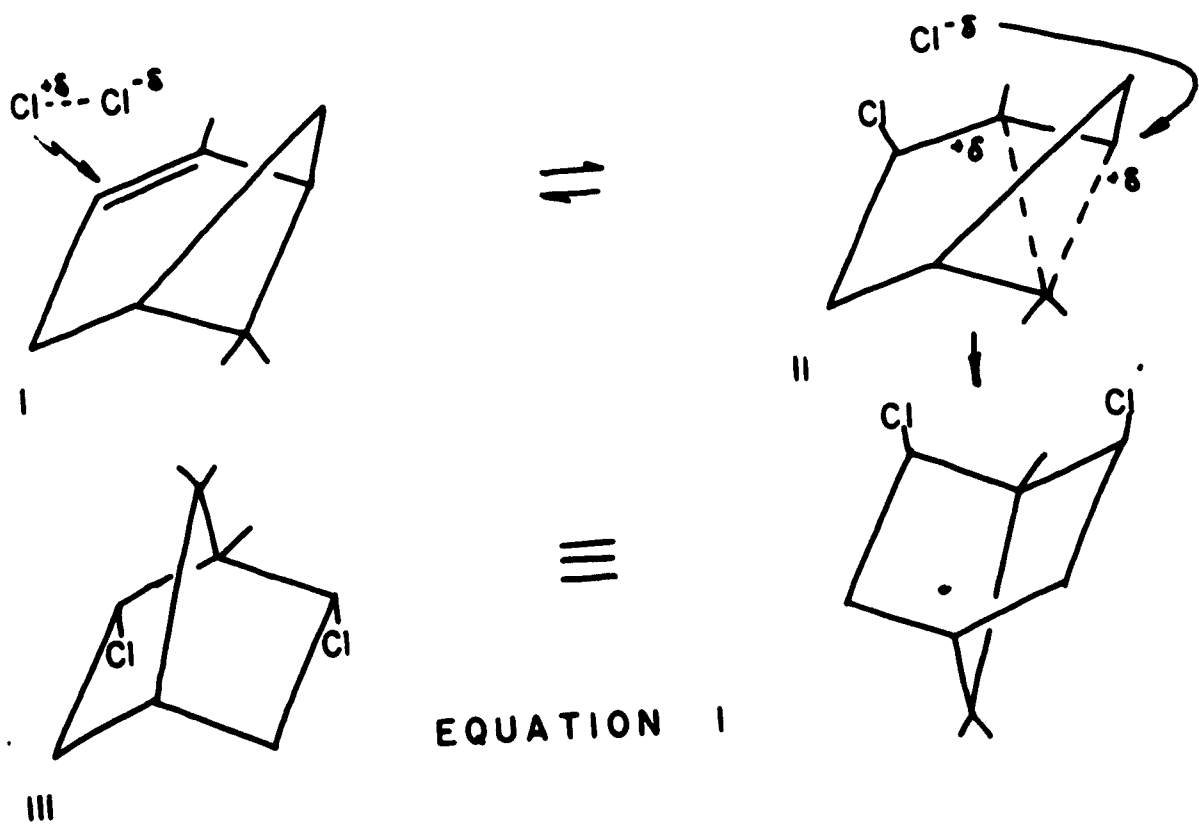
The endo-endo configuration chosen as most consistent with the data holds particular interest for the following reasons. Considering the method of formation of III from pinene, chlorination has resulted in a rearrangement of the carbon skeleton. A bridged cation intermediate (see equation I) analogous to that suggested by Neville, De Salas and Wilson and others³ to explain

(3) T. P. Neville, E. De Salas and C. L. Wilson, J. Chem. Soc., 1188 (1959). See also W. E. Doering Abstracts 115th meeting of the American Chemical Society, Chicago, Ill., April 19-23, 1948, p. 41L and S. Winstein et al, this Journal, 74, 1150 (1952)

the Wagner-Meerwein rearrangement of camphene hydrochloride accounts satisfactorily for the alteration of the carbon skeleton during this reaction.

It is seen from the purely endo-endo configuration of the product, requiring, as it does, having added the elements of chlorine from the same side of the molecule, that this confirms maintenance of configuration at the site of reaction in the bridging cation (II). The product therefore arises only on rearward displacement of the delocalized electron pair maintaining the configuration of the cation as indicated in the structural equation above. The operation of purely polar factors in this mechanism has been inferred from the observation of Henderson and Marsh⁴ that 2,6 dichlorocamphene, as

(4) G. G. Henderson and J. E. Marsh, J. Chem. Soc. 119, 1492 (1921)



would be expected in a polar halogenation⁵ also arises from the

(5) M. J. S. Dewar, THE ELECTRONIC THEORY OF ORGANIC CHEMISTRY, Oxford Univ. Press, (1949) p. 141 et seq.

chlorination of α pinene in aqueous solution alongside of pinene glycol and chlorohydrin.

