or was contaminated with selenium dioxide. No further attempts were made to purify this substance.

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The Apparent Molal Volume of Barium Chloride in Ethanol–Water Mixtures

BY RICHARD LOUIS BATEMAN

RECEIVED MAY 9, 1952

A previous publication[1] gave the density and apparent molal volume of strontium chloride in ethanol–water mixtures with a discussion of the results. The present report concerns the density and apparent molal volume of barium chloride in ethanol–water mixtures at 25.00°. The apparent molal volume of barium chloride in aqueous solutions at 25° has been reported by Geffcken[2] and at 35° by Chacravarti and Prasad.[3]

TABLE I

APPARENT MOLAL VOLUME OF BARIUM CHLORIDE IN ETHANOL–WATER MIXTURES AT 25°

Molality of $BaCl_2$	Density of soln., g./ml.	Vol. of soln. per 1000 g. solvent, ml.	Apparent molal vol. $BaCl_2$, ml.
	0% Ethanol		
0.5	1.08545	1017.21	28.56
.4	1.06812	1014.21	28.20
.3	1.05066	1011.25	27.73
.2	1.03304	1008.35	27.10
.1	1.01513	1005.59	26.60
.05	1.00615	1004.22	25.80
0	0.99708	1002.93	
	20% Ethanol		
0.5	1.05159	1049.97	30.38
.4	1.03501	1046.67	29.72
.3	1.01818	1043.51	29.10
.2	1.00122	1040.38	28.00
.1	0.98400	1037.42	26.40
.05	.97534	1036.01	24.60
0	.96639	1034.78	
	40% Ethanol		
0.5	1.01151	1091.57	36.02
.4	0.99590	1087.75	35.47
.3	.98005	1084.11	35.17
.2	.96410	1080.44	34.40
.1	.94794	1076.88	33.20
.05	.93985	1075.08	30.40
0	.93148	1073.56	
	50% Ethanol		
0.2	0.94141	1106.49	37.05
.1	.92584	1102.60	35.20
.05	.91791	1100.79	34.20
0	.90985	1099.08	
	60% Ethanol		
0.17710	0.91442	1133.91	36.70
.1	.90273	1130.81	34.00
.05	.89496	1128.99	31.60
0	.88699	1127.41	

For the same solvent, the apparent molal volume of barium chloride is greatest in the more concentrated solutions. In the more dilute solutions, with the same solute concentration, the molal volume reaches a maximum in about 50% ethanol and a minimum in about 10% ethanol in the solvent.

Experimental

Conductance water was prepared by the redistillation of water containing a little potassium permanganate through a block tin condenser and saving only the middle fraction. At 25° the specific conductance of this water was 1.0×10^{-6} ohm^{-1} cm.$^{-1}$.

Ethanol was purified by treating 95% ethanol by the method of Kiczales.[4] The purified ethanol was 99.9% absolute and at 25° the specific conductance was 2.0×10^{-7} ohm^{-1} cm.$^{-1}$.

J. T. Baker C.P. $BaCl_2 \cdot 2H_2O$ was twice recrystallized from conductance water and oven-dried to constant weight.

Ethanol–water solvents were prepared by the weight method and the exact composition determined by density measurement and interpolation with the density values from the "International Critical Tables."

Barium chloride solutions in ethanol–water mixtures were prepared from anhydrous barium chloride by the weight method and the concentrations were expressed as gram-moles per 1000 g. of solvent.

Weights were standardized against a Bureau of Standards certified set and all weighings were corrected to vacuum.

The bath temperature was constant to within 0.01° and was determined by a Beckmann thermometer that had been standardized against a thermometer certified by the Bureau of Standards.

Density determinations were made at each concentration with two pycnometers, one of 45.7941 ml. the other of 46.1905 ml., calibrated with water as a standard and considering the density of water at 25.00° as 0.9970739 g./ml. Each value given in the table was the average of two independent determinations that were interpolated to "round" solvent composition and solute concentration. Limited solubility in the strongly alcoholic solutions confined the determinations to solvents containing 60% or less ethanol.

