reaction mixture was diluted with a large volume of absolute ether and treated with an excess of methanolic hydrogen chloride. Scratching gave a white crystalline product, 70 g. (90%), melting at 120–125°. After several crystallizations from acetone–ether mixtures the pure substance melted at 124–125°. A mixture of this with the pure mono-ester (N-homoveratryl-β-alanine methyl ester)[1] of m. p. 121–122° showed a depression and melted at 105–112°.

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THE WELLCOME RESEARCH LABORATORIES
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Preparation of Homopiperonylamine by Hydrogenation of 3,4-Methylenedioxybenzyl Cyanide over Raney Cobalt Catalyst

BY WILKINS REEVE AND WILLIAM M. EARECKSON, III

The preparation of homopiperonylamine by the hydrogenation of 3,4-methylenedioxybenzyl cyanide over Raney cobalt catalyst has been studied incidental to the preparation of this compound for some synthetic work. This preparation is of interest both because it appears to be the best method of preparing the frequently used homopiperonylamine and because it provides an excellent illustration of the advantage of Raney cobalt over Raney nickel in the reduction of nitriles to primary amines. Although the use of cobalt catalysts in the reduction of nitriles has been the subject of a number of patents,[1] these catalysts do not seem to have received the recognition they deserve.

The more important methods previously used for the preparation of homopiperonylamine are (a) the hydrogenation of small amounts of 3,4-methylenedioxy-ω-nitrostyrene, dissolved in a large amount of acetic acid and in the presence of an excess of sulfuric acid and 35% of its weight of a palladium catalyst (84–93% yield)[2]; (b) the hydrogenation of 3,4-methylenedioxybenzyl cyanide, 85% yield when carried out in methanol–ammonia over Raney nickel catalyst,[3] 93% yield when carried out in acetic acid over platinum in the presence of sulfuric acid[4]; (c) the electrolytic reduction of 3,4-methylenedioxy-ω-nitrostyrene (67–75% yield)[5]; and (d) the Hofman degradation of β-(3,4-methylenedioxyphenyl)-propionamide (88% yield).[6]

Table I gives the yields we have obtained of homopiperonylamine by the hydrogenation of 3,4-methylenedioxybenzyl cyanide over Raney nickel and Raney cobalt catalysts in anhydrous ethanol–ammonia, anhydrous ethanol and in anhydrous dioxane. It is to be noted that Raney cobalt in dioxane solvent with no ammonia gives as good results as Raney nickel, even when the latter is used with the ethanol–ammonia solvent. 3,4-Methylenedioxy-ω-nitrostyrene was also reduced over Raney cobalt catalyst to the primary amine, but only in 26% yield. Under the same conditions, but with Raney nickel, a 10% yield was obtained.

TABLE I

HYDROGENATION OF 3,4-METHYLENEDIOXYBENZYL CYANIDE OVER RANEY NICKEL AND RANEY COBALT CATALYSTS

Catalyst	Solvent and conditions[a]	Yield of homopiperonylamine, %
Raney nickel	Dioxane	50[b]
Raney nickel	Ethanol–ammonia	82
Raney cobalt	Dioxane	79–87
Raney cobalt	Ethanol–ammonia	88
Raney cobalt	Anhyd. ethanol	65–69

[a] Forty-two grams of nitrile was used in the case of Raney nickel with the dioxane solvent. All other hydrogenations were carried out with 70 g. of compound dissolved in 90 ml. of solvent over 5% catalyst at 125 to 150° at a starting hydrogen pressure of 200 atmospheres at room temperature. The hydrogenations proceeded rapidly; the time necessary at the reaction temperature approximating fifteen minutes. The procedure of Icke and Redemann given in "Organic Syntheses," **23**, 72 (note 5) (1943), for the use of methanol–ammonia was followed, except anhydrous ethanol was saturated with ammonia. [b] 25% Secondary amine was also obtained.

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Experimental

All melting points are corrected.

The dioxane was purified by refluxing over sodium.

Preparation of Catalysts.—Raney nickel was prepared by the W-7 procedure of Adkins.[7] Raney cobalt was prepared by crushing and grinding the 40% cobalt–60% aluminum alloy until all passed a 100-mesh sieve, and then following the W-7 procedure. Both alloys were purchased from the Gilman Paint and Varnish Company, Chattanooga, Tennessee.

