

The proper amounts of these thermostated solutions were added to the weighed sample of perester, followed by sufficient thermostated absolute methanol to bring the solution to the desired volume.

Also, in these runs, an amount of 2 *N* methoxide sufficient to neutralize the hydrochloric acid present in the aliquot was added in addition to the 1 ml. normally used during the analysis.

That the method of analysis employed is satisfactory for determining the amount of perester present is shown by the following analyses on pure samples of the peresters using the method described above.

Decalyl perbenzoate			
Wt. taken, g.	Vol. 0.05087 <i>N</i> S <sub>2</sub> O <sub>8</sub> required, ml.	Wt. found, g.	Purity, %
0.2172	30.79	0.2148	98.9
.2784	39.70	.2770	99.4

Decalyl per- <i>p</i> -methylbenzoate			
Vol. 0.03708 <i>N</i> S <sub>2</sub> O <sub>8</sub> required, ml.			
0.1792	32.40	0.1736	96.9
Decalyl per- <i>p</i> -nitrobenzoate			
Vol. 0.02548 <i>N</i> S <sub>2</sub> O <sub>8</sub> required, ml.			
0.1270	30.83	0.1253	98.7

Similar results were obtained with the other two peresters.

The rate constants for the different runs were usually determined graphically, but in those cases in which there was any doubt as to the best straight line, the method of least squares was employed. Rate constants in all cases were reproducible to within 3%.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM CHANDLER LABORATORY, COLUMBIA UNIVERSITY]

## Mechanism of the Peracid Ketone-Ester Conversion. Analysis of Organic Compounds for Oxygen-18<sup>1</sup>

BY W. VON E. DOERING<sup>2</sup> AND EDWIN DORFMAN

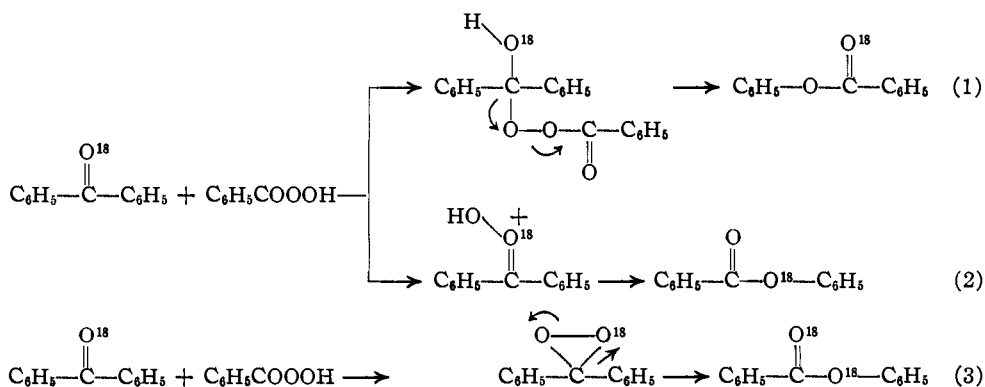
RECEIVED JULY 2, 1953

When benzophenone-O<sup>18</sup> is oxidized with perbenzoic acid, phenylbenzoate-*carbonyl*-O<sup>18</sup> results. The position of oxygen-18 is shown by reduction with lithium aluminum hydride to benzyl alcohol containing the excess oxygen-18 and phenol having the normal abundance. These analyses are carried out mass-spectrometrically on carbon dioxide obtained from the organic material by a modification of the Schütze-Untersaucher method for quantitative oxygen analysis.

At the conclusion of a paper dealing with migration aptitude in the peracid ketone-ester conversion, three consistent mechanisms were considered although, at the time, no experimentally supported distinction could be made between them.<sup>3</sup> These mechanisms were also considered to be consistent with kinetic studies.<sup>4</sup> They were in theory distinguishable by the different fates they would impose on the carbonyl oxygen atom. Using, as example, the reaction of benzophenone-O<sup>18</sup> and perbenzoic acid to give phenylbenzoate, the "Criegee" mechanism (1)<sup>5,6</sup> would lead to phenylbenzoate-*carbonyl*-O<sup>18</sup>; the "Wittig" mechanism (2)<sup>8</sup> would

give the reverse result—phenylbenzoate-*ether*-O<sup>18</sup>; whereas the "v. Baeyer" mechanism (3)<sup>7</sup> would lead to ester in which the oxygen-18 was equally distributed between both oxygen atoms. In this paper, the results of such an experiment are reported.

