Table II

Aminoanilino Alkanols

Compound	Yield, %	Cryst. from	M. p., °C.[a]	Mol. formula	Nitrogen, % Calcd.	Found
2-(*o*-Aminoanilino)-ethanol	90	Benzene	106–106.5	$C_8H_{12}ON_2$	18.42	18.28
2-(*o*-Aminoanilino)-ethanol·HCl	45	Abs. ethanol	144.5–145.5	$C_8H_{14}ON_2Cl$	14.85	14.69
2-(*p*-Aminoanilino)-ethanol·HCl	10	Abs. ethanol	198–199(d)	$C_8H_{14}ON_2Cl$	14.85	14.67
3-(*o*-Aminoanilino)-propanol-1	80	Benzene	65.5–66	$C_9H_{14}ON_2$	16.85	16.74
3-(*o*-Aminoanilino)-propanol-1·HCl	40	Abs. ethanol	146.5–147	$C_9H_{16}ON_2Cl$	13.82	13.94
3-(*o*-Aminoanilino)-propanol-2	60	Benzene	85.5–86.5	$C_9H_{14}ON_2$	16.85	16.60
3-(*p*-Aminoanilino)-2-methyl-propanol-2	60	Benzene	107.5–108	$C_{10}H_{16}ON_2$	15.54	15.63
5-(*o*-Aminoanilino)-pentanol-1	80		[b]	$C_{11}H_{18}ON_2$	14.42	

[a] Melting points are corrected. [b] Material decomposed on distillation. An impure fraction distilled over at 163–165° (2 mm.).

precipitated by passing in dry hydrogen chloride gas. Where the free base was unstable, the nitro compound was reduced as described and the entire alkaline mixture extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and then treated with dry hydrogen chloride.

The hydrochlorides were precipitated as white crystalline products in all cases. On filtering away from the ether and exposing the compounds to air, a peculiar behavior was noted. The hydrochlorides appeared to deliquesce, at the same time undergoing an effervescent reaction with bubbles of gas being blown up from the surface. After a period of time this action ceased and the materials dried up to somewhat colored, no longer deliquescent, solids. These can be recrystallized from absolute ethanol and analyze for the monohydrochlorides.

What apparently occurs here is that the dihydrochlorides are first precipitated in the ether solution; but on exposure to air, one molecule of hydrogen chloride escapes leaving the stable monohydrochloride. The hydrochlorides are included in Table II.

Summary

A new series of N-(*o*-amino- and *p*-aminophenyl)alkanolamines has been prepared by reduction of the corresponding nitro compounds resulting from the condensation of *o*- and *p*-nitrochlorobenzene with a series of amino alcohols. These compounds and their derivatives are of interest because of possible pressor and local anesthetic action.

New York, N. Y.

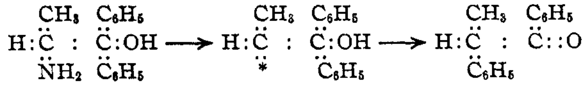
Received March 8, 1939

[Contribution from the School of Chemistry and Physics of The Pennsylvania State College]

The Common Basis of Intramolecular Rearrangements. V.[1] Inversion of Configuration in Semipinacolic Deamination. The Configurational Relationship between (+)-Alanine and (+)-Methylphenylacetic Acid

By Herbert I. Bernstein and Frank C. Whitmore

Semipinacolic deamination may take place as follows[1]



$$\underset{\ddot{N}H_2}{\overset{CH_3}{H:\ddot{C}}}\ :\ \underset{C_6H_5}{\overset{C_6H_5}{\ddot{C}:OH}} \longrightarrow \underset{*}{\overset{CH_3}{H:\ddot{C}}}\ :\ \underset{C_6H_5}{\overset{C_6H_5}{\ddot{C}:OH}} \longrightarrow \underset{C_6H_5}{\overset{CH_3}{H:\ddot{C}}}\ :\ \overset{C_6H_5}{\ddot{C}::O}$$

(I) (II)

