to 2-chlorobutane, $[\alpha]^{25}\mathrm{D} + 13.70°$. Further, Letsinger[8] recently calculated from these data and his work on the displacement of *sec*-butyl chloride with benzylsodium that the optical rotation for a pure enantiomorph must lie between $[\alpha]^{25}\mathrm{D}$ 33.8° and $[\alpha]^{25}\mathrm{D}$ 38.4°.

Since it has been shown that the (+)*sec*-butyl chloride has the same configuration as the (+)*sec*-butyl alcohol,[9] evidence presented here indicates that inversion has occurred in the pyrolysis and corroborates that provided by McElvain for a bimolecular mechanism of pyrolysis.

The high rotation of the chloride indicates that a minimum of racemization has occurred; thus this sequence of reactions involving the iminoester hydrochloride provides an excellent method for the preparation in good yield, and under mild reaction conditions, of optically active chloride with high optical purity.

Experimental

Optically active 2-butanol was prepared according to the procedure of Kantor and Hauser[10] with the following modification. In order to reduce the volume of water, the saponification of the brucine salt was carried out in diethylene glycol. From 87.2 g. of pure brucine salt, m.p. 158–159°, was obtained 7.4 g. (79%) of (+)-2-butanol, $[\alpha]^{20}\mathrm{D}+13.9°$.

One difficulty encountered in the isolation of the active alcohol resulted from the formation of the water–alcohol azeotrope. Pure alcohol was recovered from the azeotrope in this work by the use of calcium hydride, which reacted rapidly with the water but left the alcohol unchanged.

sec-**Butyl Iminoacetate Hydrochloride.**—Preliminary experiments were performed with the *dl*-2-butanol. A mixture of 2.35 g. (0.057 mole) of acetonitrile and 4.70 g. (0.063 mole) of 2-butanol was cooled to 0° and dry hydrogen chloride bubbled into the reaction mixture until 2.29 g. (0.063 mole) was dissolved. The flask was kept at 0° for 7 days after which time an equal volume of ether was added and the salt filtered, washed with ether and dried. The yield was 5.8 g. (70%), m.p. 118° dec. The salt contained 23.44% chlorine ion (calcd. 23.38%).

Using the same procedure with 2.64 g. of (+)-2-butanol, $[\alpha]^{20}\mathrm{D}$ 13.9°, 5.1 g. (59%) of the iminoester hydrochloride was isolated which melted with decomposition at 125°. (+)-2-Butyl iminoacetate hydrochloride from a similar run contained 23.09% chloride ion (calcd. 23.38%).

Pyrolysis of the Iminoester Hydrochloride.—The dry *dl*-iminoester hydrochloride (11.7 g., 0.078 mole) was placed in a 50-ml. distilling flask and heated to about 130°, at which temperature the pyrolysis took place smoothly to give 5.69 g. (80%) of *sec*-butyl chloride. The chloride was purified by distillation; essentially all of the material distilled at 67.5–68°, $n^{28}\mathrm{D}$ 1.3936, d^{28}_{4} 0.5678. The solid remaining in the distillation flask was identified as acetamide by mixture m.p. determination.

The 5.1 g. of iminoester hydrochloride prepared from (+)-2-butanol ($[\alpha]^{20}\mathrm{D}$ 13.9°) was subjected to the same pyrolysis procedure to give 2.42 g. (78%) of (−)-2-butyl chloride, $n^{25}\mathrm{D}$ 1.3941, $[\alpha]^{20}\mathrm{D}$ 31.2°.

All of the optical rotation readings were taken on the pure liquids.

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[8] R. L. Letsinger, L. G. Maury and R. L. Burwell, THIS JOURNAL, **73**, 2373 (1951).

[9] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, **59**, 1266 (1937); *J. Chem. Soc.*, 1252 (1937). For a discussion of the relationship of configuration and sign of rotation also see: H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 278; and Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 386.

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The Proximity Effect in the Alkaline Rearrangement of 1,2-Diketones. I. The Migratory Aptitudes in the Rearrangement of *o*-Chlorobenzil and 1-Chlorophenanthraquinone[1,2]

BY GRANT GILL SMITH AND DONALD G. OTT[3]

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It has been reported that the alkaline rearrangement of *m*- and *p*-chlorobenzil[4] and 2- and 3-chlorophenanthraquinone[5] results in the preferential migration of the *substituted* rings. This investigation has revealed the preferential migration of the *unsubstituted* rings in *o*-chlorobenzil and 1-chlorophenanthraquinone. Anomalies of this type have been observed with many reactions in which substituents are present in the aromatic ring *ortho* to the reacting group, and this effect has been termed an *ortho effect* or a *proximity effect*.[6] The larger migratory preference of the chloro substituted ring of *o*-chlorobenzil as compared to 1-chlorophenanthraquinone, may be attributed to the relative accessibility to hydroxide ion attack at the carbonyl groups adjacent to the substituted rings. With the quinone, if the hydroxide ion is to attack at this position, it must approach relatively close to the (electronegative) chlorine substituent. This hindrance is not so great in the case of the benzil, which is not restricted by the biphenylene linkage, and hydroxide ion can more readily approach the carbonyl group. Migratory preferences are reported in Table I.

