the one which appears in the product as $CHCl_3$. This transfer of the hydrogen from the carbonyl carbon atom to the halogen-bearing carbon apparently does *not* occur by an exchange mechanism involving the solvent.

The results obtained in the chloral and bromal experiments suggested that the isotopic purity of the product might be improved if the hydrogen atom were replaced by another group. The preparation of 99.2% $CDCl_3$ was thus accomplished using trichloroacetophenone. This represents the highest reported isotopic purity for any previous preparation of chloroform-*d*.

Acknowledgments.—The authors are greatly indebted to Professor Eugene Lieber for valuable discussions. Thanks are due to Dr. Sidney Katz for assistance with the infrared spectrophotometer. The D_2O was obtained through the courtesy of Professor Martin Kilpatrick and the Atomic Energy Commission.

Summary

1. Isotopically pure $CDCl_3$ is not obtained by the reaction of chloral with sodium deuteroxide.

2. The observed $CHCl_3$ dilution of the product does *not* occur through the previously advanced mechanism of protium exchange with the solvent.

3. A new synthesis of chloroform-*d* by the reaction of trichloroacetophenone with sodium deuteroxide has produced $CDCl_3$ of 99.2% isotopic purity.

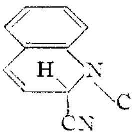
CHICAGO 16, ILLINOIS RECEIVED MAY 12, 1950

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF STANFORD UNIVERSITY AND THE UNIVERSITY OF ARIZONA]

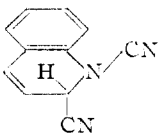
The Structure of the Isomeric Quinoline Dicyanides

BY M. G. SEELEY, R. E. YATES AND C. R. NOLLER

Quinoline reacts with bromocyanogen and hydrogen cyanide to form a dicyanide which is isomerized easily by ammonia.[1] The conclusion was drawn[2] that the isomers must differ stereochemically, and they were assigned the structures of *cis*- and *trans*-1,2-dihydro-1,2-dicyanoquinoline (I and II).



I



II

Each of the isomers necessarily would be a racemic mixture, since structures I and II would each have a non-superimposable enantiomorph. If this interpretation of the structure of the isomers is correct, they would constitute the first case in the literature of configurationally stable trivalent nitrogen which is not linked by a double bond as in the oximes, hydrazones and azo compounds, since their preparation precedes the resolution of Troeger's base.[3]

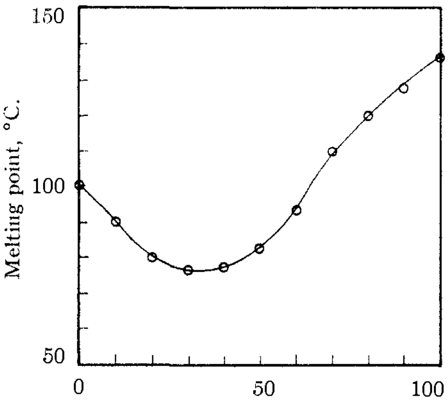


Fig. 1.—Melting point curve for mixtures of isomeric quinoline dicyanides.

Although the chemical evidence is convincing regarding the location of the cyanogen groups, it seemed desirable to examine the two isomers by physical methods to determine whether the results were compatible with the stereochemical explanation. The melting point curve for mixtures of the isomeric quinoline dicyanides (Fig. 1) showed definitely that they are not merely two crystalline forms of the same substance. Next the apparent molecular refractions of the two compounds were determined in bromobenzene solution. The observed values were 45.4 cc. for the low-melting isomer, and 42.9 cc. for the high-melting isomer. The difference of 2.5 cc. is considerably greater than that reported for *cis–trans* ring isomers, for two diastereoisomeric racemic forms, or for *syn* and *anti* oximes. For example, the difference for the *cis* and *trans* decalins is 0.40 cc.,[4] and for ethyl hexahydrophthalate it is 0.46 cc.[5]; for the two racemic forms of ethyl *sym*-dimethylsuccinate it is 0.12 cc.[5]; and for the two mesityl oxide oximes it is 0.64 cc.[6] Where a choice of several examples was possible, that pair having the highest difference in molecular refraction was selected.

More significant is the difference in the absorption of the two isomers in the ultraviolet. The low-melting isomer has three distinct bands with maxima at 229, 273 and 308 mμ and log $\epsilon_{\max.}$ 4.48, 3.67 and 3.32, respectively (Fig. 2). The high-melting isomer has only two maxima at 224 and 284 mμ with log $\epsilon_{\max.}$ 4.18 and 3.46, respectively (Fig. 3). It seems unlikely that the spectra of two structurally identical racemic forms would differ to this extent.

Assuming that the above results point to a structural difference in the two isomers, the ques-

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[1] Mumm and Herrendörfer, *Ber.*, **47**, 758 (1914).

