gently for 2 hours. A precipitate (NaCl) was formed during this period. The mixture was poured onto ice-water and left standing in the cold for 12 hours. The precipitate, 1,2-bis-(thiophenesulfonyl)-ethane, melted at 207–208° after recrystallization from an ethanol–water solution.

Anal. Calcd. for $C_{10}H_{10}O_4S_4$: C, 37.27; H, 3.12; S, 39.75. Found: C, 37.35; H, 3.17; S, 39.69.

This compound was also obtained by treating 1-(2-thiophenesulfonyl)-2-methanesulfonylethane (1.0 g., 0.004 mole) with excess lithium 2-thiophenesulfinate (1.2 g., 0.008 mole). Both compounds were dissolved in 80 ml. of absolute alcohol and refluxed for 12 hours, with stirring. The solution was poured into water and the precipitate formed was filtered off and recrystallized from ethanol. This compound, m.p. 207–208°, was found to be 1,2-bis-(thiophene-

sulfonyl)-ethane by comparison with an authentic sample It weighed 0.7 g. (yield, 54%).

Independent Synthesis of 1,2-Bis-(thiophenesulfonyl)-ethane.—1,2-Dibromoethane (1.9 g., 0.01 mole) was dissolved in 30 ml. of absolute ethanol and 3 g. of lithium 2-thiophenesulfinate (0.02 mole) was added with stirring. The mixture was refluxed and stirred for 3 hours. A precipitate (NaBr) was formed during this time. After pouring the mixture into water and allowing it to stand for 10 hours in the cold, a solid compound was isolated. The crude material, weighing 3 g., was recrystallized from an ethanol–water mixture to give 2.4 g. (75%) of a slightly yellow flaky solid, m.p. 207–208°. A mixed melting point with the cleavage products obtained above, was 206–208°.

LAFAYETTE, INDIANA

Nucleophilic Displacement *via* Frontal Attack. The Stereochemistry of the Stevens Rearrangement
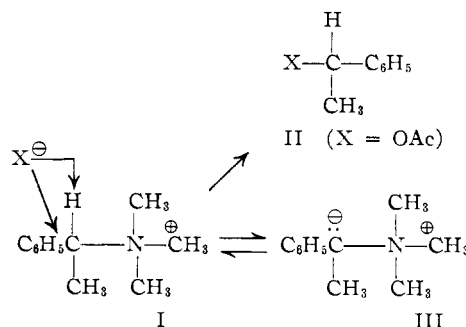
BY JAMES H. BREWSTER AND MILTON W. KLINE[1]

The relation of the Stevens rearrangement to the amine replacement and alkylide-forming reactions of quaternary ammonium salts is discussed. *d*-α-Dimethylamino-β-phenylbutyrophenone, prepared by the Stevens rearrangement of the phenacyl bromide derivative of *l*-N,N-dimethyl-α-phenylethylamine, has been degraded to *l*-β-methylhydrocinnamic acid *via* Beckmann rearrangement of the oxime of the ketone formed by reductive deamination of the rearrangement product. The previously established configurational relation of *l*-N,N-dimethyl-α-phenylethylamine to *l*-β-methylhydrocinnamic acid shows that the α-phenylethyl group retains its original configuration during its intramolecular migration from nitrogen to carbon. The rearrangement occurs with little racemization; racemic forms of several of the degradation products are, however, concentrated by recrystallization. These findings lend strong support to the concept that nucleophilic displacement can occur by frontal as well as by lateral and rearward attack.

Quaternary ammonium salts have been used in the benzylation of many inorganic and organic anions.[2] It has been suggested that such "amine replacement" reactions are typical S_N2 reactions on the basis of kinetic[3] and stereochemical[4,5] studies of the formation of alcohols[3,4] and an ester[5] (II, X = OAc) from quaternary ammonium compounds. An attempt to demonstrate inversion of configuration in the alkylation of sodiomalonic ester by means of *d*-I was, however, frustrated by racemization of the quaternary salt.[5] It seems likely that this racemization resulted from anionic attack on the α-hydrogen atom, which is activated by both the quaternary nitrogen atom and the phenyl group, to give the internal salt (III). Salts of this nature, termed "alkylides" by Wittig, have been postulated as intermediates in some of the reactions of 'onium salts with strong bases.[6] Thus,

quaternary ammonium salts (*e.g.*, I) appear to be able to react with Lewis bases by either a displacement mechanism (to form II) or an alkylide-forming mechanism (to form III).