It is conceivable that the removal of the amino group and the shift of phenyl may be essentially simultaneous. Evidence for this is the fact that the optically active aminoalcohol I gives the ketone II in optically active form.[2] If the indicated intermediate existed independently, the three groups around the electronically deficient carbon could occupy a single plane and racemization would seem inevitable. We decided to study this change in order to find out whether the shifting phenyl group actually takes the place of the removed amino group or takes part in a Walden inversion by approaching the back of the adjacent carbon atom, the front being considered as the corner holding the amino group. In the case of the ordinary pinacolic rearrangement the group removed is the hydroxyl group. The general case may be represented as follows: X being the group removed with a complete octet of electrons, thus leaving the carbon with only six electrons (C*). The two possible ways for a group to shift with its complete octet to the electronically deficient carbon would then be

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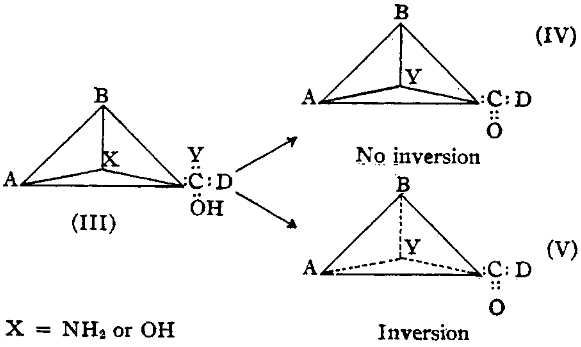
(1) *Cf.* Whitmore, This Journal, **54**, 3274 (1932); **60**, 2002 (1938).

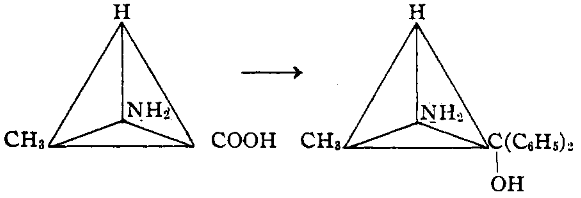
(2) (a) McKenzie, Roger and Wills, *J. Chem. Soc.*, 779 (1926); (b) McKenzie and Dennler, *Ber.*, **60**, 220 (1927); (c) Roger and McKenzie, *ibid.*, **62**, 272 (1929).



The ketones IV and V are enantiomorphs.

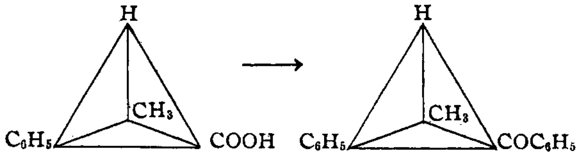
This study appeared important because of the strong indications that the replacement of groups in organic molecules involves an attack on the back of the carbon with a net result as in the conversion of III to V resembling that of the turning inside out of an umbrella.[3]

We have been able to show that inversion of configuration occurs during semipinacolic deamination. (−)-1,1-Diphenyl-2-amino-1-propanol (VI) has been converted to (+)-methylphenylacetophenone (VII) in 94% yield by treatment with nitrous acid.[2a] To find out whether or not inversion took place in this change it was necessary to study the configurational relationship of VI and VII. Compound VI has the same configuration as (+)-alanine (VIII).[2a]



(VIII) (VI)

(+)-Methylphenylacetic acid (IX) has been converted to (+)-methylphenylacetophenone (VII), thus establishing the configurational relationship of these two compounds.[4]