[2] Mumm and Ludwig, *Ann.*, **514**, 34 (1934).

[3] Prelog and Wieland, *Helv. Chim. Acta*, **27**, 1127 (1944).

[4] Hückel, *Ann.*, **441**, 44 (1925).

[5] Auwers and Ottens, *Ber.*, **57**, 442 (1924).

[6] Auwers and Ottens, *ibid.*, **57**, 458 (1924).

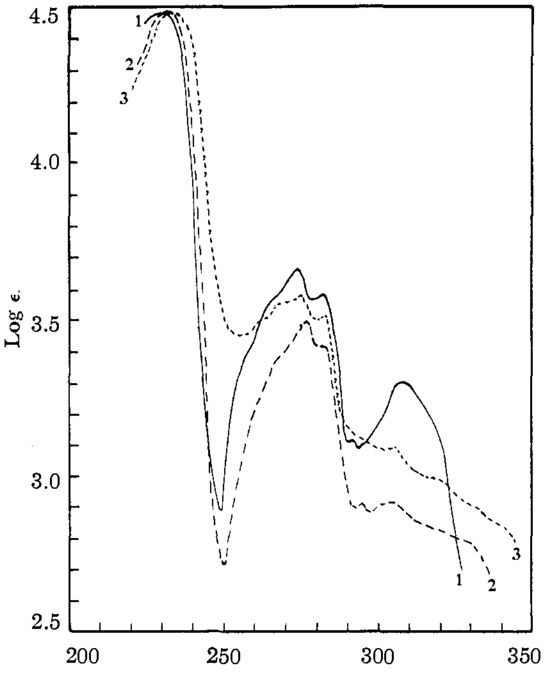
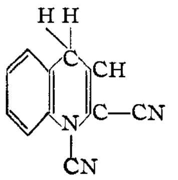
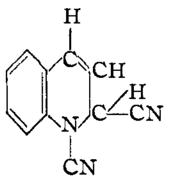


Fig. 2.—Absorption spectra of (1) low-melting quinoline dicyanide, (2) phenylcyanamide, (3) N-methylphenylcyanamide.

tion of the nature of this difference remains. A possibility apparently not considered by Mumm and his co-workers is that one isomer is a 1,4-dihydroquinoline derivative (III) whereas the other is a 1,2-dihydro derivative (IV).



III



IV

As models for structure III, phenylcyanamide and N-methyl phenylcyanamide were prepared and their ultraviolet absorption spectra determined. These spectra bear a striking resemblance to that of the low-melting quinoline dicyanide (Fig. 2). As a model for structure IV, N-methyl-*o*-styrylcyanamide was prepared. Here the absorption spectrum is very similar to that of the high-melting quinoline dicyanide (Fig. 3). Accordingly, it appears that the low-melting isomer is 1,2-dicyano-1,4-dihydroquinoline and that the high-melting isomer is 1,2-dicyano-1,2-dihydroquinoline.

In addition to being isomerized readily by ammonia, the low-melting isomer is converted completely to the high-melting isomer on standing for one week in ethyl alcohol as indicated by the change in the absorption spectrum. No change in the melting point of the low-melting isomer was observed after standing in the solid state for over a year.

All attempts to prepare a dicyanide from benzalaniline were unsuccessful and quinoline does not react with cyanogen. One of the authors (M.G.S.) hopes to be able to investigate further the mechanism of the formation of the quinoline dicyanides.

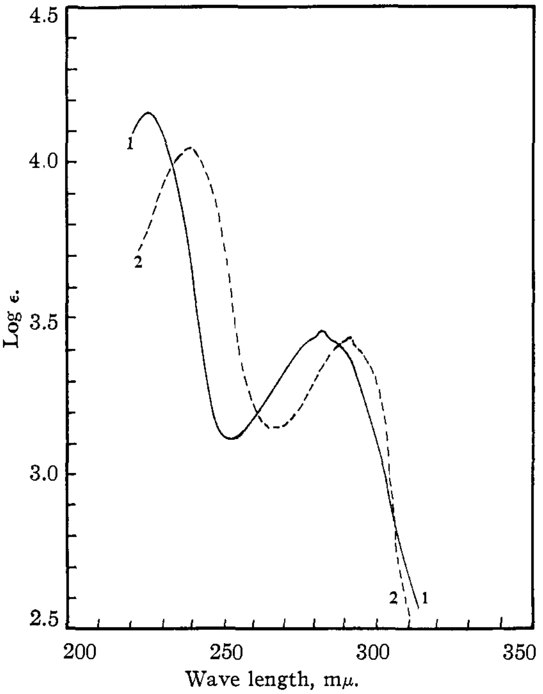


Fig. 3.—Absorption spectrum of (1) high-melting quinoline dicyanide, (2) N-methyl-*o*-styrylcyanamide.

