mined experimentally on a carefully purified sample of the nonane are reported. Empirical equations relating molecular structure to boiling point, density, and refractive index for the symmetrical series $(CH_3)_{4-n}C(C_2H_5)_n$ are presented.

PAULSBORO, N. J. RECEIVED JUNE 27, 1946

NOTES

Attempted Asymmetric Synthesis in a Metathetical Grignard Reaction

BY WILLIAM A. BONNER

In connection with another problem it became desirable to investigate the possibility of producing an asymmetric synthesis in a metathetical replacement reaction involving the Grignard reagent. The reaction selected was the formation of ethyl α-phenylethyl ether by the action of phenylmagnesium bromide on ethyl α-chloroethyl ether. The replacement was carried out in the presence of a variety of optically active agents including methyl tetramethyl-α-D-glucoside, tetraacetylglucosyl chloride, brucine, and *d*-bromocamphor. In each instance the ethyl α-phenylethyl ether obtained showed no optical activity beyond experimental error.

The well known investigations of McKenzie and others, wherein asymmetric syntheses have been achieved via the Grignard reagent, have been confined to the addition of the Grignard to carbonyl groups in molecules *already* possessing asymmetric centers. Very few Grignard reactions have been conducted to test the possibility of asymmetric synthesis in the presence of *external* asymmetric molecules. Betti and Lucchi[1] claimed in 1940 to have prepared optically active α-phenylethanols by the action of Grignard reagents on aldehydes in the presence of dimethylbornylamine. Tarbell and Paulson[2] showed later, however, that the activity of the Betti and Lucchi alcohols was due to an active impurity, and were further unable to prepare active alcohols under a variety of conditions, even using an optically active ether as solvent. The present attempted asymmetric synthesis apparently fails for the same possible reason, namely, because the asymmetric center supposedly imparting an asymmetric bias to the reaction is present only externally, and not as part of the reacting molecule. Several instances of successful asymmetric synthesis in the presence of external optically active agents have been reported, but none of these employs the Grignard reagent.

Experimental

Ethyl α-Phenylethyl Ether.—Ethyl α-chloroethyl ether was prepared according to the directions of Swallen and Boord.[3] The material boiling from 44–51° (170 mm.) was used in the reaction described below. The chloro ether hydrolyzes rapidly and fumes in moist air, but can be stored with no apparent decomposition in a glass-stoppered flask at 0°.

Phenylmagnesium bromide (50% excess) was prepared from magnesium (3.6 g.) and bromobenzene (23.2 g.) in dry ether (75 ml.). Ethyl α-chloroethyl ether (12 g.) was dissolved in dry ether (60 ml.) and the mixture placed in a three-necked flask equipped with a mercury-sealed Hershberg stirrer, a reflux condenser protected with a calcium chloride tube, and a dropping funnel similarly protected. The solution was cooled in ice and the Grignard reagent added dropwise with stirring over the course of thirty minutes. A grayish precipitate formed immediately, and the reaction proceeded with a hissing sound. The mixture was stirred under reflux for an additional hour, cooled and poured into ice water. The residue remaining in the reaction flask was dissolved with dilute sulfuric acid and the solution added to the ice water. The ether layer was separated, washed twice with water, with sodium bicarbonate solution until neutral, again

TABLE I

ATTEMPTED ASYMMETRIC SYNTHESES

Run	α-Chloro ether, moles	Optically active agent	Active agent, moles	α-Phenyl ether Yield, %	$[\alpha]^{23}D$
1	0.074	Methyl tetramethyl-α-D-glucoside	0.074	69	0.00°
2	.074	Brucine	.038	..[a]	− .08
3	.068	Tetraacetylglucosyl chloride	.034	88[b]	.00
4	.055	*d*-Bromocamphor	.055	80	2.85[c]
5	.074	Methyl tetramethyl-α-D-glucoside and activated alumina	.074	56	0.00