The Stevens rearrangement[7] of phenacylbenzyldialkylammonium bromides (*e.g.*, IV) to α-dialkylaminoketones (*e.g.*, VI) under the influence of alkali seems to be simply an amine replacement reaction which proceeds *via* an alkylide (*e.g.*, V).[7d,6c,8] Evidence suggesting that this rearrangement is

(1) Purdue Research Foundation Fellow, 1951–1952.

(2) (a) W. Michler and A. Gradmann, *Ber.*, **10**, 2078 (1877); (b) E. von Meyer, *Abhandl. math.-phys. Klasse sachs. Gesellschaft Wiss.*, **31**, 179 (1908) *Chem. Zentr.*, **80**, II, 1800 (1909); (c) J. von Braun, *Ann.*, **382**, 1 (1911); (d) Hla Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926) (*C. A.*, **20**, 3695 (1926)); (e) H. R. Snyder and J. C. Speck, THIS JOURNAL, **61**, 668, 2895 (1939); (f) H. R. Snyder, C. W. Smith and J. M. Stewart, *ibid.*, **66**, 200 (1944).

(3) (a) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 69 (1933); (b) E. D. Hughes, C. K. Ingold and C. S. Patel, *ibid.*, 526 (1933).

(4) J. Read and J. Walker, *ibid.*, 308 (1934).

(5) H. R. Snyder and J. H. Brewster, THIS JOURNAL, **71**, 291 (1949).

(6) (a) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929); 713 (1930); (b) F. Krollpfeiffer and K. Schneider, *Ann.*, **530**, 38 (1937); (c) G. Wittig and co-workers, *ibid.*, **555**, 133 (1944); **557**, 193 (1947); **560**, 116 (1948); *Angew. Chem.*, **63**, 15 (1951); (d) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2011 (1946); **69**, 723 (1947); (e) A. Novelli and A. de Varela, *Ciencia e invest.*, **4**, 82 (1948); (*C. A.*, **42**, 5912 (1948)).

(7) (a) T. S. Stevens, E. M. Creighton, A. B. Gordon and M. MacNicol, *J. Chem. Soc.*, 3193 (1928); (b) T. S. Stevens, W. W. Snedden, E. T. Stiller and T. Thomson, *ibid.*, 2119 (1930); (c) J. Dunn and T. S. Stevens, *ibid.*, 1926 (1932); 279 (1934); (d) T. Thomson and T. S. Stevens, *ibid.*, **69**, 1932 (1932).

(8) (a) H. B. Watson, "Modern Theories of Organic Chemistry," Oxford University Press, London, England, 1941, p. 205; (b) C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951), have discussed possible mechanisms for the Stevens rearrangement and a number of other reactions apparently occurring by 1,2-rearrangement of a carbanion. This important paper should be consulted for a more detailed discussion of possible alternate mechanisms for this type of rearrangement.

intramolecular has been presented by Stevens.[9,10] The rearrangement of optically active IV has been shown to occur without racemization of C*.[11] This result indicates that the migrating group does not become fully detached from the rest of the molecule *in an intramolecular reaction*. Other pertinent arguments against the migration of the benzyl group as an ion have been presented by Hauser and Kantor.[8b] In view of the elements of uncertainty in previous demonstrations of the intramolecular nature of the reaction,[9,10] bimolecular mechanisms in which retention of optical *activity* but inversion of *configuration* at C* would occur might be entertained.
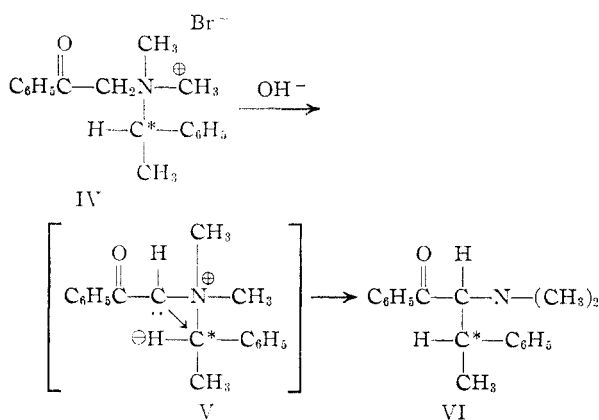
Because of the significance of this reaction to theories of the mechanisms of amine replacement reactions in particular and of nucleophilic displacements in general it seemed desirable to test the prediction[12,8b] that an *intramolecular* rearrangement of an alkylide such as V would occur with retention of configuration at the migrating carbon atom, C*.[13] It was also hoped that such a study would serve to dispel lingering doubts as to the intramolecular nature of the reaction.