The portion of this work done at the University of Arizona was made possible by a grant from the Research Corporation, New York City.

Experimental

Preparation of Compounds.—The quinoline dicyanides were prepared by the procedure of Mumm and Herrendörfer[1] and melted at 99.5–100.5° and 134–136°. **Phenylcyanamide** was prepared according to Baum[7] and melted at 46–47°. **N-Methylcyanamide** was prepared by the method of von Braun.[8] It melted at 25–28° and boiled at 132–134° (10 mm.).

β-(*o*-Dimethylaminophenyl)-ethyl alcohol was prepared by adding a solution of 12.6 g. (0.1 mole) of methyl sulfate in 25 cc. of anhydrous benzene to a solution of 13.7 g. (0.1 mole) of β-(*o*-aminophenyl)-ethyl alcohol[9] in 75 cc. of benzene. An oil separated immediately. The mixture was allowed to stand for 24 hours and then refluxed for 4 hours. A solution of 11.2 g. of potassium hydroxide in water was added to destroy unreacted methyl sulfate and to neutralize the sulfuric acid formed. The benzene layer was separated from the aqueous solution which was extracted three times with 25-cc. portions of benzene. The combined benzene solution was dried over magnesium sulfate, the benzene removed and the residue distilled at reduced pressure. The highest boiling fraction distilled at 122–124° (6 mm.). The yield of colorless liquid was 4.0 g. (24%).

The alcohol was dehydrated by distilling 2.8 g. (0.017 mole) from 2.4 g. of powdered anhydrous potassium hydroxide at 50 mm.[9] Redistillation gave 1.5 g. (60%) of **o-dimethylaminostyrene**, b.p. 78–80° (3 mm.).

Anal. Calcd. for $C_{10}H_{13}N$: N, 9.52. Found: N, 9.49.

N-Methyl-*o*-styrylcyanamide was prepared by adding a solution of 1.1 g. (0.1 mole) of cyanogen bromide in 5 cc. of anhydrous ether to 2.7 g. (0.018 mole) of *o*-dimethylaminostyrene. After a short time a white solid separated. The mixture was refluxed for 15 minutes. The precipitate was

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[7] Baum, *Ber.*, **41**, 524 (1908).

[8] von Braun, *ibid.*, **33**, 1438 (1900).

[9] Sabetay, Bleger and de Lestrange, *Bull. soc. chim.*, [4] **49**, 3 (1931).

removed by filtration and the ether evaporated. Two fractions were obtained from the residue, one boiling at 60–61° (4 mm.) and the other at 122–123° (4 mm.). The second fraction solidified on standing to colorless crystals which melted at 52–53° and proved to be N-methyl-*o*-styrylcyanamide. The yield was 0.75 g. (24%).

Anal. Calcd. for $C_{10}H_{10}N_2$: N, 17.72; mol. wt., 158. Found: N, 17.65; mol. wt., 156.

Mixed Melting Point Determinations.—The various mixtures of the quinoline dicyanides were prepared by dissolving weighed amounts of the two isomers in purified ether, allowing the ether to evaporate at room temperature and heating the residue at 60° for 3 minutes. The melting points were determined in capillary tubes heated in a Hershberg melting point apparatus.[10]

Molecular Refraction Determinations.—Densities were determined at 20° using a 10-cc. calibrated pycnometer. The refractive indices were measured at 20° with an Abbe refractometer. For the purified bromobenzene used as a solvent, d^{20}_4 1.492 and n^{20}_D 1.560 from which MR_D 34.03 cc. A solution of 0.3521 g. of the low-melting isomer in 10.46 g. of bromobenzene gave d^{20}_4 1.486 and n^{20}_D 1.561 from which $MR_{D\ \mathrm{app.}}$ 45.4 cc. for the compound. A solution of 0.3540 g. of the high-melting isomer in 16.85 g. of bromobenzene gave d^{20}_4 1.490 and n^{20}_D 1.560 from which $MR_{D\ \mathrm{app.}}$ 42.9 cc.

Absorption Spectra.—The ultraviolet absorption spectra were determined with a Beckman model DU spectrophotometer. The solvent was 95% ethyl alcohol and the concentrations were between 10^{-4} and 10^{-5} molar. The slit width was adjusted to the minimum value for each wave length in order to obtain the maximum amount of fine structure.

Summary

Molecular refractions and ultraviolet absorption spectra indicate that the isomeric quinoline dicyanides are structural isomers rather than stereochemical isomers. A comparison of the spectra of the two dicyanides with those of phenylcyanamide, N-methylphenylcyanamide, and N-methyl-*o*-styrylcyanamide indicates that the low-melting isomer is 1,2-dicyano-1,4-dihydroquinoline and that the high-melting isomer is 1,2-dicyano-1,2-dihydroquinoline.