The endo-endo configuration, deduced for 2,6 dichloro-camphane would at first glance suggest that the elements of chlorine had added from the endo side and this in turn construed as a contradiction of the rule of exo addition substantiated in the work of Alder and Linstead and their collaborators.⁶ However, in the re-

(6) K. Alder and G. Stein, Ann., 515, 161 (1935)
Ibid., 526, 183 (1936)
 R. Linstead et al, This Journal, 64, 1985 (1942)

action mechanism represented in equation (1) initial attack at the double bond in α pinene by the electrophilic reagent has been depicted as occurring from the exo side of the molecule if one accepts the unsubstituted methylene bridge as the frame of reference. Curiously, the exo addition reference disappears in forming the product (III) which contains only a disubstituted methylene bridge. This interesting situation occurs often in the chemistry of α pinene. Thus the structure of α pinene oxide obtained⁷ by the action of

(7) W. Prileschaev, Ber., 42, 4814 (1909)

perbenzoic acid on α pinene can be assigned as IV, in view of the course of addition described above for the chlorination of α pinene. Indeed, the mechanism of acid catalyzed rearrangement of this oxide to VI observed by Arbusov⁸ can be deduced in consonance with the

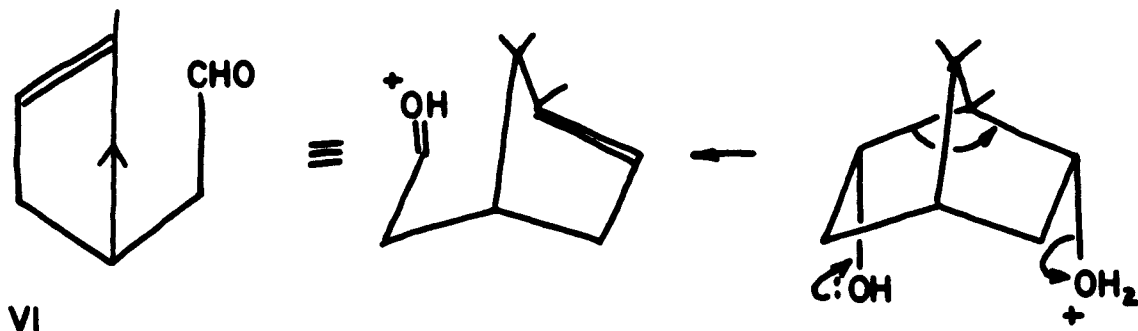
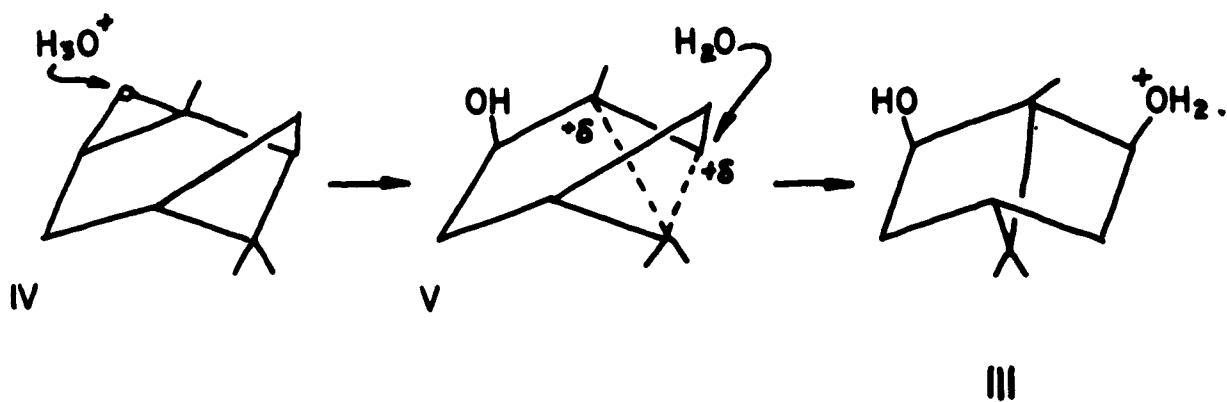
(8) B. Arbusov, Ber., 68, 1450 (1935). We are indebted to Dr. W. E. Doering for this suggestion.

stereochemical results of the chlorination reaction. (See equation 2). The formation of the bridged ion intermediate V in this rearrangement, analogous to the formation of II in equation (2), involves the participation of the neighboring disubstituted methylene bridge located trans and nearly coplanar with respect to the rupturing oxonium ion bond.