[a] The product obtained from Run 2 was not ethyl α-phenylethyl ether as indicated by b. p. (91–97° (17 mm.)) and refractive index ($n^{21}D$ 1.5308). The product rapidly decolorized bromine in carbon tetrachloride and slowly decolorized permanganate in acetone. *Anal.* C, 78.07, 78.20; H, 7.93, 7.85. Its identity is being established. [b] Tetraacetylglucosylbenzene was isolated by acetylation of the residue on evaporation of the water layer; yield, 43%. [c] The rotation here was due to contamination by camphor derivatives. When the crude product was redistilled into two fractions the first (b. p. 72–74° (17 mm.)) had $[\alpha]^{23}D$ 0.43°, and the second (b. p. 74–76° (17 mm.)) had $[\alpha]^{23}D$ 2.23°. The undistilled residue had a strong camphor-like odor.

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(1) Betti and Lucchi, *Boll. sci. facolta chim. ind., Bologna*, No. 1-2, 2 (1940); *C. A.*, **34**, 2354 (1940).

(2) Tarbell and Paulson, THIS JOURNAL, **64**, 2842 (1942).

(3) Swallen and Boord, *ibid.*, **52**, 654 (1930).

with water, and dried over anhydrous sodium sulfate. Removal of the solvent gave 20.1 g. of crude product. This was distilled through a three-inch Vigreux column and the fraction boiling from 74–92° (17 mm.) (mostly 75° (17 mm.)) collected. The yield was 11.6 g. (70%). The residue weighed 3.6 g. On redistillation the b. p. was 76–79° (17 mm.). The boiling point and density (d^{27}_{25} 0.939) agree with literature values[4] obtained for the product prepared by different methods. Refractive index n^{21}D 1.4929.

Attempted Asymmetric Syntheses.—Attempts were made to impart an asymmetric bias to the above reaction by conducting it, in the same manner, in the presence of various optically active agents. The quantities of reagents and results are given in Table I. The amount of phenylmagnesium bromide used in each case was sufficient to react completely with the optically active agent and the ethyl α-chloroethyl ether, plus a 100% excess of the quantity required for the latter reaction. All rotations were taken in 95% ethanol.

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[4] Beilstein, "Handbuch der organische Chemie," 4th ed., Vol. VI, p. 475, (236).

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7-Chloro-4-(1-diethylamino-4-pentylamino)-quinazoline

BY M. K. MCKEE, R. L. MCKEE[1] AND R. W. BOST

Our attention has been called to the preparation of 7-chloro-4-(1-diethylamino-4-pentylamino)-quinazoline by Price and co-workers.[2] We wish to record an alternative route for the preparation of this compound which had been worked out in our Laboratory when this article[2] appeared.

7-Chloro-4-hydroxyquinazoline.—A mixture of 19.5 g. of 4-chloro-anthranilamide,[3] 75 cc. of ethyl orthoformate, and 45 cc. of diethylene glycol was heated to 105–110° for three hours and to 120° for twenty-four hours. The resulting gel was warmed with dilute hydrochloric acid, made alkaline (sodium hydroxide), treated with Norite and filtered. The filtrate was acidified (acetic acid) and finally made faintly alkaline with ammonium hydroxide. The product was recrystallized from alcohol, giving 18.9 g. (87% yield) of white material melting at 250–253°. A small sample was sublimed at atmospheric pressure, giving a product melting at 251.5–253° for analysis.

Anal. Calcd. for $C_8H_5ClN_2O$: N, 15.51. Found: N, 15.52.

7-Chloro-4-(1-diethylamino-4-pentylamino)-quinazoline.—Five grams (0.028 mole) of the above quinazolone was refluxed with 6.3 g. (0.030 mole) of phosphorus pentachloride in 25 cc. of freshly distilled phosphorus oxychloride for twenty-four hours. After removal of excess solvent by distillation (water pump), 11 g. (0.07 mole) of 1-diethylamino-4-aminopentane was added and refluxed for two hours. Aqueous alkali was added, and the product was extracted with ether, dried over sodium hydroxide and distilled. The material boiling from 210–215° at 4.5 mm. was recrystallized from benzene–petroleum ether to yield 7.1 g. (80% yield based on the quinazolone) of white crystals melting at 117–118°.