STANFORD, CALIF.
TUCSON, ARIZONA

RECEIVED JULY 10, 1950

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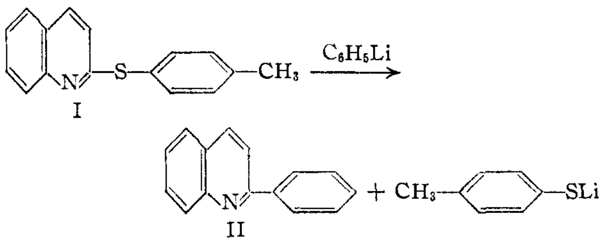
[10] Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Some Organometallic Compounds with 2-Substituted Quinolines[1a]

BY HENRY GILMAN AND JOHN A. BEEL

As a result of some investigations into the reactions of organometallic compounds with benzothiazole,[1b] it was considered of interest to determine the effect of phenyllithium on *p*-tolyl 2-quinolyl sulfide (I), a compound which, like benzothiazole, contains the $-N{=}\overset{|}{C}-S-$ grouping. The preliminary reaction gave a 57% yield of *p*-thiocresol and a 47% yield of 2-phenylquinoline (II).

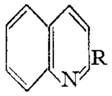


Regardless of the reaction mechanism, the over-all reaction resulted in a cleavage of the sulfide between the 2-carbon of quinoline and the sulfur atom. This suggested similar cleavage reactions with other 2-substituted quinolines and with other organometallic compounds.

In Table I are given the data on the reactions of phenyllithium with other 2-substituted quinolines. With the exceptions of 2-(N-piperidyl)-quinoline and 2-benzylquinoline, reactions similar to (1) were obtained with the production of varying amounts of 2-phenylquinoline. The yield varied from 10.6% in the case of 2-allyloxyquinoline to 70.2% in the case of 2-phenoxyquinoline. Of the organometallic compounds used, phenyllithium gave the best yields of cleavage products because it was quite reactive, but did not give extensive side reactions. 2-Chloroquinoline gave a good yield (65%) of 2-phenylquinoline, and it is interesting to note that under the same conditions 2-chlorobenzothiazole, containing a more reactive halogen atom, gave a 47.8% yield of 2-phenylbenzothiazole. Although no 2-

TABLE I

REACTIONS OF PHENYLLITHIUM WITH 2-SUBSTITUTED QUINOLINES



No.	R	Yield of 2-phenylquinoline,[a] %	Yield of cleavage product, %	Reaction time, hr.	T, °C.	Recovery of starting material, %
1	$CH_3C_6H_4S-$	47.4	*p*-Thiocresol[b] (57)	5	28	...
2	C_6H_5O-[c]	70.2	Phenol[d] (72.3)	18	28	...
3	C_2H_5O-[e]	41.5	(Ethanol)[f]	18	28	54.8[g]
4	Cl–	65.7	....	30	28	8.0[h]
5	$C_5H_{10}N-$	..	Piperidine (trace)	18	28	10.0[i]
6	$C_6H_5CH_2O-$[j]	12.2	Benzyl alcohol (24.8)[k]	6	0	17.0[l]
7	C_3H_5O-	10.6	(Allyl alcohol)[f]	18	28	15.6[m]
8	$C_6H_5CH_2-$	..	....	18	28	82.6[n]

[a] Identified by m.p. (81–83°) and mixed m.p. determination with an authentic specimen. The picrate (m.p. 191°) was also identified by a mixed m.p. determination. [b] Identified by m.p. (43–45°) and mixed m.p. determination. [c] Friedländer and Ostermaier, *Ber.*, **15**, 332 (1882). [d] Identified by m.p. (41–42°) and mixed m.p. determination. [e] Bogert and May, THIS JOURNAL, **31**, 507 (1909). [f] Not isolated. [g] B.p. 74° at 0.4 mm.; n^{20}_D 1.5892. [h] B.p. 115° at 0.03 mm. [i] Identified by m.p. (50°) and mixed m.p. determination. [j] Prepared from 2-chloroquinoline and sodium benzyloxide. [k] B.p. 60° at 0.03 mm.; n^{20}_D 1.5424. Identified by m.p. of the 3,5-dinitrobenzoate and mixed m.p. determination with an authentic specimen. [l] Identified by m.p. and mixed m.p. determination. [m] B.p. 145° at 0.1 mm.; n^{20}_D 1.5948. [n] B.p. 170–176° at 0.1 mm.; n^{20}_D 1.6339–1.6370. Identified by m.p. of picrate (152–154°) and mixed m.p. determination.

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[1] (a) Paper LXVII in the series: The Relative Reactivities of Organometallic Compounds; the preceding paper with Webb is in THIS JOURNAL, **71**, 4062 (1949); (b) Gilman and Beel, *ibid.*, **71**, 2328 (1949).