(9) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 55 (1932), report that the rearrangement is first order with respect to the quaternary salt and zero order with respect to alkali, indicating that the rearrangement of the alkylide is the rate-controlling step. This evidence is not wholly unequivocal since in each run only five measurements were made, by isolation of the product and the unreacted starting material. The data so obtained were consistent with an assumption that the reaction had the kinetic orders indicated above and *that a side-reaction which consumed 10–15% of the starting material was simultaneous with the slow step*. Reactions were carried to 60% completion and it was noted that, with aqueous sodium hydroxide, "the [rate] coefficients fell off steadily as the reaction proceeded."

(10) T. Stevens, *ibid.*, 2107 (1930), reported that when a mixture of two isomeric brominated phenacylbenzyldimethylammonium bromides was treated with alkali the two substances rearranged independently. Although his results strongly suggest this interpretation, they, again, are not wholly unequivocal. The ratio of products was not that to be expected from the independently determined rate coefficients of the two compounds. About 12% of the starting material could not be accounted for either as recovered quaternary salts (42.9%; theor. 45.9%, based on alkali consumed) or as *crude tertiary amines* (45.2%; theor. 54.1%, based on alkali consumed). Thus 21% of the *consumed* starting material was not accounted for; according to Stevens most of this defect probably represents the formation of "neutral by-products."

(11) A. Campbell, A. H. Houston and T. Kenyon, *ibid.*, 93 (1947).

(12) J. H. Brewster, Ph.D. Thesis, University of Illinois, 1948.

(13) Retention of configuration has been noted in other 1,2-rearrangements in which, however, migration of a group to an *electron deficient* atom appears to occur, *i.e.*, the Hofmann, Lossen, Curtius, Wolff and Beckmann rearrangements and the Arndt–Eistert synthesis, *cf.* G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 519.

Accordingly, *l*-IV was prepared from *l*-α-phenylethylamine by methylation[5] and treatment with phenacyl bromide[11] and converted to *d*-VI by reaction with sodium hydroxide solution.[11] The α-dimethylamino ketone (VI) could not be degraded to optically active products of lower molecular weight by oxidation with permanganate, chromic acid or lead tetraacetate. Reduction of *d*-VI by means of zinc and acetic acid, however, afforded the unsubstituted ketone *l*-VII.[14] The oxime of this ketone (*l*-VIII) was converted to *l*-β-methylhydrocinnamanilide (IX) by means of a Beckmann rearrangement; the anilide was hydrolyzed to *l*-β-methylhydrocinnamic acid (X). It has previously been shown that *l*-α-phenylethylamine and *l*-X have the same steric configuration.[15]
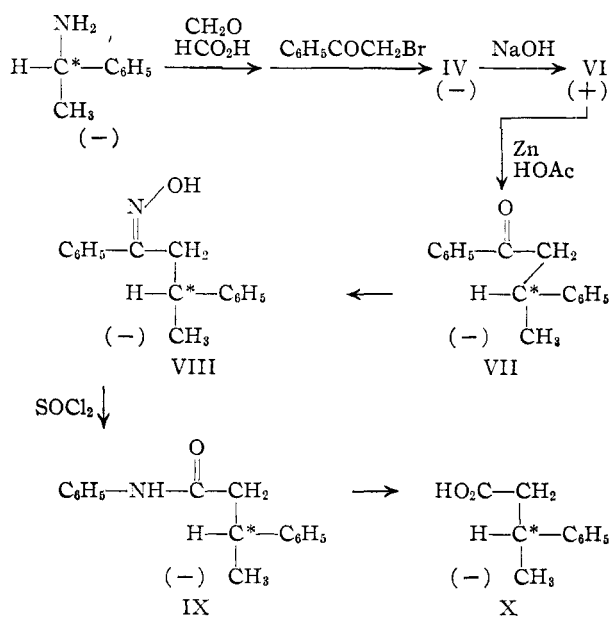
When this reaction sequence was first carried out, the intermediates were isolated and crystallized. The β-methylhydrocinnamic acid (X) so obtained, from α-phenylethylamine of about 98% optical purity, had a lower specific rotation ($[\alpha]^{30}$D −31°) than that reported as a maximum in the literature ($[\alpha]^{25}$D − 46.8°),[16] indicating that partial racemization had occurred during the chemical operations described. When the degradation was repeated, using precipitation rather than crystallization in the isolation of intermediates, the acid (X) was obtained in about 97% optical purity. This finding indicates that little racemization occurs in the Stevens rearrangement, but that crystallization of some of the reaction intermediates results in concentration of racemic forms.