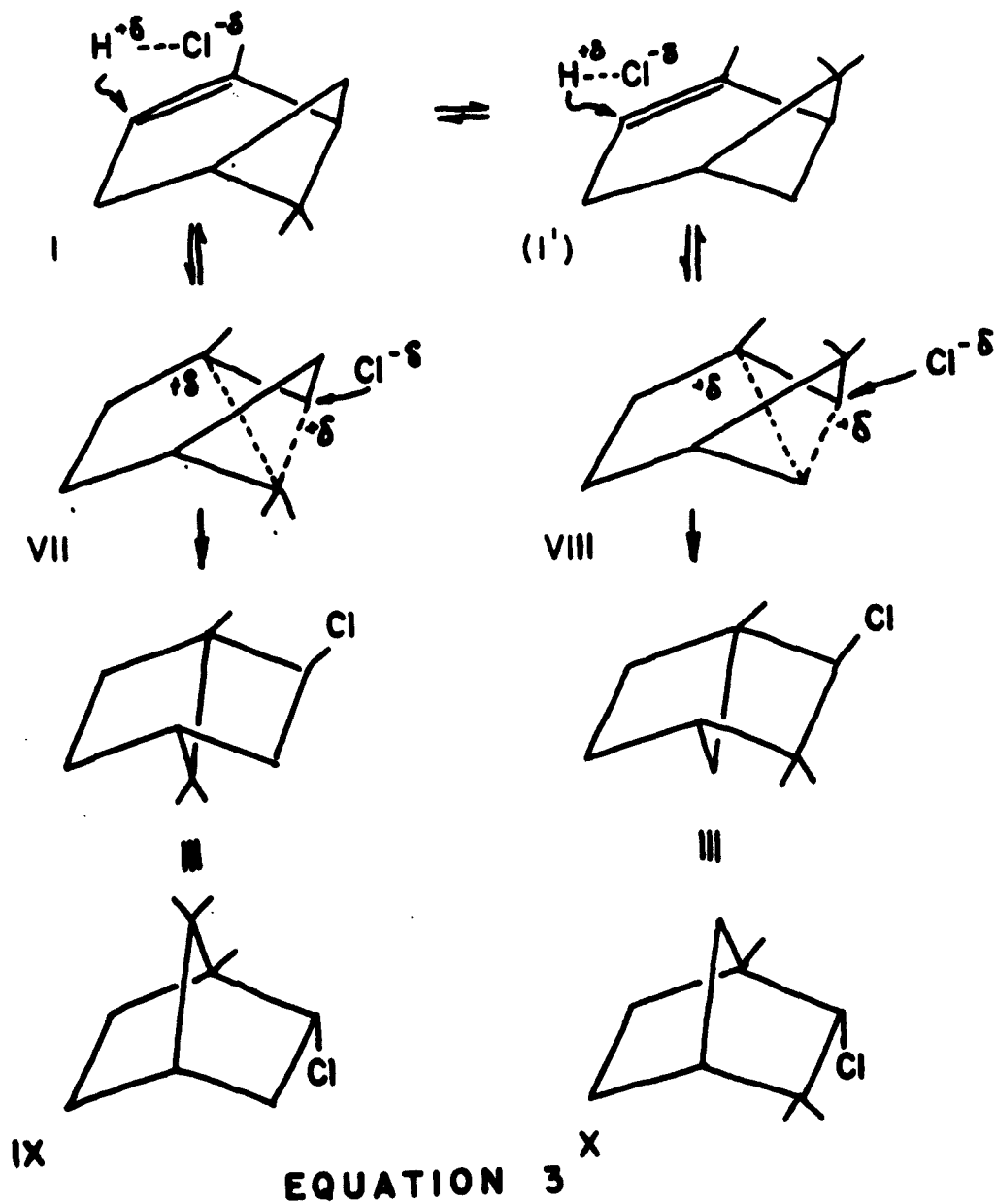
Often, however, the course of addition to the double bond in α pinene may be inferred by regarding the disubstituted methylene bridge as the frame of reference for exo attack by the electrophilic reagent. The addition of hydrogen chloride to α pinene⁹ is a case

(9) O. Aschen, Ber., 40, 2750 (1907), Ann., 387, 1 (1912)

in point where both the substituted and unsubstituted bridges simultaneously direct the course of addition resulting in two different reaction products. The mechanism formulated in equation (3) appears to afford an adequate explanation for simultaneous formation of the two products in terms of two different bridged ion intermediates;



EQUATION 2



the one (VII) arising from the unsubstituted methylene bridge orientation leads to the preponderant product, bornyl chloride (IX), the other (VIII) arising from the disubstituted methylene bridge orientation leads to the minor product, α fenchyl chloride (X).

