starting material there was obtained 0.5 g. of the acid; colorless plates melting at 197°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.37. Found: C, 75.9; H, 7.31.

p-Cyclopentylbenzamide was prepared by the method of reference 1, p. 157. It was recrystallized from dilute alcohol and formed glistening flakes, m. p. 189–190°.

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.2; H, 7.94; N, 7.41. Found: C, 76.1; H, 8.12; N, 7.30.

The melting points given are uncorrected.

2211 BURLING STREET
CHICAGO 14, ILLINOIS RICHARD D. KLEENE

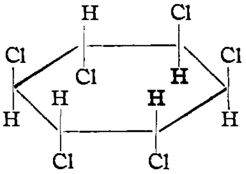
RECEIVED JANUARY 4, 1949

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF α-BENZENE HEXACHLORIDE

Sir:

The structures of the isomers of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) are of considerable interest due to the insecticidal activity of one of them.[1] Of the five known isomers, one, the β-isomer, is of established configuration,[2] being the isomer with all vicinal chlorine (or hydrogen) atoms *trans* to each other. The α-isomer has been assigned the structure



by Burrage and Slade[1] on the basis of a statistical treatment of chlorine addition, whereas Melander[3] has assigned the above structure to the γ-isomer on the basis of dipole moment data.

We wish to report preliminary data at this time regarding the structure of the α-isomer.

The above structure has no element of symmetry and should therefore exist as a racemate capable of resolution.[4] Lucas and Gould[5] have shown that *dl*-dibromoalkanes may be partially resolved by preferred reaction of one modification with optically active bases. With this rate method we have obtained optically active α-benzene hexachloride by the reaction

$$dl\text{-}C_6H_6Cl_6 + 3/2\text{brucine} \longrightarrow 1/2\text{active-}C_6H_6Cl_6 + 3/2\text{brucine}\cdot HCl + 1/2C_6H_3Cl_3$$

The α, γ and δ isomers were treated separately in dioxane with one-half of the amount of brucine required for complete dehydrochlorination. Five grams (0.018 mole) of each isomer, 12.4 g. (0.027 mole) of brucine, and 50 ml. of dioxane were allowed to stand at room temperature for several days. The alkaloid and alkaloid hydrochloride were removed by washing with water and dilute acid, and the residual (ether extraction) oily solids tested for optical activity. (Specific rotations (ethereal solutions): α, −14.6°; γ, −0.1°; δ, −1.3°.)

The optical activity of the α-product was concentrated by distillation, steam distillation, chromatography on alumina, and fractional distillation to give material of m. p. 128–132° (specific rotation over 120° (in acetone)). [*Anal.* calcd. for $C_6H_6Cl_6$: C, 24.78; H, 2.08; Cl, 73.14. Found (Clark Microanalytical Laboratories): C, 24.94; H, 2.32; Cl, 73.04. Hydrolyzable chlorine, calcd., 36.6; found, 36.2.] The activity is unaffected by recrystallization from concd. nitric acid, and is lost in a few minutes upon treatment with 2.5% methanolic sodium hydroxide.[6]

We are presently attempting the isolation of the levorotatory α-isomer with other optically active bases for a study of the phase diagram, as our present preliminary data suggest that the inactive material is a racemic compound.

We wish to acknowledge the assistance of the Office of Naval Research, for partial support of this work, as well as of the Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, where initial phases of this research were done.

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[1] Slade, *Chemistry and Industry*, 314 (1945).

[2] Hendricks and Bilicke, THIS JOURNAL, **48**, 3007 (1926); Dickinson and Bilicke, *ibid.*, **50**, 764 (1928).

[3] Melander, *Svensk Kem. Tid.*, **58**, 231 (1946).

[4] The only structure for a hexachlorocyclohexane capable of resolution. See Shriner, Adams and Marvel in Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, 2nd ed., pp. 324, 337.

[5] Lucas and Gould, THIS JOURNAL, **64**, 601 (1942).

(6) *Cf.* Cristol, *ibid.*, **69**, 338 (1947).

DEPARTMENT OF CHEMISTRY STANLEY J. CRISTOL
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RECEIVED MARCH 11, 1949

THE EXCHANGE REACTION BETWEEN THE TWO OXIDATION STATES OF CERIUM IN NITRIC ACID SOLUTIONS[1]

Sir:

We have studied the exchange reaction between cerous and ceric ions in nitric acid solutions

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[1] This work was carried out under the auspices of the Atomic Energy Commission.

and have found the rate to be measurable. In view of current interest in electron transfer reactions, it is felt that a preliminary report may be of interest at this time.