The results are summarized in Table I. The ethanol percentages are weight percentages ethanol in the solvent.

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(1) R. L. Bateman, THIS JOURNAL, **71**, 2291 (1949).

(2) W. Geffcken, *Z. physik. Chem.*, **A155**, 12 (1931).

(3) A. S. Chacravarti and B. Prasad, *Trans. Faraday Soc.*, **35**, 1469 (1939).

(4) S. Kiczales, *Ind. Eng. Chem.*, **20**, 493 (1928).

Identification and Properties of the Colored Compound Formed in Parathion Estimations[1]

BY R. C. BLINN, F. A. GUNTHER AND M. J. KOLBEZEN

RECEIVED MARCH 29, 1952

With the widespread use of the insecticidal material O,O-diethyl O-*p*-nitrophenyl thiophosphate (parathion) has coincided the development and exploitation of a sensitive method for its quantitative estimation upon foodstuffs.[2] This method is based upon the quantitative reduction of the nitro to the amino group with subsequent diazotization and coupling with N-1-naphthylethylenediamine to produce an intense magenta color. It has been established[3] that various substituted nitrobenzenes or anilines also give magenta colors

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(1) Paper No. 732, University of California Citrus Experiment Station, Riverside, California. Presented at the 121st Meeting of the American Chemical Society, Milwaukee, Wisconsin, April, 1952.

(2) (a) P. R. Averell and M. V. Norris, *Anal. Chem.*, **20**, 753 (1948); (b) F. A. Gunther and R. C. Blinn, *Advances in Chemistry Series*, **1**, 72 (1950); (c) J. C. Gage, *Analyst*, **75**, 189 (1950).

(3) (a) F. I. Edwards, Jr., *Anal. Chem.*, **21**, 1415 (1949); (b) R. C. Blinn and F. A. Gunther, *ibid.*, **22**, 1219 (1950); (c) M. V. Norris and P. R. Averell, private communications.

that are visually very similar to that produced by parathion when subjected to this same colorimetric procedure. Because of these facts, it was considered of interest to study some of the physical characteristics of the parathion and nitrobenzene colored compounds and to elucidate their structures.

Colored compounds of parathion and of nitrobenzene were prepared in a manner as nearly identical with that used in the analytical method[2a] as was practicable. Only tarry products resulted from attempts to obtain the colored compound from technical-grade parathion, but N-[4-(O-*p*-phenylazo-O,O-diethyl thiophosphate)-1-naphthyl]-ethylenediamine (I) (for convenience, hereafter referred to as "parathion dye") was obtained from parathion that had been purified by molecular distillation.[4] N-(4-Benzeneazo-1-naphthyl)-ethylenediamine (II) (hereafter referred to as "nitrobenzene dye") was prepared from purified aniline. Both hydrochlorides occurred as very small platelets, deep purple in color, with a golden sheen. Compound II·HCl melted at 188° (dec.), and I·HCl melted at 170° (dec.).

The free base of each compound was liberated by treatment with sodium bicarbonate, II occurring as dark-red prisms, m.p. 107–108°,[5] and I as dark-orange micro-crystals, m.p. 103–105°. Aqueous solutions of both compounds exhibited indicator properties, changing from magenta to yellow as the *p*H was increased. The color transition range for II was *p*H 2.8–4.5, while that for I was *p*H 2.0–3.9.

Absorption characteristics were obtained for these compounds and for 4-benzeneazo-1-naphthylamine (III) and 2-benzeneazo-1-naphthylamine (IV)[6] as shown in Table I. The similarity of the structures of III and IV to those of I and II is evidenced in their similar absorption characteristics.