Anal. Calcd. for $C_{17}H_{25}ClN_4$: N, 17.46. Found: N, 17.23.

Acnkowledgment.—The authors wish to take this opportunity to express their appreciation to The Wm. S. Merrell Co., whose generous support made this work possible.

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[1] The Wm. S. Merrell Co., Postdoctoral Fellow.

[2] Price, Leonard and Curtin, THIS JOURNAL, **68**, 1305 (1946).

[3] Hunn, *ibid.*, **45**, 1024 (1923).

Electron Deficient Molecules. III. The Entropy of Diborane

BY KENNETH S. PITZER

In order to see whether measurement of the entropy of diborane would contribute further definite evidence concerning its structure, the writer calculated the translational-rotational entropy for both ethanelike and protonated double bond[1] models using distances and angles given by Bauer.[2] Much to his surprise the difference in moments of inertia almost compensated the difference in symmetry number so that the total entropies differ hardly more than the expected experimental error.

This makes it unlikely that an entropy measurement would contribute significantly to the structural problem. For the same reason, the calculated entropy is reasonably certain even if one may doubt which structure is correct. Since this entropy value may be of interest in thermodynamic calculations, it seems worthwhile to present it at this time.

Table I itemizes the calculations for the two separate models. It should be noted that the experimental heat capacity data of Stitt[3] were used to compute the vibrational contribution. Thus no assumption was needed with respect to the actual vibrational assignment. Likewise, if there is an electronic contribution, it is included within that labelled vibrational. The estimates of error are based, respectively, on the uncertainties in bond distances and in the experimental heat capacities together with their extrapolation to a point where the vibrational contribution is negligible.

TABLE I

ENTROPY OF DIBORANE AT 298.16°K

Model	Ethane-like	Protonated double bond
Moments of inertia	1.44	1.08
× 10^{39} g. sq. cm.	5.67	4.73
	5.67	5.05
Symmetry no.	6	4
$S_{trans. + rot.}$	53.09 ± 0.1	53.31 ± 0.1
$S_{vibr.}$	2.15 ± .1	2.15 ± .1
S_{total} (cal. per degree mole)	55.24 ± .2	55.46 ± .2

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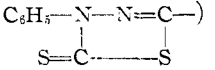
[1] K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945) (paper I of this series).

[2] S. H. Bauer, *Chem. Rev.*, **31**, 43 (1942); private communication reported by Longuet-Higgins and Bell, *J. Chem. Soc.* (London), 250 (1943).

[3] F. Stitt, *J. Chem. Phys.*, **8**, 981 (1940).

Metal Salts of 2-Mercapto-4-phenyl-Δ^2-1,3,4-thiadiazoline-5-thione

BY GEORGE W. WATT AND MARY E. BOYD

Metal salts of 2-mercapto-4-phenyl-Δ^2-thiadiazoline-5-thione (represented as RSH, where R is ) have been prepared by Ray[1a] and by Ray and Guha.[1b] More recently the possible use of these salts in qualitative and quantitative analysis has been suggested.[2] The present note is concerned with the preparation of unreported salts of RSH and with the formation of coördination compounds of these salts upon treatment with ammonia, pyridine and ethylenediamine (en).

Experimental

The salt RSK was prepared according to the method of Busch.[3] Repeated crystallization from absolute ethanol gave an 85% yield of the white crystalline salt, m. p. 245°; reported by Busch, 240°.

Anal. Calcd. for $C_8H_5N_2S_3K$: N, 10.6. Found: N, 10.4.

The heavy metal salts of RSH were formed at room temperature by addition of an aqueous solution of slightly more than one equivalent of the specified inorganic salt to an agitated aqueous solution of 1/40 mole of RSK. The precipitated salts were separated by filtration, purified by repeated extraction with water, ethanol and acetone, and dried *in vacuo* over concentrated sulfuric acid. When the dry salts were heated, slow decomposition occurred and none exhibited a sharp melting temperature. However, with nickel chloride the normal salt was precipitated only after four hours of heating and the use of nickel nitrate or sulfate resulted largely in the formation of the disulfide, RSSR, m. p. 124°.