The fact that α fenchyl derivatives always accompany the corresponding bornyl derivatives obtained in addition reactions of α pinene¹⁰ is best understood in terms of the equilibrium of α pinene

(10) M. Dalepina, *Compt. Rend.* 178, 2088 (1924), 179, 175 (1924)

structures (I) and (I') and maintenance of configuration in the distinctive bridged ion intermediates (VII) and (VIII). The configurational relationship of bornyl and α fenchyl structures has been previously suggested by Hückel and coworkers.¹¹ The mechanism

(11) W. Hückel, H. Kindler and H. Wolowski, *Ber.*, 77, 220 (1944).
See also H. Schmidt and K. Todenhöfer *Schweizerische Reports*, 115,
(1937) and G. Komppa and S. Beckmann, *Ann.*, 522, 157 (1936)

depicted in equation (3) is seen to be entirely consistent with this structural relationship.

A second consequence of the configurational assignment (III) suggested here for bornyl dichloride bears on the long contested question of whether a bornyl structure corresponds to the

exo or endo configuration¹² and vice versa for the isobornyl con-

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- (12) K. Alder and G. Stein, Ann. 514, 211 (1934)
 H. Bode, Ber., 70, 1167 (1937)
 G. Komppa and G. A. Nyman, *ibid.*, 69, 354 (1936)
 W. Hückel, Die Chemie, 55, 227 (1942)
-

figuration.

Consideration¹ of the chemical reactivity of 2,6 dichloro-
 camphane has heretofore suggested a relationship to the inertness
 of the bornyl halides and prompted the name bornyl dichloride. The
 present endo assignment supports the view that a bornyl configura-
 tion in a suitably substituted camphane is always endo.

β -Dichlorocamphane resulting from rearrangement of 2,2'
 dichlorocamphane with electrophilic reagents has been shown by Houben
 and Pfankuch,¹³ to be 2,4 dichlorocamphane. The 2-exo structure we

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- (13) J. Houben and E. Pfankuch, Ann., 501, 219 (1933)
-

have assigned to XI does not result from as clear a choice of struc-
 tures (see Table I) as was the case with (III) since it is seen that
 a 2-endo structure is not excluded by the dipole moment data. How-
 ever, Houben and Pfankuch¹⁴ from considerations of optical activity

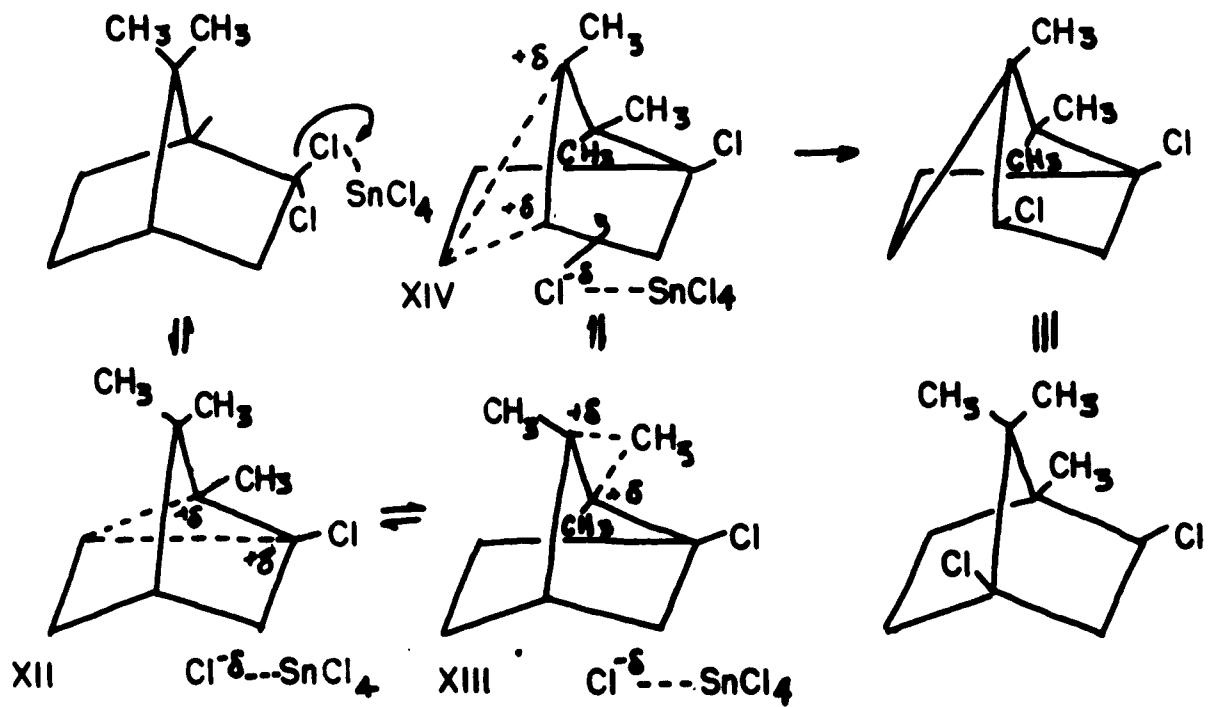
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- (14) J. Houben and E. Pfankuch, Ann., 489, 204 (1931). See also
 reference (10).
-