The bulk of the work was concerned with developing a general method of getting oxygen-18 out of organic molecules in a form suitable for mass-spectrometric analysis. The ter Meulen method of oxygen analysis<sup>9</sup> has been used by Urey and Roberts<sup>9</sup> for the analysis of methanol-O<sup>18</sup> and by Bunton and Frei<sup>10</sup> for phenol-O<sup>18</sup>. The latter workers re-



(1) Taken from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

(3) W. von E. Doering and L. Speers, *THIS JOURNAL*, **72**, 5515 (1950).

(4) S. L. Friess and A. H. Soloway, *ibid.*, **73**, 3968 (1951).

(5) R. Criegee, *Ann.*, **560**, 127 (1948).

(6) S. L. Friess, *THIS JOURNAL*, **71**, 2671 (1949).

port a 10% isotope dilution, a result which would accord with the large blank usually observed when the method is used for oxygen analyses.<sup>11</sup> Another method which was considered was a modification

(7) A. v. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899).

(8) H. ter Meulen, *Rec. trav. chim.*, **41**, 509 (1922).

(9) H. C. Urey and I. Roberts, *THIS JOURNAL*, **60**, 2391 (1938).

(10) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951).

(11) A. O. Maylott and J. B. Lewis, *Anal. Chem.*, **22**, 1050 (1950).

of the procedure of oxygen analysis originated by Grosse, Hindin and Kirshenbaum<sup>12</sup> in which oxygen-containing material is burned with oxygen-18 in a platinum tube at high temperature. It was thought that pyrolysis in the tube would give carbon monoxide which could be analyzed directly for oxygen-18.

After experiments with the ter Meulen and platinum tube methods gave unsatisfactory results, attention was turned to the possibility of adapting the Schütze-Untersaucher method<sup>13-15</sup> to oxygen-18 analysis. *A priori* unpromising because of the likelihood of exchange with the hot quartz tube and with the iodine pentoxide, this method became more inviting when it was found that carbon dioxide-O<sup>18</sup> and iodine pentoxide did not exchange on long heating. An apparatus very similar to that described by Steyermark<sup>16</sup> was assembled and modified so that the final product, carbon dioxide, was collected in a liquid nitrogen trap by freezing and could be analyzed directly in the mass spectrograph.

Several experiments indicated that the apparatus had at most a very small memory for the immediately preceding analysis (Table I: A, D) and it was found that three consecutive pyrolyses of a given sample sufficed to remove the memory if it did indeed exist. The accuracy of the method

TABLE I  
OXYGEN-18 ANALYSES

Sample <sup>a</sup>	Ratio <sup>b</sup> 46/44 × 10 <sup>6</sup>	Atom % oxygen-18
A. Tank CO <sub>2</sub>	419	0.204 <sup>c</sup>
1. H <sub>2</sub> O <sup>18</sup>	1818	1.54
2. H <sub>2</sub> O	441	0.225
3. H <sub>2</sub> O	429	0.214
B. Tank CO <sub>2</sub>	424	0.204 <sup>c</sup>
CO <sub>2</sub> -H <sub>2</sub> O <sup>18</sup> exchange	3300	1.52
1. H <sub>2</sub> O <sup>18</sup>	1806	1.52
2. H <sub>2</sub> O <sup>18</sup>	1799	1.51
C. CO <sub>2</sub> -H <sub>2</sub> O <sup>18</sup> exchange	3230	1.55
Tank CO <sub>2</sub>	406	0.204 <sup>c</sup>
1. H <sub>2</sub> O <sup>18</sup>	1781	1.57
2. H <sub>2</sub> O <sup>18</sup>	1772	1.56
D. Tank CO <sub>2</sub>	417	0.204 <sup>c</sup>
1. H <sub>2</sub> O <sup>18</sup>	1777	1.52
2. H <sub>2</sub> O <sup>18</sup>	1778	1.52
CO <sub>2</sub> -H <sub>2</sub> O <sup>18</sup> exchange	3280	1.52
3. H <sub>2</sub> O	439	0.227
E. Tank CO <sub>2</sub>	356	0.204 <sup>c</sup>
3. C <sub>6</sub> H <sub>17</sub> O <sup>18</sup> H	1169	1.12
2. C <sub>8</sub> H <sub>17</sub> O <sup>18</sup> H	1131	1.08
1. C <sub>8</sub> H <sub>17</sub> O <sup>18</sup> H	1098	1.04
F. Tank CO <sub>2</sub>	411	0.204 <sup>c</sup>
Phenol	403	0.196
Benzyl alcohol	408	0.201
Benzoic acid	411	0.204