TABLE I

ABSORPTION CHARACTERISTICS

Compound	Maxima		Compound	Maxima	
	mμ	log ε		mμ	log ε
Nitrobenzene dye (II)	253	4.12	Parathion dye (I) hydrochloride	250	4.11
	282	4.16		272	4.06
	337	3.49		295	3.96
	350	3.50		360	3.83
	450	4.38		563	4.53
Nitrobenzene dye (II) hydrochloride	255	4.00	4-Benzeneazo-1-naphthylamine (III)	248	4.17
	265	4.00		280	4.16
	272	4.03		336	3.57
	300	3.88		352	3.59
	352	3.77		437	4.36
	560	4.64	4-Benzeneazo-1-naphthylamine (III) hydrochloride	250	4.03
Parathion dye (I)	250	4.13		266	4.01
	284	4.18		271	4.03
	333	3.62		302	3.97
	350	3.60		347	3.89
	470	4.37		540	4.66
			2-Benzeneazo-1-naphthylamine (IV)[6]	232	4.41
				309	4.39
				315.5	4.39
				377	3.36
				468	4.16

From the absorption characteristics of I and II as compared with those established for the 2- and 4-benzeneazo-1-naphthylamines, it is clear that the 4-position is the major coupling site. This contradicts the structure presumed by Gunther and Blinn.[2b] Turner[6] has shown that variously 2-coupled 1-naphthylamines exhibit absorption maxima in the region of 225 mμ and 320 mμ, while the corresponding 4-coupled 1-naphthylamines exhibit minima in these regions. I and II possess minima in these regions; they also have maxima and other minima corresponding closely with those of the 4-benzeneazo-1-naphthylamine.

Experimental

Measurements.—All measurements were made with a Beckman model DU quartz spectrophotometer. In the regions of maximum extinction, readings were obtained at 1-mμ intervals in the ultraviolet region and at 2-mμ intervals in the visible region.

Preparation of Parathion Dye (I).—To 3.35 g. (0.0129 mole) of purified parathion[4] in 480 ml. of 50% ethyl alcohol was added 3.0 g. of zinc dust (0.046 mole) and 48 ml. of 6 *N* hydrochloric acid and refluxed for 4 hours. This mixture cleared slowly, turning successively brown, violet, blue and finally clear and colorless. The final solution was cooled to 10° and 100 g. of potassium hydroxide in 700 ml. of water was added, with cooling, keeping the temperature below 15°. The resulting cloudy, purple mixture was extracted with three 150-ml. portions of ether and the combined purple ether extracts were washed twice with water, then with two 25-ml. portions of concentrated hydrochloric acid. The purple acid extract was cooled to 0°, and 1.85 g. of sodium nitrite in 20 ml. of water was added, with cooling, keeping the temperature below 5°. This mixture was stirred for 30 minutes; 3.65 g. of ammonium sulfamate in 20 ml. of water was then added, again keeping the temperature below 5° and this was followed by the addition of 3.0 g. (0.0116 mole) of N-1-naphthylethylenediamine dihydrochloride in 100 ml. of water. A purple solid quickly separated. After being allowed to stand overnight, the purple solid was filtered and washed successively with cold dilute hydrochloric acid and boiling 5% hydrochloric acid. The residue was then dissolved in a minimum quantity of hot water and cooled and 80 ml. of cold, concentrated hydrochloric acid was added. The solid which separated was filtered and air-dried, then redissolved in hot, dilute hydrochloric acid and allowed to cool slowly. The resulting tiny purple platelets were dried under reduced pressure to give 1.6 g. (23.5%), m.p. 170° (dec.).

Anal. Calcd. for $C_{22}H_{29}Cl_2N_4O_3PS$: C, 49.72; H, 5.50; Cl, 13.34. Found: C, 49.85; H, 5.78; Cl, 13.00.

The free base (I) was obtained by adding an excess of sodium bicarbonate to an aqueous solution of the hydrochloride and extracting into ether; the resulting oil was crystallized from cyclohexane to yield orange microcrystals, m.p. 103–105°.

Anal. Calcd. for $C_{22}H_{27}N_4O_3PS$: C, 57.63; H, 5.94. Found: C, 58.13; H, 6.02.