of β dichlorocamphane have proven an isobornyl configuration for the 2-chlorine atom. Since the evidence discussed above in connection with the structure of 2,6 dichlorocamphane indicates that the isobornyl configuration is exo, the 2-exo model is chosen. This selection is also consistent with the mechanism represented in equation 4 for the rearrangement reaction by which XI is formed. A series of bridged cation intermediates act to preserve the stereochemical purity of the reaction product in such the same manner as in the chlorination of α pinene. No less than three (XII, XIII, and XIV) such bridged cations are involved in the rearrangement with the remarkable result of a single stereoisomer as the product.

The stereochemical course of the Wagner-Meerwein and Nametkin¹⁵ rearrangements, which these examples illustrate, is thus

(15) S. Nametkin et al, J. pr. Chem. (ii), 124, 144 (1950); Ber., 66, 511 (1935)

characterized by complete maintenance of configuration in bridged ion intermediates and by rearward displacement of the participating bonds either by other participating electron pairs located trans and nearly coplanar with respect to the bridged loci, leading to an equilibrium of such intermediates or ultimately by anions, leading to products.



EQUATION 4

Experimental

Isobornyl Chloride was prepared according to Meerwein and van Emster.¹⁶ The product thus obtained was recrystallized once from

(16) H. Meerwein and K. van Emster, Ber., 55, 2526 (1922)

n-nyl alcohol (dried over calcium oxide) and twice from nitromethane (Eastman white label dried over anhydrous calcium sulfate. m.p. 162° (uncorr.)). It was dried thoroughly in vacuum before use. The camphene used in this synthesis was provided through the courtesy of the Hercules Powder Company Experimental Station.

Bornyl Chloride was prepared by the addition of dry HCl to α pinene (Hercules grade distilled over sodium) according to the procedure discussed by Thurber and Thielke.¹⁷ It was recrystallized

(17) F. H. Thurber and R. C. Thielke, This Journal, 53, 1032 (1931)

twice from low boiling 30-60° petroleum ether (distilled from sodium) m.p. 131° (uncorr.) and stored in a vacuum desiccator over calcium chloride before use.

2,6 Dichlorocamphane¹⁸ was prepared according to the method

(18) This preparation was carried out by Mr. Donald Pascale and Mr. Lloyd Kaplan.

of Aaschen.¹ For dipole moment measurements it was recrystallized

three times from absolute ethanol and stored in a vacuum desiccator over calcium chloride before use. m.p. $170-171^{\circ}$ (uncorr.).

2.4 Dichlorocamphane was prepared from synthetic camphor (U.S.P. du Pont) by the procedure suggested by Doering and Schoenewaldt.¹⁹ The product was recrystallized twice from absolute methanol

(19) W. E. Doering and E. F. Schoenewaldt, *This Journal*, 75, 2333 (1951)

saturated with dry hydrogen chloride and stored in a vacuum desiccator over calcium chloride before use. m.p. 178° dec. (uncorr.).

Dipole Moment Measurements

Pure, dry carbon tetrachloride used as the solvent in these experiments was prepared from C. P. Baker grade by the method of Vogel.²⁰

(20) A. I. Vogel, *TEXTBOOK OF PRACTICAL ORGANIC CHEMISTRY*, Longmans Green Co., 1951, p. 174-5

The dipole moments were computed from the data tabulated in tables II, III and IV by the method of Guggenheim²¹ using the

(21) E. A. Guggenheim, *Trans. Farad. Soc.*, 45, 714 (1949)
 J. W. Smith, *ibid.*, 46, 394 (1950)
 F. A. Guggenheim, *ibid.*, 47, 573 (1951)

equation:

$$\mu = 0.0222 \left(\frac{S_0 T}{(\epsilon_0 - 2)(n_0^2 - 2)} \right)^{\frac{1}{2}} \text{ where}$$

μ = the dipole moment in Debyes

S_0 = slope of the plot in the accompanying figures I, II and III

T = absolute temperature

ϵ_0 = dielectric of solvent; ϵ = dielectric of solution

n_0 = refractive index of solvent; n = refractive index of solution

Analysis of the error introduced by using this simplified computation according to the suggestion of Palet²² indicates that an error of no

(22) S. R. Palit, This Journal, 74, 3952 (1952)

greater than 5 per cent could arise by ignoring consideration of the solution densities in the results reported here. This magnitude of possible error lies beyond the limit which would have significance in our considerations above.