The individual steps were examined in more detail. It was found that the phenacyl bromide salt (IV) prepared from *d*-α-phenylethylamine of about 45% optical purity could be almost completely resolved by four crystallizations from alcohol–ether. It seems probable, then, that the recrystallized salt (IV) originally used was optically pure. If so, a small amount of racemization must occur in the Stevens rearrangement to permit the formation of X with a low rotation in the first degradation. Repetition of these degradations with *d*-*dl* IV (45% optical purity) and with *d*-IV yielded products of the same order of optical purity as the starting materials, confirming the observation that little racemization occurs in the rearrangement.

(14) Reductive removal of a substituent from the carbon atom adjacent to a carbonyl group by means of a metal and an acid has been reported a number of times in the literature, *cf.*, S. S. Jenkins, THIS JOURNAL, **56**, 1137 (1934), and preceding papers; N. J. Leonard and W. C. Wildman, *ibid.*, **71**, 3100 (1949) and preceding papers.

(15) (a) *d*-Hydratropic acid has been converted to *l*-α-phenylethylamine by Hofmann rearrangement of its amide [C. L. Arcus and J. Kenyon, *J. Chem. Soc.*, 916 (1939)]; this reaction is known to occur with retention of configuration (see 13). (b) *d*-Hydratropic acid has also been converted to *l*-β-methylhydrocinnamic acid by reduction of the ester, bromination of the alcohol and carbonation of the Grignard reagent of the halide [P. A. Levene, R. E. Marker and A. Rothen, *J. Biol. Chem.*, **100**, 595 (1933)]. The same configurational relation was shown by reduction of *l*-hydratroponitrile to the amine which can be prepared by Hofmann rearrangement of the amide of *l*-β-methylhydrocinnamic acid. (c) A third correlation is provided by reaction of *d*-α-phenylethyl chloride [related to *d*-α-phenylethylamine by E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937)] with sodiomalonic ester to yield *l*-β-methylhydrocinnamic acid [E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937)], inversion of configuration undoubtedly occurring in the alkylation step.

(16) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **100**, 694 (1933).

NH_2
|
H—$\overset{|}{\underset{|}{C}}$*—$C_6H_5$ $\xrightarrow{\underset{HCO_2H}{CH_2O}}$ $C_6H_5COCH_2Br$ $\xrightarrow{}$ IV $\xrightarrow{NaOH}$ VI
| (−)   (+)
CH_3
(−)

$\overset{OH}{\underset{\parallel}{N}}$

C_6H_5—$\overset{\parallel}{C}$—CH_2

H—$\overset{|}{C}$*—C_6H_5 $\longleftarrow$
|
(−) CH_3
VIII

$\underset{\downarrow}{SOCl_2}$

$\overset{O}{\underset{\parallel}{}}$

C_6H_5—NH—$\overset{\parallel}{C}$—CH_2 $\longrightarrow$ HO_2C—CH_2

H—$\overset{|}{C}$*—C_6H_5 H—$\overset{|}{C}$*—C_6H_5
| |
(−) CH_3 (−) CH_3
IX   X

Zn HOAc (applies to VI → VII)

O
‖
C_6H_5—$\overset{\parallel}{C}$—CH_2

H—$\overset{|}{C}$*—C_6H_5
|
(−) CH_3
VII

The aminoketone (VI) has two asymmetric centers and is obtained as a mixture of diastereomers.[10,11] These isomers were separated by crystallization from methanol[11]; the optically active "α"-isomers had higher rotations and melting points than those previously reported (see Experimental). These isomers could be degraded to VII of high optical purity. This ketone (VII), when of high optical purity, was obtained erratically in a low melting (50–51°) and high melting (72–73°) form (see Experimental). The oxime, VIII, as usually obtained required several crystallizations for purification; these crystallizations were accompanied by an appreciable decrease in magnitude of rotation. The impurity necessitating these recrystallizations could not be identified on the scale employed. Since Beckmann rearrangement of the crude oxime appeared to produce only one amide, it seems likely that this impurity was unreacted ketone. Recrystallization of the amide also resulted in a diminution of rotatory power. Thus the large apparent racemization observed in the initial experiments, when rather large crystallization losses were accepted, appears to be due very largely to a concentration of the racemic forms of VIII and IX on recrystallization.