3,4-Methylenedioxybenzyl Cyanide.—This was prepared by a modification of the procedures of Bills and Noller,[3] and Kobayashi.[8] 3,4-Methylenedioxybenzyl chloride was prepared from piperonyl alcohol (1.0 mole), concentrated hydrochloric acid (250 ml.) and calcium chloride (sufficient to saturate the aqueous layer). The aqueous layer was extracted twice with 100 ml. portions of benzene, and the benzene solution of the chloride treated directly with 3.5 moles of sodium cyanide and 0.025 mole of mercuric cyanide dissolved in 250 ml. of water. After

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(1) Schmidt, German Patent 648,297 (July 27, 1937), *C. A.*, **31**, 7067 (1937), U. S. Patent 2,160,578 (May 30, 1939), *C. A.*, **33**, 7315 (1939); and U. S. Patent 2,165,515 (July 11, 1939); *C. A.*, **33**, 8211 (1939); British Patent 536,940 (June 3, 1941), *C. A.*, **36**, 1331 (1942); Signaigo, U. S. Patent 2,166,183 (July 18, 1939), *C. A.*, **33**, 8211 (1939), Canadian Patent 408,981 (Dec. 1, 1942), *C. A.*, **37**, 1447 (1943; Howk, U. S. Patents 2,166,150, 2,166,151, and 2,166,152 (July 18, 1939), *C. A.*, **33**, 8211 (1939), Canadian Patent 408,983 (Dec. 1, 1942), *C. A.*, **37**, 1449 (1943); Gresham, U. S. Patent 2,429,-876 (Oct. 28, 1947), *C. A.*, **42**, 1316 (1948).

(2) Kinder, Brandt and Gehlhaar, *Ann.*, **511**, 211 (1934); Schales, *Ber.*, **68**, 1581 (1935).

(3) Bills and Noller, THIS JOURNAL, **70**, 957 (1948).

(4) Hahn and Schales, *Ber.*, **67B**, 1486 (1934).

(5) Slotta and Haberland, *Angew. Chem.*, **46**, 766 (1933); Tanaka and Midzuno, *J. Pharm. Soc. Japan*, **49**, 255 (1929), *C. A.*, **23**, 3214 (1929).

(6) Faltis, Wagner and Adler, *Ber.*, **77B**, 691 (1944).

(7) Adkins and Billica, THIS JOURNAL, **70**, 698 (1948).

(8) Kobayashi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokio*), **6**, 164 (1927).

refluxing for six hours with stirring, the benzene layer was washed thoroughly until free of halide and mercuric ions. The nitrile was distilled from Raney nickel. The yield was 85%, based on the piperonyl alcohol.

Dihomopiperonylamine was isolated as the hydrochloride by dissolving the non-volatile residue from the Raney nickel catalyzed hydrogenation in dry ether and bubbling in dry hydrogen chloride. The hydrochloride, after recrystallizing twice from water and once from 95% ethanol melted at 261-262° with dec. *Anal.* Calcd. for $C_{18}H_{20}O_4NCl$: C, 61.82; H, 5.73; N, 4.00. Found: C, 62.08; H, 5.84; N (Dumas), 4.15.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
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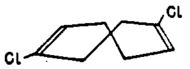
The Dipole Moment and Molecular Configuration of 1,6-Dichloro-1,5-cycloöctadiene

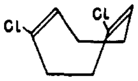
BY JOHN D. ROBERTS

The structure of the eight-membered ring dimer (I) of chloroprene (2-chloro-1,3-butadiene) has been established as 1,6-dichloro-1,5-cycloöctadiene (the product of "head-to-head" dimerization)[1] with probably the *cis–cis* configuration of double bonds.[2] Inspection of Fisher–Hirschfelder models reveals that this substance might be expected to exist in three strainless forms analogous to the boat and chair forms of cyclohexane.[3]