Dipole Moment Data

Table II

Isobornyl Chloride $S_0 = .0535$

(Moles/cc) 10^4

6.989	2.6121	1.4616	2.1565	0.476
5.494	2.4187	1.4594	2.1238	0.287
1.747	2.5208	1.4594	2.1263	0.194
0.874	2.2725	1.4579	2.1255	0.147
0.000	2.2250	1.4574	2.1240	0.101

Bornyl Chloride $S_0 = .0535$

(Moles/cc) 10^4

10.0463	2.7952	1.4626	2.1332	0.654
5.0235	2.5372	1.4502	2.1522	0.375
2.5117	2.5650	1.4588	2.1281	0.237
1.2558	2.2965	1.4581	2.1261	0.170
0.0000	2.2250	1.4574	2.1240	0.101

Table III

2,6 Dichlorocamphane $S_0 = .198 \times 10^5$

Mole %

1.51	2.5450	1.4594	2.1298	0.415
2.20	2.5534	1.4607	2.1536	0.520
4.11	3.0242	1.4651	2.1406	0.894
6.05	3.4015	1.4548	2.1456	1.256
0.00	2.2372	1.4575	2.1245	0.113

Table IV

2,4 Dichlorocamphane $S_0 = 7.203 \times 10^2$

(Moles/cc) 10^3

4.5094	2.565	1.4609	2.1542	0.451
2.2547	2.3919	1.4597	2.1507	0.261
1.1274	2.3094	1.4588	2.1281	0.181
0.5637	2.2687	1.4595	2.1266	0.142
0.000	2.2324	1.4578	2.1252	0.107