(12) A. V. Grosse, S. G. Hindin and A. D. Kirshenbaum, *THIS JOURNAL*, **68**, 2119 (1946).

(13) M. Schütze, *Z. anal. Chem.*, **118**, 241 (1939).

(14) J. Untersaucher, *Ber.*, **73**, 391 (1940).

(15) For references, see V. A. Aluise, *et al.*, *Anal. Chem.*, **23**, 530 (1951).

(16) A. Steyermark, "Quantitative Organic Microanalysis," Blakiston Co., Philadelphia, Pa., 1951, pp. 208-221.

G. Tank CO <sub>2</sub>	396	0.204 <sup>c</sup>
Phenylbenzoate	393	0.186
Benzophenone	398	0.205
H. Tank CO <sub>2</sub>	411	0.204 <sup>c</sup>
1. Benzophenone-O <sup>18</sup>	1679	1.44
2. Benzophenone-O <sup>18</sup>	1662	1.42
3. Benzophenone-O <sup>18</sup>	1686	1.45
I. Tank CO <sub>2</sub>	377	0.204 <sup>c</sup>
1. Benzophenone-O <sup>18</sup>	1518	1.42
2. Benzophenone-O <sup>18</sup>	1498	1.40
3. Benzophenone-O <sup>18</sup>	1521	1.42
4. Benzophenone-O <sup>18</sup>	1523	1.42
5. Benzophenone-O <sup>18</sup>	1522	1.42
J. Tank CO <sub>2</sub>	427	0.204 <sup>c</sup>
1. Benzophenone-O <sup>18</sup>	1563	1.27
2. Benzophenone-O <sup>18</sup>	1662	1.37
3. Benzophenone-O <sup>18</sup>	1684	1.39
6. Benzyl alcohol-O <sup>18</sup>	1620	1.33
5. Benzyl alcohol-O <sup>18</sup>	1604 <sup>d</sup>	....
4. Benzyl alcohol-O <sup>18</sup>	1609	1.32
K. Tank CO <sub>2</sub>	408	0.204 <sup>c</sup>
2. Benzophenone-O <sup>18e</sup>	1638	1.42
1. Benzophenone-O <sup>18e</sup>	1603	1.38
L. Tank CO <sub>2</sub>	382	0.204 <sup>c</sup>
1. Benzophenone-O <sup>18e</sup>	1532	1.42
2. Benzophenone-O <sup>18e</sup>	1556	1.44
3. Benzophenone-O <sup>18e</sup>	1541	1.43
M. Tank CO <sub>2</sub>	406	0.204 <sup>c</sup>
1. Phenylbenzoate-O <sup>18</sup>	1008	1.40
2. Phenylbenzoate-O <sup>18</sup>	1007	1.40
3. Phenylbenzoate-O <sup>18</sup>	1008	1.40
N. Tank CO <sub>2</sub>	414	0.204 <sup>c</sup>
1. Phenylbenzoate-O <sup>18</sup>	1026	1.40
2. Phenylbenzoate-O <sup>18</sup>	1007	1.36
O. Tank CO <sub>2</sub>	391	0.204 <sup>c</sup>
1. Phenylbenzoate-O <sup>18</sup>	959	1.38
2. Phenylbenzoate-O <sup>18</sup>	971	1.41
3. Phenylbenzoate-O <sup>18</sup>	972	1.41
P. Tank CO <sub>2</sub>	380	0.204 <sup>c</sup>
1. Phenol	375	0.200
2. Phenol	381	0.205
3. Phenol	381	0.205