The mechanism proposed for the rearrangement would predict that the chloro substituent would tend to lower the electron density at the adjacent carbonyl group which would favor preferential migration of the substituted ring. The proximity effect of the *o*-chloro group, however, overshadows the electronic effects transmitted within the molecule, and the hydroxide ion attacks more readily at the carbonyl group adjacent to the unsubstituted ring. In order to study the proximity effect further, other substituted aromatic 1,2-diketones are being studied.

Experimental[7]

o-**Chlorophenylacetic acid-carboxyl-C^{14}** (I) was obtained from *o*-chlorobenzyl chloride by a method described for the preparation of 2-phenyl-5-chloro-α-toluic acid-carboxyl-C^{14}.[5] A 68.7% yield of the acid was obtained; m.p. 94.5–95.5°.

Anal. Calcd. for $C_8H_7O_2Cl$: C, 56.33; H, 4.34; Cl, 20.78. Found: C, 56.20; H, 4.14; Cl, 20.67.

o-**Chlorodesoxybenzoin** (II).—Compound I was converted

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[1] Presented in part before the Division of Organic Chemistry, 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15, 1953.

[2] Abstracted in part from a thesis presented to the Graduate Faculty of the State College of Washington by Donald G. Ott in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1953. Supported in part by a grant from the State College of Washington Isotopes Research Fund.

[3] Atomic Energy Commission Predoctoral Fellow, 1951–1953.

[4] M. T. Clark, E. C. Hendley and O. K. Neville, THIS JOURNAL, in press.

[5] Donald G. Ott and Grant G. Smith, *ibid.*, **76**, 2325 (1954).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 204.

[7] All melting points are corrected. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn. The yields given for the carbon-14 compounds are comparable to those obtained with non-labeled analogs.

TABLE I

MIGRATORY PREFERENCES IN THE ALKALINE REARRANGEMENT OF THE CHLORO SUBSTITUTED α-DIKETONES

Compound	Counts/min., $BaCO_3$ plates[a]	Migratory preference[b] Migration ratio subst./unsubst.	Migratory preference[b] Migration substd. ring, %
2-*o*-Chlorophenyl-2-phenylglycolic acid-1,2-C^{14}[c]	1315 ± 11	0.454 ± 0.002	31.2
o-Chlorobenzophenone carbonyl-C^{14}	442 ± 2	....	..
1-Chlorophenanthraquinone-9-C^{14}	1531 ± 10	$(1.60 \pm 0.03)(10^{-2})$	1.6
1-Chlorofluorenone-9-C^{14}	26 ± 1	....	..
2-Chlorophenanthraquinone-9-C^{14}[d]	2411 ± 11	4.93 ± 0.23	83.1
2-Chlorofluorenone-9-C^{14}[d]	2158 ± 3	....	..
3-Chlorophenanthraquinone-9-C^{14}[d]	756 ± 6	2.01 ± 0.03	66.8
3-Chlorofluorenone-9-C^{14}[d]	543 ± 7	....	..
m-Chlorobenzil[e]		4.10	81.2
p-Chlorobenzil[e]		2.05	67.2

[a] Plates of infinite thickness having an area of 2.4 cm.^{2}. Carbon-14 analyses were performed in the manner outlined in reference 5. [b] Ratio of the activity per labeled position of the fluorenone to the difference of the activities per labeled position of the phenanthraquinone and the fluorenone. [c] *o*-Chlorobenzil could not be completely purified; therefore the activity of the *o*-chlorobenzilic acid was measured. The acid is singly labeled at both the carboxyl and α-carbon atoms. [d] Reference 5. [e] Reference 4.

TABLE II

Product	Yield, %	M.p., °C.	Emp. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Methyl-3-chlorobiphenyl[a]	11		$C_{13}H_{11}Cl$	77.03	76.97	5.47	5.55
2-Chloromethyl-3-chlorobiphenyl[b]	85	56-59					
2-Phenyl-6-chloro-α-toluic acid-carboxyl-C^{14}	79[c]	148	$C_{14}H_{11}O_2Cl$	68.20	68.45	4.49	4.60
1-Chloro-9-phenanthryl acetate-9-C^{14}	86	119–120	$C_{16}H_{11}O_2Cl$	70.98	70.69	4.10	4.35
1-Chloro-9-phenanthrol-9-C^{14}[d]	99.5	211–212					
1-Chlorophenanthraquinone-9-C^{14}	27	228–230[e]					
1-Chloro-9-hydroxy-9-fluorenecarboxylic acid[f]		Not purified					
1-Chlorofluorenone-9-C^{14}	92	139.5–140[g]					