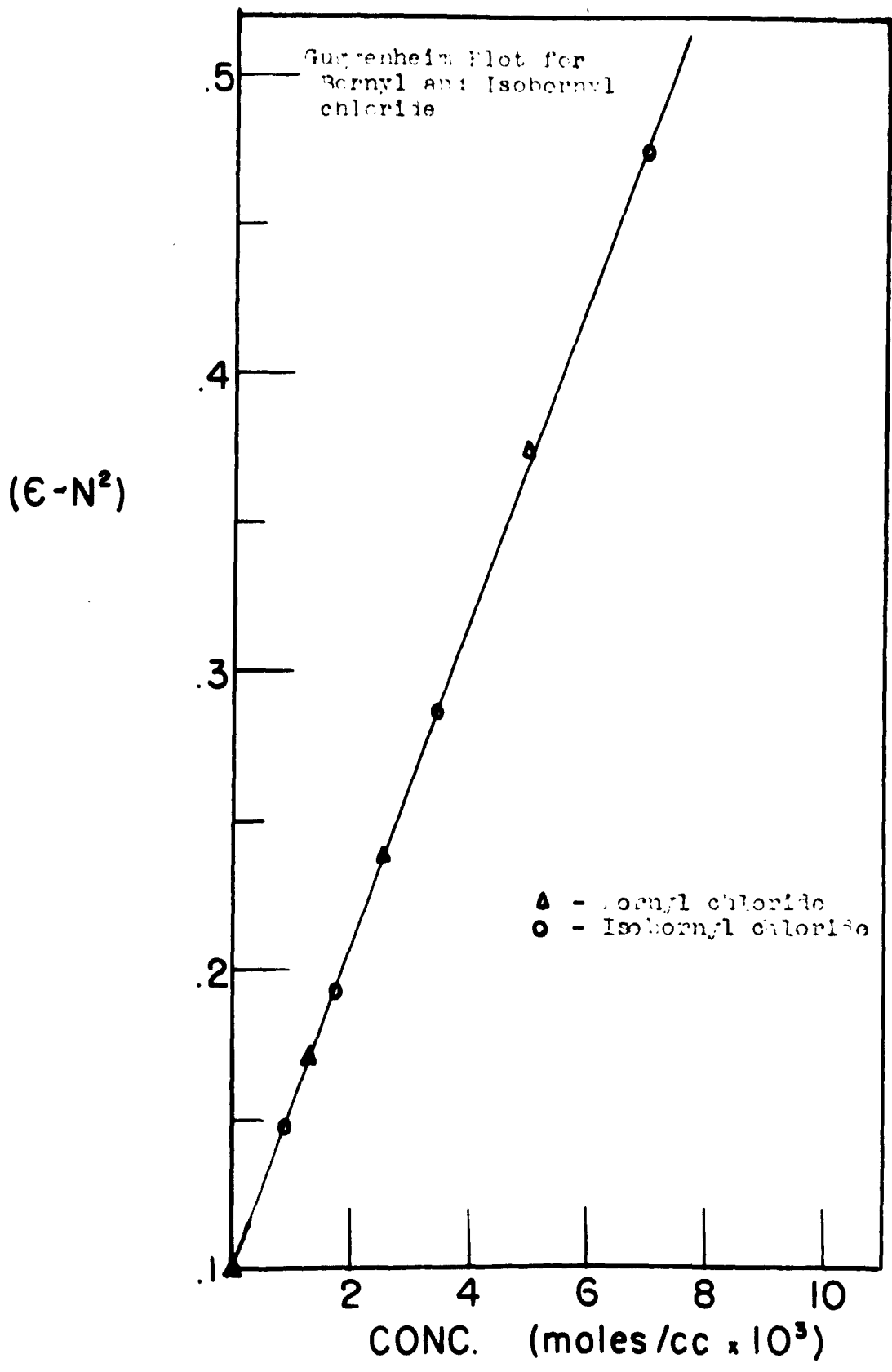


Fig. I

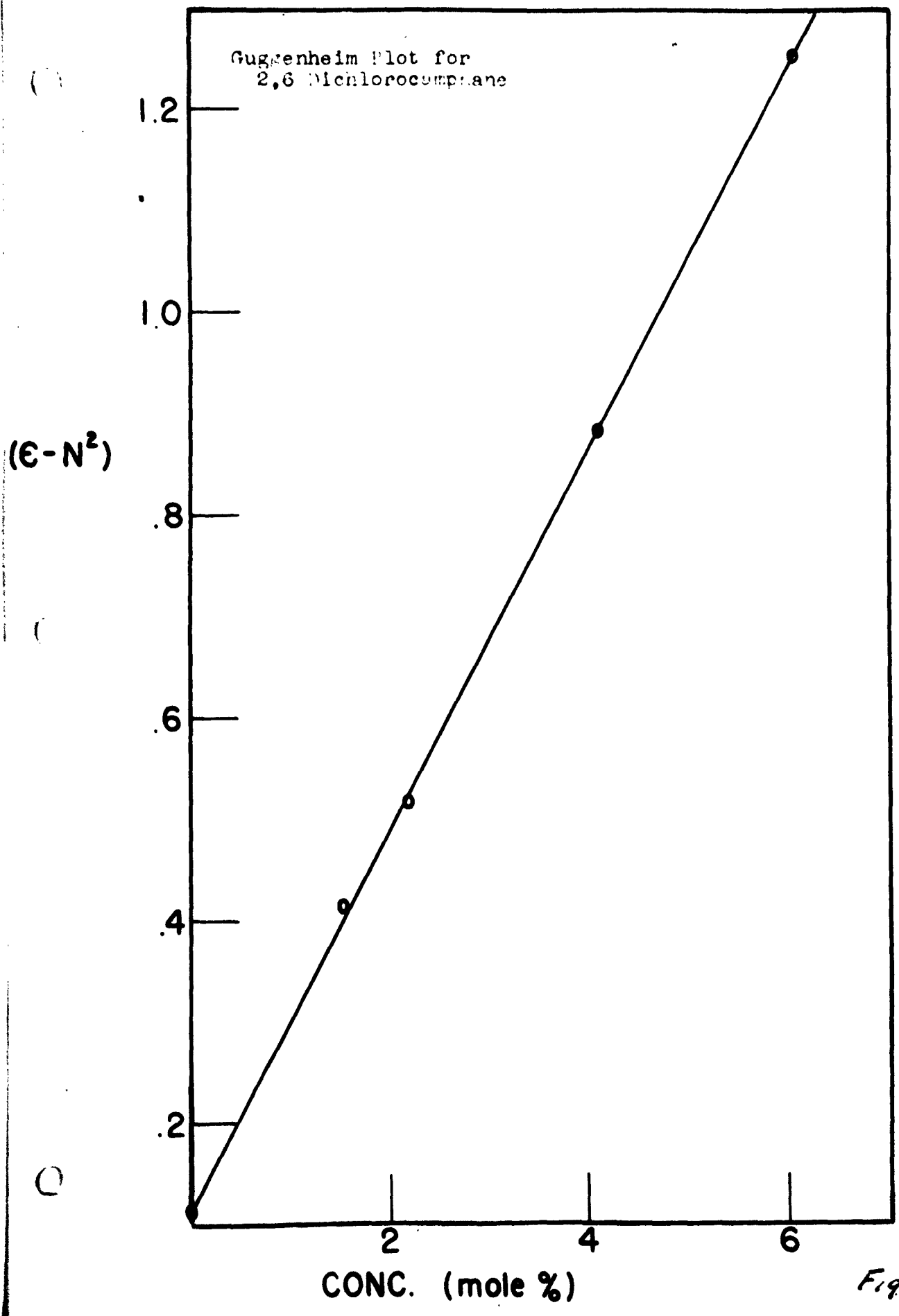