Oak Ridge cerium 144 (275 day half-life) was purified by the procedure described by Newton.[2]

Several experiments were performed in which a diffusion separation[3] was employed. The ceric and cerous concentrations were each 0.005 *f*, the solvent was variously 1 *f* sulfuric acid, 2 *f* perchloric acid, or 6 *f* perchloric acid. The results indicated complete exchange within two hours,[4] but the poor separation factor and the possibility of reduction of ceric ion in the diffusate indicated that another approach would be desirable.

The second method employed was to extract ceric cerium from nitric acid solution with diethyl ether. Stock solutions of active cerous and inactive ceric nitrates were mixed in a thermostated bath, and the ceric nitrate was extracted into analytical reagent ether. The ethereal phase was washed with nitric acid, and the cerium reextracted into water. The resultant solution was diluted to constant volume and counted with a dipping Geiger–Müller tube. In all cases the 17-minute praseodymium daughter was allowed to grow into the sample before counting. It was found that no significant amount of cerous ion is extracted and that the extraction of ceric nitrate is essentially complete.

The results obtained with solutions 6.18 *f* in nitric acid are given in Table I. Ceric concentration was determined by titration with ferrous ion; cerous by a second titration after oxidation with ammonium peroxysulfate and silver catalyst.

The expected exponential time dependence[5] of the extent of exchange was observed in each run.

TABLE I

Run	Cerous conc., *f*	Ceric conc., *f*	Temp., °C.	Half time of reaction. minutes	k, mol.$^{-1}$ min.$^{-1}$
1	0.00198	0.00187	25.03 ± 0.02	11.2 ± 0.3	16
2	.00198	.00187	0.0 ± 0.2	88 ± 4	2.0
3	.00198	.0187	.0 ± 0.2	20.0 ± 0.5	1.7
4	.0198	.00187	.0 ± 0.2	16.7 ± 0.5	1.9

From these data we calculate the experimental energy of activation to be 13.4 ± 0.7 kcal. and conclude that the reaction is first order with respect to both cerous and ceric concentrations. The last column gives the calculated bimolecular rate constant.

Experiments are in progress to determine the effect of concentration of reactants, ionic strength, and nitrate and hydrogen ion concentration. Additional experiments are planned with sulfuric and perchloric acid systems.

We are indebted to Dr. Jerome J. Howland, Jr., for information about the ether extraction of cerium.

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RECEIVED APRIL 11, 1949

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[2] A. S. Newton, *Phys. Rev.*, **75**, 17 (1949).

[3] C. L. Van Alten and C. N. Rice, THIS JOURNAL, **70**, 883 (1948).

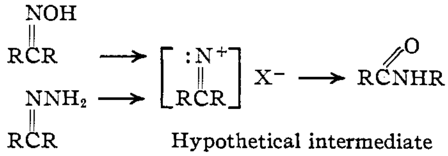
[4] Through the kindness of Professor A. C. Wahl, we have learned that similar conclusions have been reached in his laboratory.

[5] (a) H. A. C. McKay, *Nature*, **142**, 997 (1938); (b) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

THE REARRANGEMENT OF HYDRAZONES

Sir:

Structural and chemical analogy suggests that ketone hydrazones should undergo a rearrangement similar to the Beckmann rearrangement of ketoximes. Consideration of the mechanism of the Beckmann rearrangement[1] suggests a common intermediate or reaction path



Sidgwick,[2] however, states that there is no general reaction of the hydrazones, such as the Beckmann transformation of oximes. Search of the literature also has not revealed any examples.

Attempted deamination with nitrous acid, which is similar to the semi-pinacolinic, deamination process of McKenzie[3] yielded only the ketone; attempted deamination with sodium nitrite in glacial acetic acid, without mineral acid, yielded chiefly the azine.

It was observed by electrometric titration that benzophenone hydrazone is an extremely weak base which fails to titrate sharply in aqueous solution with mineral acids. Instead, it undergoes moderately rapid and quantitative hydrolysis to the ketone. Accordingly, it appeared that the hydrazone had failed to undergo "diazotization." It was thus indicated that a relatively strong, anhydrous acid should be used as a medium for "diazotization," not only to prevent hydrolysis but also to convert the hydrazone to a salt which would be "diazotizable."[4]

An equivalent of benzophenone hydrazone was dissolved in twenty times its weight of concentrated sulfuric acid, and the mixture cooled to 0°. A slight excess of one equivalent of solid sodium nitrite was added to the stirred mixture in small enough portions to keep the temperature below 8°. After the completion of the addition (sixty minutes), the mixture was poured on to ice, neutralized with ammonium hydroxide, and the pre-

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[1] Pearson and Ball, *J. Org. Chem.*, **14**, 118 (1949).

[2] Taylor and Baker in Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1937, p. 397.

[3] McKenzie and Mills, *Ber.*, **62B**, 284 (1929).

[4] Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1948, p. 315.