One of the referees has suggested that the formation of an alkylide similar to III from IV could account for the small amount of racemization that occurs during the rearrangement.

These findings confirm the view that the Stevens rearrangement is intramolecular in mechanism, since bimolecular displacement would result in inversion of configuration. The observed high retention of optical activity indicates that the migrating group does not separate as an ion[8b] and suggests that the reaction occurs by nucleophilic displacement. Thus, evidence that such displacements can occur by frontal,[8b] as well as by rearward (S_N2) and lateral (S_Ni),[17] attack is also provided by this work.

(17) W. A. Cowdrey, E. A. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, J. Chem. Soc., 1267 (1937).

Experimental

The reactions described below were carried out with both racemic and optically active materials using identical procedures. All melting points were taken with a calibrated partial immersion thermometer.

l-α-**Phenylethylamine**, $n^{26}D$ 1.5238, $α^{27}D$ −37.9° (*l* 1, homogeneous) was prepared by resolution of α-phenylethylamine[18] by means of tartaric acid.[11] Based on Holmberg's value ($α^{19}D$ −38.73°, *l* 1, homog.),[19] this product was about 97.9% optically pure.

d-dl-α-**Phenylethylamine**, $n^{19}D$ 1.5261, $α^{28}D$ +17.5° (*l* 1, homog.) was obtained from the mother liquors of the tartaric acid resolution of α-phenylethylamine. This substance had an optical purity lying between 45.2 and 46.4% based on the values of Holmberg[19] (above) and of Marckwald and Meth ($α^{22}D$ +37.70°, *l* 1, homog.).[20]

l-N,N-**Dimethyl-α-phenylethylamine**, b.p. 65° (8 mm.), $n^{27}D$ 1.5000, $α^{24}D$ −65.3° (*l* 1, homog.) was prepared by the methylation of α-phenylethylamine by means of formic acid and formaldehyde.[5,21] *d-dl*-Compound, b.p. 50–53° (4 mm.), $n^{25}D$ 1.5005, $α^{28}D$ +30.3° (*l* 1, homog.).

l-**Phenacyl-α-phenylethyldimethylammonium bromide** (IV) was prepared from the *l*-amine by reaction with phenacyl bromide.[11] The large white plates had m.p. 119.5–120°, $[α]^{26}D$ −79.9° (*l* 1, *c* 7.108 in 95% ethanol); lit.[11] m.p. 126°, $[α]D$ −71.0° (*c* 7.104 in ethanol).

Anal. Calcd. for $C_{18}H_{22}ONBr$: Br, 22.9. Found: Br, 22.7.

Racemic compound, m.p. 100–102.5° (lit.[10] m.p. 155–157°); this melting point did not change appreciably on repeated crystallization from ethanol–ether.

d-dl-Compound, m.p. 97–110° (after one crystallization from ethanol–ether), $[α]^{27}D$ +16.0° (*l* 1, *c* 7.12 in 95% ethanol). When 10.0 g. of the *d-dl* compound was recrystallized four times from ethanol–ether, the *d-compound* was obtained, m.p. 119.5–120°, $[α]^{29}D$ +80.3° (*l* 1, *c* 6.989 in 95% ethanol).

d-α-**Dimethylamino-β-phenylbutyrophenone** (VI) was obtained by heating the quaternary salt (*l*-IV) with a slight excess of N sodium hydroxide solution.[11] The melting range of the product varied considerably in different preparations, but was generally about 65–85°, $[α]^{25}D$ +24.9° (*l* 1, *c* 1.69 in methanol); lit.[11] m.p. 90–93°, $[α]D$ +25° (*c* 1.66 in methanol).

Anal. Calcd. for $C_{18}H_{21}ON$: N, 5.24. Found: N, 5.43.[22]

Racemic compound, m.p. 75–84°; lit.[10] m.p. "about 90°."

l-Compound, m.p. 70–82°, $[α]^{27}D$ −23.8° (*l* 1, *c* 1.68 in methanol).

l-dl-Compound, m.p. 74–80°, $[α]^{28}D$ −11.2° (*l* 1, *c* 1.78 in methanol).