Preparation of Nitrobenzene Dye (II).—Exactly 1.07 g. (0.0115 mole) of aniline was dissolved in 50 ml. of concentrated hydrochloric acid and cooled to 5°. Then 1.85 g. of sodium nitrite in 20 ml. of water was added, while the temperature was maintained below 0°. After the resulting solution had been stirred for one-half hour, 3.6 g. of ammonium sulfamate in 20 ml. of water was added and stirred 10 minutes. Then 3 g. (0.0116 mole) of N-1-naphthylethylenediamine dihydrochloride in 100 ml. of water was added, and the resultant deep-purple solution was stirred for two hours. The dark-purple solid which resulted was separated. Two recrystallizations from 5% hydrochloric acid gave 2.5 g. (60%), m.p. 188° (dec.).

Anal. Calcd. for $C_{18}H_{20}Cl_2N_4$: C, 59.51; H, 5.55; Cl, 19.52. Found: C, 60.00; H, 5.53; Cl, 19.15.

The free base (II) was obtained by adding an excess of sodium bicarbonate to an aqueous solution of the hydrochloride, extracting into ether, and recrystallizing several times from petroleum ether (b.p. 60–70°) to give dark-red prisms, m.p. 107–108°.

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(4) Supplied by the American Cyanamid Company.

(5) A. L. Yaroslavtseo, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 2274 (1950); [*C. A.*, **45**, 7084 (1951), gave m.p. 102–103°].

(6) H. S. Turner, *J. Chem. Soc.*, 2282 (1949).

Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.45; H, 6.25. Found: C, 74.16; H, 6.21.

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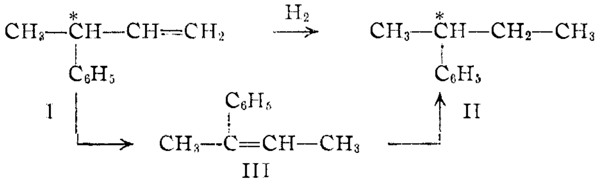
Racemization of an Optically Active Olefin during Catalytic Hydrogenation

BY DONALD J. CRAM

RECEIVED MAY 24, 1952

The syntheses and relative configurations of optically pure (−)-3-phenyl-1-butene (I) and (−)-2-phenylbutane (II) have been previously reported.[1] It has now been observed that when I is reduced catalytically to give II, from 1 to 11% loss of optical activity attends the reaction. Since compound II has been demonstrated not to racemize to any detectable extent under the conditions of the experiment, the racemization appears to take place either before or during the reduction. Possibly I isomerizes to III which is subsequently reduced, either with or without leaving the catalyst surface. The results are recorded in Table I.



The palladium-on-calcium carbonate catalyst gives more racemization than the other two catalysts, and the addition of conjugated olefin (2-phenyl-2-butene) to the mixture does not seem to effect the degree of racemization with this catalyst. The results are duplicatable within a few per cent.

TABLE I

DEGREE OF RACEMIZATION OF OPTICALLY ACTIVE 3-PHENYL-1-BUTENE WHEN REDUCED IN THE PRESENCE OF DIFFERENT CATALYSTS[a]

Catalyst	Starting material	Racem. of active material,[b] %
Pd-$CaCO_3$[c]	Opt. pure I	9.1
Pd-$CaCO_3$[c]	86% racemized I[d]	11.1
Pd-$CaCO_3$	15% opt. pure I + 85% III[e]	11.3
Raney Ni	Opt. pure I	2.5
Raney Ni	86% racemized I[d]	1.1
PtO_2[f]	86% racemized I[d]	3.5

[a] The solvent was in each case ethanol, 6 ml. per g. of olefin. The 2-phenylbutane isolated in each case had $n^{25}D$ 1.4878 (see ref. 1b). The hydrogen uptake was the theoretical ±2%. [b] Calculated on the basis that for optically pure 2-phenylbutane, $\alpha^{25}D$ 24.3° (neat, l 1 dm.). [c] 0.5% palladium-on-calcium carbonate, 1 g. per g. of olefin [I. M. Heilbron, E. R. H. Jones, J. T. McCombie and B. C. Weedon, *J. Chem. Soc.*, 84 (1945)]. [d] Prepared by diluting optically pure 3-phenyl-1-butene with pure racemic material (see ref. 1a). [e] Equal molar mixture of *cis*- and *trans*-2-phenyl-2-butene. [f] 0.1 g. of PtO_2 per g. of olefin.