[a] B.p. 102–105° (0.65 mm.), n^{25}D 1.5995, d^{25} 1.137. *Anal.* Calcd. Cl, 17.49. Found: Cl, 17.30. [b] B.p. 114–117° (0.28 mm.). It was not found possible to fractionate this compound through either a glass helices-packed column or an all-glass Dufton column without encountering flooding; consequently, it was not submitted for microanalysis. [c] 42% after recrystallization from benzene. [d] The acetate was hydrolyzed with 8.5% ethanolic potassium hydroxide before the quinone was obtained by chromic anhydride oxidation. Since the phenanthrols are subject to oxidation by air this compound was not submitted for microanalysis. [e] L. F. Fieser [THIS JOURNAL, **53**, 4120 (1931)] reported 217–218°. [f] The acid is doubly labeled at both the carboxyl and carbon atoms. [g] E. H. Hunter, *et al.* [*ibid.*, **64**, 2845 (1942)] reported 137–138°.

into radioactive *o*-chlorodesoxybenzoin in 80.5% yield by standard procedures[8]; m.p. 68.5–69.2°.

Anal. Calcd. for $C_{14}H_{11}OCl$: C, 72.90; H, 4.81; Cl, 15.37. Found: C, 72.81; H, 4.80; Cl, 15.32.

1-(*o*-Chlorophenyl)-2-phenyl-1,2-ethanedione-2-C^{14} (III).—A mixture of 4.61 g. (0.02 mole) of II dissolved in 15 ml. of dioxane, 4 ml. of water and 2.43 g. (1.1 molar excess) of selenium dioxide was stirred and heated under reflux for a period of 18 hours. The reaction mixture was cooled to 10° and filtered through a Gooch crucible; the precipitate was washed with cold dioxane. To the filtrate was added dry ether and Norite, and the mixture was warmed gently for 15 minutes on the steam-bath. The cooled ethereal solution was dried over magnesium sulfate, filtered through Celite filter aid and evaporated under reduced pressure. The yield of the crude III was quantitative and was rearranged without purification[9] to the corresponding benzilic acid (IV).

2-*o*-Chlorophenyl-2-phenylglycolic Acid-1,2-C^{14} (IV).—To the total yield of crude III (5.43 g.) were added 2.24 g. of potassium hydroxide pellets, 64 ml. of ethyl ether and 13 ml. of 95% methanol. The mixture was shaken at room temperature for 21 hours producing a dark red solution that was extracted with three 25-ml. portions of water. The aqueous extract was subsequently acidified to a *p*H of 1 with 5% hydrochloric acid. A dark red oil formed which was extracted with three 25-ml. portions of ether. The ether layer was filtered to remove the red selenium, treated with Norite and anhydrous magnesium sulfate and allowed to stand two hours. Concentration of the ether yielded 2.43 g. (44.5%) of a pale yellow oil which was crystallized from a minimum of 95% ethanol, m.p. 125–130°, and recrystallized from a mixture of chloroform and petroleum ether (30–60°) which produced white crystals, m.p. 137.5–138.5°.

Anal. Calcd. for $C_{14}H_{11}O_3Cl$: C, 64.01; H, 4.22; Cl, 13.50. Found: C, 63.95; H, 4.38; Cl, 13.32.

***o*-Chlorobenzophenone (V).**—IV was quantitatively oxidized to V by a procedure already reported for the oxidation of *p*-methoxybenzilic acid using chromic anhydride and acetic acid.[10] The crude V was recrystallized from low boiling petroleum ether in a recovery of 66.6%, m.p. 44–45°.[11]

1-Chlorophenanthraquinone-9-C^{14} was prepared and rearranged by procedures analogous to those reported[5] for the 2- and 3-chlorophenanthraquinone-9-C^{14}. Yields and physical constants of intermediates and final products are given in Table II.

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(8) C. F. H. Allen and W. E. Barker, "Organic Synthesis," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 156.

(9) Several methods were tried to purify III free from traces of selenium; none, however, was completely satisfactory. A 50% recovery of crystalline III, m.p. 41.5–43°, was obtained by inducing crystallization of a solution of the crude material dissolved in 90% ethanol by adding small Dry Ice chips. However, since this material could not be freed of red selenium it was not submitted for microanalysis.

(10) J. D. Roberts, D. S. Smith and C. C. Lee, THIS JOURNAL, **73**, 618 (1951).

(11) C. Graebe and S. Keller, [*Ber.*, **32**, 1687 (1899)] reported 45.5°.