"Chair" form



"Skew" form



"Boat" form

In the "chair" form of I, the C–Cl bonds (barring minor perturbations) lie within parallel planes with the projection of one bond on the plane of the other bond forming an angle of 120°[4] with the latter. If it is assumed that (a) only the C–Cl moments make important contributions to the dipole moment of the molecule and (b) the vector moment of each C–Cl is equal to 1.5*D*,[5] the calculated moment of this form is 1.5*D*. In the "skew" configuration the C=C—Cl groups lie in two intersecting planes inclined at about 45°, the line of intersection of the planes passing through the mid-points of each of the C=C bonds and perpendicular to them. The resultant of the C–Cl vectors in the skew form is 1.4*D*. In the "boat" configuration the C–Cl bonds lie within the same plane at an angle of 40°. The value of the angle is readily obtained if the equivalence is recognized between this angle and the one formed by the extensions of the Cl–C8 and C6–C7 bonds. The calculated moment for a 40° angle is 2.8*D*.

The dipole moment of pure I[1] in benzene solution was found to be 2.60*D* by the method previously described.[6] The data are given in Table I. The experimental value for the dipole moment is in good agreement with the value calculated for the boat configuration and indicates that this is the actual configuration for at least 85% of the molecules formed by the dimerization of chloroprene. The boat configuration could hardly have been expected *a priori* to be the most stable form since the dipole–dipole repulsions of the C–Cl bonds (operating across a medium of unit dielectric constant) would amount to about 500 cal./mole.

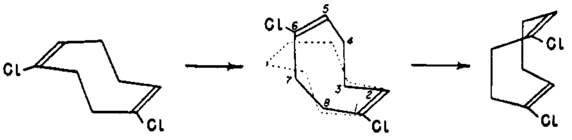
TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN BENZENE AT 25° OF 1,6-DICHLORO-1,5-CYCLOÖCTADIENE

f_2	ϵ	d	P_2
0.00000	2.2760	0.87308	(P_1 = 26.697)
.00596	2.3329	.87654	182.0
.01027	2.3756	.87882	183.4
.02562	2.5270	.88751	181.1
.05918	2.8716	.90496	178.0

$P_\infty = 183.0$, $MR_D = 48.15$, $\mu = 2.60D$

In order to test a provisional hypothesis, that (a) the forms might not be readily interconvertible and (b) the boat form is produced almost exclusively in the dimerization, approximate calculations have been made of the energy barriers to interconversion of the three forms. It was expected that the boat and chair forms should not be easily convertible since they correspond to the reported isomeric salicylides.[7] This expectation was not verified on calculation of the strain energy involved in the interconversion process. From inspection of scale models, the most energetically favorable interconversion route appeared to be that shown below with a transition state having C-3,4,5,6,7 and 8 lying in one plane. The strain



in this transition state results from changes in the valence angles of C-1,2,4,5,6 and 7. No particular strain seems to be involved in angles of C3 and 8 if free rotation exists around the C2-C3 and C1-C8 bonds.

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[1] Cope and Schmitz, THIS JOURNAL, **72**, 3056 (1950).

[2] Cope, Stevens and Hochstein, *ibid.*, **72**, 2510 (1950).

[3] Baker, Banks, Lyon and Mann, *J. Chem. Soc.*, 27 (1945), have previously suggested the possibility of similar isomeric forms for the analogously constituted *sym*-dibenzocycloöctadiene. The X-ray crystallographic data were reported to indicate that *sym*-dibenzocycloöctadiene exists as a centro-symmetrical form.

[4] Throughout this paper the following values are assumed for the normal bond angles and bond lengths: ∠C-C-C, ∠C-C-H = 109.5°; ∠C=C-C, ∠C=C-Cl, ∠C=C-H = 120°; C-H = 1.09 Å.; C=C = 1.34 Å.; C-C = 1.54 Å., =C-Cl = 1.70 Å.

[5] This moment is obtained from the average moments (2.1*D*) of secondary alkyl chlorides in benzene and the 0.6*D* difference between ethyl chloride and vinyl chloride, Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

[6] Rogers and Roberts, THIS JOURNAL, **68**, 843 (1946); Roberts, Armstrong, Trimble and Burg, *ibid.*, **71**, 843 (1949).

[7] *Cf.* Schönberg, *J. Chem. Soc.*, 891 (1948), for references and discussion. Note, however, that Baker, Ollis and Zealley, *Nature*, **164**, 1049 (1949), have very recently presented evidence that the *β*-salicylide is actually a trimer.