Experimental Part

Reduction of Optically Pure 3-Phenyl-1-butene in Presence of Raney Nickel.—The procedure for the experiments reported in Table I is illustrated as follows. A mixture of 1.0 g. of optically pure (−)-3-phenyl-1-butene ($[\alpha]^{22}D$ −6.39°, ref. 1a), 1 ml. (roughly) of freshly prepared Raney nickel catalyst[2] and 6 ml. of absolute ethanol was agitated in an atmosphere of hydrogen with a magnetic stirrer at room temperature until no more hydrogen was absorbed (two hours). A total of 183 ml. (temperature 26°, pressure 752 mm.) was taken up, or 98% of theory. The reduction mixture was filtered, and the catalyst was washed with ethanol (3 ml.). The filtrate was shaken with five volumes of water and two of pure pentane. The pentane layer was washed three times with water, dried, and the solvent was evaporated through a short column. The product was twice flash distilled to give 0.83 g. of pure 2-phenylbutane, $n^{25}D$ 1.4878, $\alpha^{23}D$ −23.7 (neat, l 1 dm.), or 2.5% racemized.

When optically active 2-phenylbutane ($n^{25}D$ 1.4878, $\alpha^{23}D$ −22.4°, neat, l 1 dm.) was submitted to the above procedure utilizing 0.5% palladium-on-calcium carbonate catalyst, an 84% recovery of the 2-phenylbutane was experienced ($n^{25}D$ 1.4878, $\alpha^{23}D$ −22.4° (neat, l 1 dm.)).

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(1) D. J. Cram, (a) THIS JOURNAL, **74**, 2137 (1952); (b) *ibid.*, **74**, 2149 (1952).

(2) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

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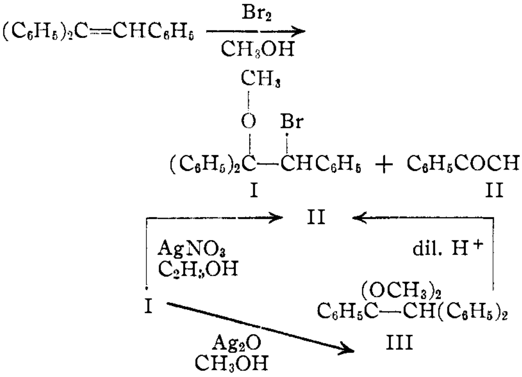
Rearrangement of 2-Bromo-1-methoxy-1,1,2-triphenylethane and 1-*p*-Anisyl-2-bromo-1-methoxy-1,2-diphenylethane[1]

BY DAVID Y. CURTIN[2] AND ESTELLE K. MEISLICH

RECEIVED JUNE 19, 1952

The synthesis of 2-bromo-1-methoxy-1,1,2-triphenylethane (I) was accomplished in 40% yield by the bromination of triphenylethylene in the presence of methanol. Its formation was accompanied by a rearrangement which gave benzhydryl phenyl ketone (II) in 45% yield. It was found that the yield of I was increased to 56% by the addition of sodium bicarbonate.

I reacted with silver nitrate in ethanol to give a 99% yield of II. With silver oxide suspended in ethanol the product was III, the diethyl ketal of II. III was characterized by its ready hydrolysis to II with 0.04% hydrochloric acid. The isomeric ether, triphenylethylene glycol dimethyl ether (IV) was synthesized and found to be stable under the same conditions.



It is possible that benzhydryl phenyl ketone diethyl ketal is an intermediate in the conversion of I to II with aqueous ethanolic silver nitrate but that it is hydrolyzed to II by the nitric acid formed during the reaction.

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(1) Part of the Ph.D. Thesis submitted by Estelle K. Meislich to Columbia University.

(2) Department of Chemistry, University of Illinois, Urbana, Illinois.