The α-dimethylamino-β-phenylbutyrophenones are obtained as mixtures of diastereomers.[10,11] The individual isomers were obtained by fractional crystallization from methanol,[11] the "α"-forms being obtained in the first fractions as pale yellow fibrous needles, while the "β"-forms crystallize in the later fractions as yellow-orange prisms.[23]

d-"α"-Compound, m.p. 119.5–120°, $[α]^{26}D$ +60.4° (*l* 1, *c* 1.855 in methanol).

(18) A. W. Ingersoll, in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 503.

(19) B. Holmberg, *Ber.*, **45**, 999 (1912).

(20) W. Marckwald and R. Meth, *ibid.*, **38**, 808 (1905).

(21) Essentially the method of R. W. Icke, B. B. Wisegarver and G. A. Alles, in *Org. Syntheses*, **25**, 89 (1945).

(22) Nitrogen analysis by Miss Helen D'Agostino.

(23) It has previously been reported[10,11] that the pure "α"-form may be obtained by isomerization of the "β"-form with sodium methoxide. It has been our experience that such treatment, as applied to mixtures of the two forms, leads only to slightly altered mixtures of the isomers. It seems likely that the low rotations and melting points previously reported for the "α"-form[11] are actually the constants for an equilibrium mixture (in methanol) of the "α"- and "β"-forms. Due to the difficulty in obtaining these isomers in quantity for our principal purpose, this point was not further investigated.

d-"β"-Compound, m.p. 111–112°, $[\alpha]^{28}$D +7.0° (l 2, c 0.200 in methanol).[24]

Lit.[11] "α"-form, m.p. 108°, $[\alpha]^{21}$D +47.7° (c 1.814 in methanol); "β"-form, m.p. 108°, $[\alpha]$D +5.0° (c 2.258 in methanol). 1-"α"-Compound, m.p. 119.5–120°, $[\alpha]^{28}$D −61.6° (l 2, c 1.088 in methanol). 1-"β"-Compound, m.p. 111–112°, $[\alpha]^{28}$D −4.4° (l 2, c 9.040 in methanol).[24]

l-β-Phenylbutyrophenone (VII).—A stirred solution of 1.0 g. (3.8 mmoles) of the d-aminoketone (VI) in 30 ml. of glacial acetic acid was heated under reflux with 0.75 g. (11.4 mmoles) of zinc dust for 30 minutes. The hot solution was filtered from the inorganic precipitate and excess zinc. The filtrate was diluted with water (100 ml.), giving a white precipitate, 0.7 g. (84%), m.p. 44–45°, $[\alpha]^{28}$D −10.6° (l 2, c 2.961 in carbon tetrachloride), of the deaminated ketone. When recrystallized from methanol and water the product had the following properties: m.p. 50–51°, $[\alpha]^{27}$D −9.8° (l 1, c 7.160 in carbon tetrachloride).

l-Compound (from "α"-d-VI), m.p. 45–55°, $[\alpha]^{27}$D −12.2° (l 2, c 1.025 in carbon tetrachloride).

d-Compound (from l-VI), m.p. 48–70°, $[\alpha]^{28}$D +10.6° (l 2, c 2.780 in carbon tetrachloride).

Racemic compound (from dl-VI), m.p. 72–73°; lit. m.p. 72°,[25] 74°.[26]

A mixture of l-VII (0.03 g.) and d-VII (0.03 g.) was dissolved in 3 ml. of hot 95% ethanol. When the solution was cooled, 0.05 g. of flakes, m.p. 72–73°, formed. A mixture of this material with authentic β-phenylbutyrophenone (see below) showed no depression of melting point. The infrared spectra[27] of the low melting l-compound and of the high melting racemic compound (15 mg./ml. in carbon tetrachloride) were identical.

d-dl-Compound (from l-dl-VI), m.p. 45–70°, $[\alpha]^{27}$D +5.3° (l 2, c 6.827 in carbon tetrachloride).

dl-β-Phenylbutyrophenone (Authentic Sample).—β-Methylhydrocinnamic acid, m.p. 37°, was prepared from α-phenylethyl chloride and sodiomalonic ester[28] and converted to β-methylhydrocinnamoyl chloride, b.p. 81–83° (22 mm.), n^{18}D 1.5198, by reaction with thionyl chloride. The acid chloride was treated with phenylcadmium, following the general procedure of Cason,[29] to form the ketone in 54% yield, m.p. 71–72°.