Fig II

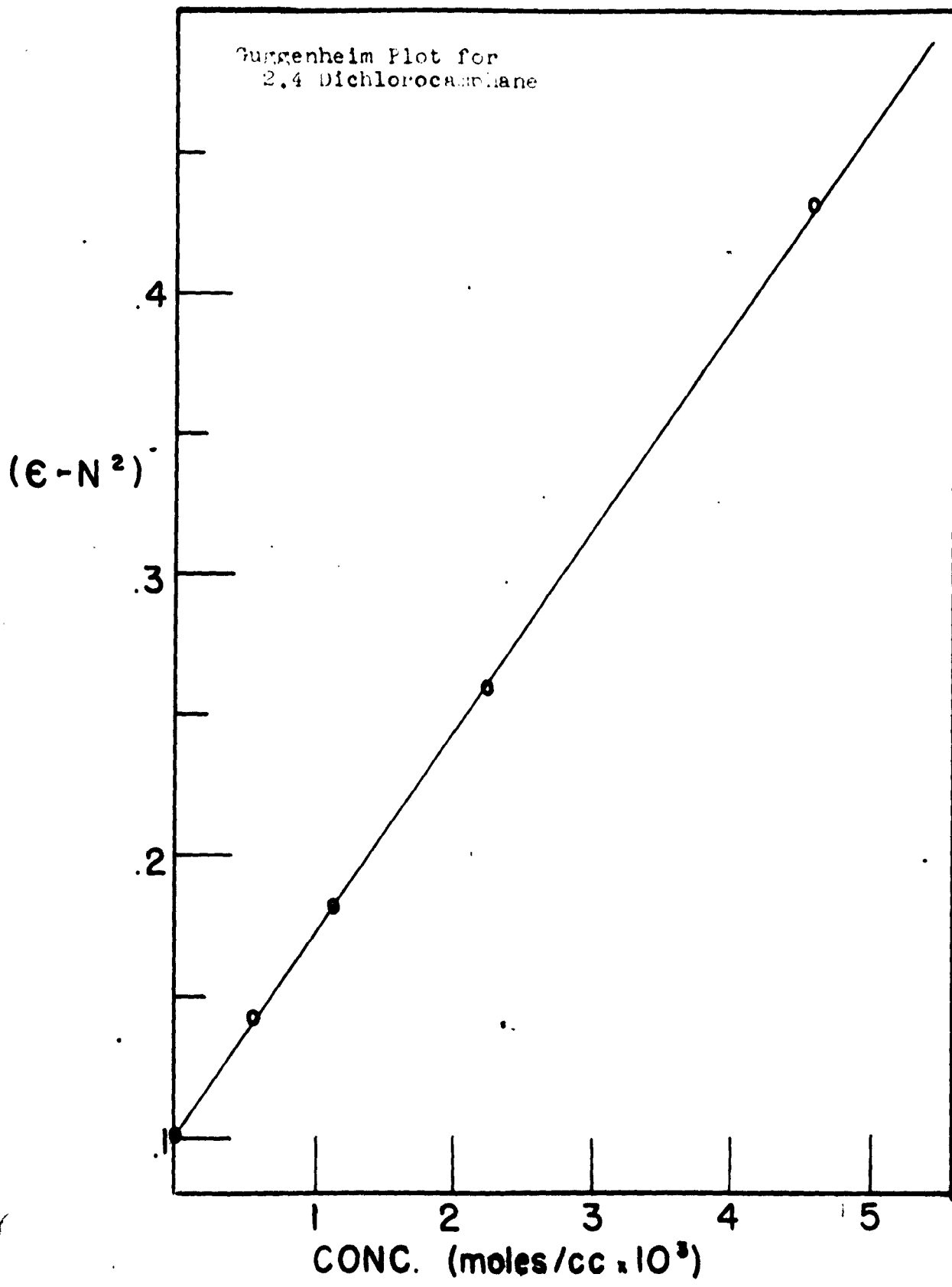


Fig III