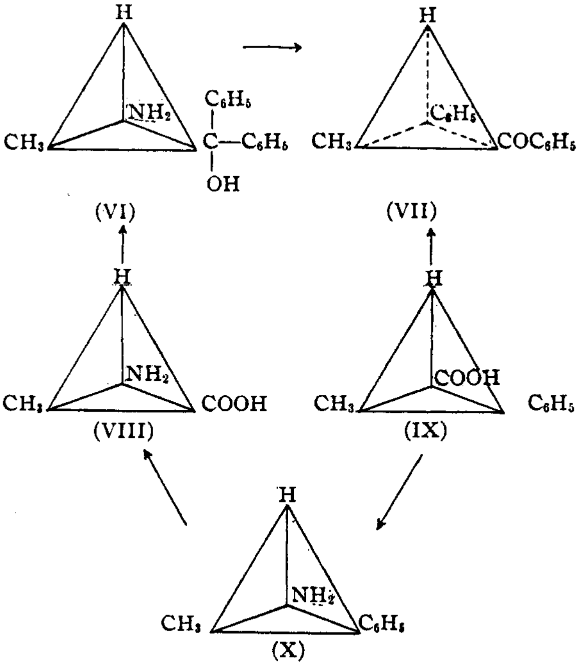


(IX) (VII)

It thus remained only to establish the configurational relationship of (+)-alanine (VIII) and (+)-methylphenylacetic acid (IX). We have converted (+)-methylphenylacetic acid (IX) to its azide and then by the Curtius rearrangement to the hydrochloride of (−)-α-phenylethylamine (X) and finally to the benzoyl derivative. It is assumed that no change in configuration of the *migrating group* occurs in the Hofmann–Curtius–Lossen type of rearrangement, which must not be confused with the pinacolic Wagner–Meerwein type of rearrangement in which an optically active carbon is directly involved.[5]

The phenyl in the benzoyl derivative of (−)-α-phenylethylamine (X) has been oxidized to the carboxyl group giving the benzoyl derivative of (+)-alanine[6] (VIII).

The configurational relations involved may be summarized as follows



Thus (+)-alanine (VIII) and (+)-methylphenylacetic acid (IX) have opposite configurations and the conversion of the aminoalcohol VI to the ketone VII by pinacolic deamination involves a Walden inversion. This gives additional evidence for the "rearward" attack on a carbon atom during replacement of a group.[3]

We wish to thank the Mallinckrodt Chemical Works for kindly furnishing the strychnine alka-

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[3] Olson and Long, THIS JOURNAL, **56**, 1294 (1934); Hughes, Juliusberger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935); Bartlett and Pöckel, THIS JOURNAL, **59**, 820 (1937); **60**, 2416 (1938); Criegee and Plate, *Ber.*, **72**, 178 (1939).

[4] Conant and Carlson, THIS JOURNAL, **54**, 4055 (1932).

[5] *Cf.* Whitmore and co-workers, THIS JOURNAL, 1932–; also Wallis and Moyer, *ibid.*, **55**, 2598 (1933); Wallis and Whitmore, *ibid.*, **56**, 1427 (1934); Shriner, Adams and Marvel, Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, p. 308.

[6] Leithe, *Ber.*, **64**, 2827 (1931).

loid and ethyl phenylmalonate used in this work. We are also grateful to our colleague R. E. Marker for helpful advice and suggestions.

Experimental

Preparation and Resolution of Methylphenylacetic Acid.—*dl*-Methylphenylacetic acid was prepared in 78% yield by a malonic ester synthesis involving ethyl phenylmalonate and methyl iodide. Physical constants for the racemic acid are b. p. 124–125° (3–4 mm.), $n^{20}\text{D}$ 1.5211, d^{20}_4 1.097. Resolution of the acid was accomplished by three recrystallizations of the strychnine salt from 75% ethyl alcohol.[7] Decomposition of the strychnine salt with hydrochloric acid yielded a pure acid with $[\alpha]^{25.5}\text{D}$ 86.1°.

Preparation of *l*-Methylphenylcarbinylisocyanate.—(+)-Methylphenylacetyl chloride was prepared from 9.1 g. of (+)-methylphenylacetic acid and 7.9 g. of thionyl chloride. The excess thionyl chloride was removed by suction. The acid chloride was dissolved in 125 cc. of dry ether, and 11 g. of sodium azide freshly precipitated by addition of acetone to a saturated aqueous solution was added. This mixture was stirred for twenty-four hours at room temperature. The solid was filtered, washed with ether, and ether evaporated from the filtrate using suction only. The residue had the unmistakable isocyanate odor.