l-β-Phenylbutyrophenone Oxime (VIII).—A solution of 0.57 g. (8 mmoles) of hydroxylamine hydrochloride and 1.1

g. (8 mmoles) of sodium acetate in 10 ml. of water was added to a solution of 1.0 g. (4.5 mmoles) of the ketone (VII) in 20 ml. of 95% ethanol. The mixture was heated under reflux for 1.5 hours and then diluted with 100 ml. of water, precipitating a white solid. This solid was dried over calcium chloride *in vacuo*; m.p. 70–82°, yield 1.0 g. (93%), $[\alpha]^{27}$D −49.8° (l 2, c 1.385 in methanol). Some of this solid was recrystallized three times from 95% ethanol, giving fine white needles, m.p. 87–89.5°, $[\alpha]^{28}$D −40.5° (l 2, c 0.766 in methanol).

Racemic compound, m.p. 93–94°; lit.[30] m.p. 93.5–94°.

d-dl-Compound (from d-dl-VII), m.p. 73–86°, $[\alpha]^{2?}$D +21.1° (l 2, c 4.459 in methanol).

l-β-Methylhydrocinnamic Acid (X).—Thionyl chloride (0.5 ml.) was added to a solution of 1.00 g. (4.2 mmoles) of the oxime (l-VIII) in 25 ml. of ether. After the vigorous reaction had subsided, the ether and thionyl chloride were evaporated in a stream of air, leaving a brown oil. This oil was heated under reflux with 50 ml. of 18 N sulfuric acid for 2.5 hours. After the reaction mixture had cooled, it was extracted with three 40-ml. portions of ether. The combined ethereal extract was washed with a saturated solution of sodium bicarbonate until the ether was neutral to Hydrion paper. The sodium bicarbonate solution was then acidified with 15 ml. of 18 N sulfuric acid. The acid solution was extracted with three 25-ml. portions of ether and the combined ether extract was dried over sodium sulfate. After the ether had been distilled, the residual oil was distilled under vacuum, b.p. 107–108° (0.3 mm.), yield 0.3 g. (43%), $[\alpha]^{26.5}$D −45.5° (l 2, c 1.615 in benzene). Based on the literature value ($[\alpha]^{25}$D −46.8°[16]), this product is 97.2% optically pure. A sample of this material was eventually caused to crystallize, m.p. 37–38°; lit.[31] m.p. 37–38°.

d-dl-Compound, b.p. 107–108° (0.3 mm.), $[\alpha]^{27}$D +21.1° (l 2, c 12.235 in benzene), optical purity 45.1%.

dl-β-Methylhydrocinnamanilide (IX) was prepared by the Beckmann rearrangement of racemic VIII as described for l-VIII. The oil obtained after evaporation of the ether and thionyl chloride was crystallized from ethanol, m.p. 135–136°; lit. m.p. 136–137°.[32]

l-Compound, m.p. 139.5–140.5°, $[\alpha]^{30}$D −32.2° (l 1, c 1.180 in 95% ethanol), was prepared from l-VIII as described above. This product was obtained in the initial degradation study, in which all intermediates were thoroughly recrystallized. Hydrolysis of this anilide by the method described above afforded l-β-methylhydrocinnamic acid, $[\alpha]^{30}$D −31° (l 1, c 5.58 in benzene). This product is about 67% optically pure, on the basis of the literature value cited above.

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(24) The specific rotations of the d-"β"- and l-"β"-compounds merely indicate the order of magnitude observed; the low concentrations and the intense yellow color of the solutions made more precise measurements difficult.

(25) C. Harries, *Ann. chim.*, **330**, 232 (1909).

(26) M. A. Spielman and C. W. Mortinson, THIS JOURNAL, **61**, 666 (1939).

(27) Determined by Mr. Thomas Riethof of this department.

(28) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **97**, 379 (1932).

(29) J. Cason, *Chem. Revs.*, **40**, 15 (1947).

(30) E. P. Kohler, *Am. Chem. J.*, **31**, 655 (1904).

(31) L. Eijkman, *Chem. Weekblad.*, **5**, 655 (1908).

(32) F. F. Blicke and D. Sheets, THIS JOURNAL, **70**, 3768 (1948).