The reaction between RSK and mercury (II) cyanide in absolute ethanol led to the formation of a double salt of the type $(RSK)_2Hg(CN)_2$ which was converted to the yellow normal mercury (II) salt upon treatment with water. When the same reactants were brought together in aqueous solution they reacted to form a white solid (presumably the double salt) which decomposed yielding the normal yellow salt slowly at room temperature and more rapidly at elevated temperatures. When mercury (II) bromide was used, the normal yellow salt was obtained immediately.

The salts were insoluble in water and in the common organic solvents, soluble or sparingly soluble in liquid ammonia, and soluble (usually with decomposition) in pyridine or ethylenediamine. Coördination compounds with ammonia were formed by allowing the excess solvent to evaporate from solutions of the salts in liquid ammonia. Coördination compounds with ethylenediamine were precipitated by diluting solutions of the heavy metal salts in that solvent with water. In the di-solvate $(RS)_2Hg(en)_2$ the central mercury atom is presumably 6-covalent. Coördination compounds of reproducible composition were obtained only after extended desiccation *in vacuo* over concentrated sulfuric acid at room temperature. Stable solvates with pyridine were not obtained in any case.

TABLE I

METAL SALTS OF 2-MERCAPTO-4-PHENYL-Δ^2-1,3,4-THIADIAZOLINE-5-THIONE AND THEIR COÖRDINATION COMPOUNDS

($R = C_8H_5N_2S_2$)

				Percentage composition				Coörd.			
				Nitrogen		Metal		cpd.		Nitrogen, %	
Product	Inorg. salt	Yield	Color	Calcd.	Found	Calcd.	Found	with	Color	Calcd.	Found
$(RS)_2Hg$[a,b]	$HgBr_2$	Quant.	Yellow	8.6	8.8	30.8	31.0	0.5 NH_3	Yellow	9.6	9.7
$(RS)_2Hg$[c]	$Hg(CN)_2$	....	Yellow	8.6	8.6	30.8	30.4	......	.....	..	..
$(RS)_2Cu$[d]	$CuSO_4$	Quant.	Orange[e]	10.7	10.7	12.4	12.7	NH_3	Dk. br.	12.9	13.0
$(RS)_2Ni$	$NiCl_2$	[f]	Brown	11.0	11.0	11.5	11.4	NH_3[g]	Dk. br.	13.3	13.1
RS Ag[h]	$AgNO_3$	Quant.	Yellow	8.4	8.6	32.4	32.5	0.5 en[i]	Cream	..	..

[a] M. p., 110° (dec.). [b] Coörd. cpd. with 2 en: formed after forty-eight hours of desiccation over concd. sulfuric acid; color, white. *Anal.* Nitrogen %, calcd. 14.6; found 14.5. Coörd. cpd. with 1 en; formed after one hundred and forty hours desiccation: color, white; *anal.* nitrogen %, calcd. 11.8; found, 11.8. [c] After decompn. of the white double salt which formed first. [d] Small amounts of disulfide, RSSR, formed as by-product. [e] After heating at 90° for one hour; original ppt. was tan. [f] Precipitated only after four hours of heating. Original dark brown ppt. lightened in color as heating continued. [g] An olive-green ppt. (probably a higher ammonate) formed first but was not isolated. [h] Dec. on exposure to light, air or hot ethanol; m. p. 150° (dec.). [i] Some evidence for the formation of a compound corresponding to this formula was obtained but analytical data on separate preparations were not conclusive.

Data relative to the metal salts and their coördination compounds are given in Table I.

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[1] (a) Ray, *J. Chem. Soc.*, **115**, 875 (1919); (b) Ray and Guha, *ibid.*, **115**, 261 (1919).

[2] (a) Majumdar, *J. Indian Chem. Soc.*, **19**, 396 (1942); (b) Kuras, *Chem. Obzor.*, **16**, 17, 124 (1941).

[3] Busch, *Ber.*, **27**, 2510 (1894).