Preparation of (−)-α-Phenylethylamine Hydrochloride and its Benzoyl Derivative.—One-third of the above residue was mixed with 25 cc. of concd. hydrochloric acid and stirred vigorously for four hours. The flask became warm and there was a slight evolution of gas. This mixture was then diluted with 100 cc. of water, allowed to stand, and the resulting precipitate (0.1 g., m. p. 104–113°) filtered off. The aqueous filtrate was extracted with 30 cc. of ether, and this aqueous solution was then evaporated to dryness. The residue had a m. p. of 154–158°. The m. p. of (−)α-phenylethylamine hydrochloride is 171°,[8] (+)-α-phenylethylamine hydrochloride 159–160°;[9] $[\alpha]^{24}\text{D}$ −5° in water.

The crude amine hydrochloride was converted by the Schotten–Baumann reaction to 1.6 g. of white needles of (−)-benzoyl-α-phenylethylamine. One recrystallization from benzene yielded a product of m. p. 120–121.° Marckwald and Meth,[8] after repeated recrystallization, report 125.5°. Pope and Read,[10] however, report 119.5°. The specific rotation was $[\alpha]^{27}\text{D}$ −39.2° in benzene with c 2.44, l 2, and α −1.91°. Marckwald and Meth[8] report $[\alpha]\text{D}$ −39.9° in benzene, c = 3.005; Pope and Read,[10] $[\alpha]^{20}\text{D}$ −43.7° in benzene, c 2.4.

Summary

1. (+)-Methylphenylacetic acid has a configuration opposite to that of (+)-alanine.

2. A semipinacolic deamination rearrangement has been shown to involve a Walden inversion.

3. Additional support is given to the conception of a "rearward" attack on the carbon atom in replacement of groups.

STATE COLLEGE, PENNA. RECEIVED FEBRUARY 21, 1939

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(7) Raper, *J. Chem. Soc.*, **123**, 2558 (1923).

(8) Marckwald and Meth, *Ber.*, **38**, 801 (1905).

(9) Hunter and Kipping, *J. Chem. Soc.*, **83**, 1147 (1903).

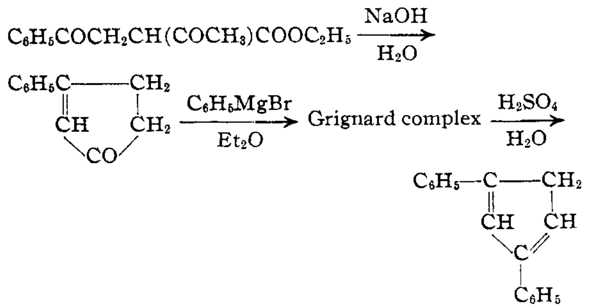
(10) Pope and Read, *ibid.*, **103**, 451 (1913).

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Some 1,4-Diaryl-1,3-cyclopentadienes

BY NATHAN L. DRAKE AND JOHN R. ADAMS, JR.[1]

Some years ago Borsche and Menz[2] described a hydrocarbon, $C_{17}H_{14}$, which they called 1,3-diphenyl-1,3-cyclopentadiene, and synthesized according to the following scheme



Borsche and Menz offered no proof of the structure of the diene, apparently assuming that their method of synthesis was in itself sufficient proof.

During a recent study of the condensation of ethyl β-benzoylpropionate with acetophenone in the presence of sodium ethoxide, we obtained this same diene, and it is with this compound, which we have shown beyond all reasonable doubt to be 1,4-diphenyl-1,3-cyclopentadiene, that the present paper deals.

When ethyl β-benzoylpropionate and acetophenone are allowed to react for some time in dry benzene in the presence of two equivalents of sodium ethoxide, and the mixture is cooled, poured into ice water and the layers separated, a crystalline substance separates from the aqueous layer when it is subsequently warmed to about 60°.

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(1) From the Doctor's dissertation of J. R. Adams, Jr. This paper was presented at the Milwaukee meeting of the Society, September, 1938.

(2) Borsche and Menz, *Ber.*, **41**, 209 (1908).