<sup>a</sup> The samples in each set are listed in the order they were analyzed in the mass spectrometer. The number of the sample indicates the order in which it was decomposed in pyrolysis train. <sup>b</sup> Each ratio was obtained from four sets of readings. <sup>c</sup> The standard, normal oxygen-18 abundance is taken as 0.204 atom %. <sup>d</sup> Air leaked into the sample. <sup>e</sup> Recrystallized from absolute ethanol.

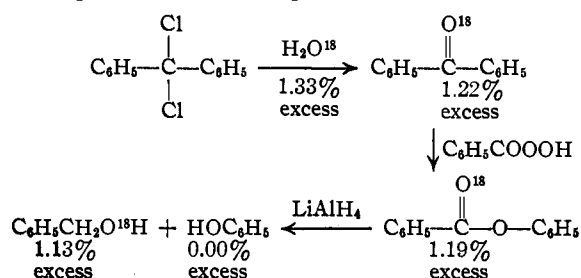
was determined in two ways. In the first of these, a portion of a sample of enriched water was equilibrated with carbon dioxide according to the method of Cohn and Urey<sup>17</sup> and analyzed mass-spectrometrically. Another portion of the water was then converted to carbon dioxide *via* the pyrolysis apparatus and analyzed. Three experiments of this type (Table I: B, C, D) show excellent agreement. In the second independent test, a sample of methyl-ethylisobutylcarbinol-O<sup>18</sup> was pyrolyzed and found to contain 0.88 atom % excess oxygen-18 (Table I: E). This same sample had been analyzed by Dr.

(17) M. Cohn and H. C. Urey, *THIS JOURNAL*, **60**, 679 (1938).

L. Friedman<sup>18</sup> and been found to contain  $0.92 \pm 0.09$  atom % excess of oxygen-18. Finally, it may be mentioned that compounds containing the normal abundance of oxygen-18 gave excellent results by this method indicating that no spurious, disturbing impurities of either mass 44 or 46 survived the pyrolysis and oxidation (Table I: F, G).

This adaptation of the Schütze-Untersaucher method therefore appears suitable for the determination of oxygen-18 in samples (10–20 mg.) from which all oxygen can be volatilized on pyrolysis. It is applied here to analyze the oxygen-18 content of the compounds involved in a study of the mechanism of the peracid ketone-ester conversion.

Benzophenone-O<sup>18</sup> was prepared from diphenyldichloromethane with water-O<sup>18</sup> containing 1.33 atom % excess oxygen-18. Treatment of the benzophenone-O<sup>18</sup> with perbenzoic acid in benzene



solution gave phenylbenzoate-carbonyl-O<sup>18</sup> containing 1.19 atom % excess of oxygen-18. The position of labeling was determined by reducing the ester to phenol and benzyl alcohol with lithium aluminum hydride. Phenol containing no excess of oxygen-18 was obtained whereas the benzyl alcohol contained 1.13 atom % excess indicating that the oxygen-18 of the benzophenone appeared exclusively in the carbonyl oxygen of the phenylbenzoate. This isotopic condition is incompatible with mechanisms (2) and (3) and is completely consistent with the "Criegee" mechanism (1).

We wish to acknowledge the assistance of Professor T. Ivan Taylor in the mass spectrometric analyses.

### Experimental<sup>19</sup>

**Apparatus and Procedure for Analysis of Oxygen-18.**—The apparatus and procedure is essentially that described by Steyermark.<sup>18</sup> The furnace to heat the carbon black at 1120° was a 550-watt type (Hoskins Electric Furnace FD303A) recommended by Dinerstein and Klipp.<sup>20</sup> The effluent gases from the decomposition were passed through a bubbler tube containing 2–3% of bromine in 1:1 chloroform-carbon tetrachloride and cooled in a Dry Ice-acetone-bath; a trap consisting of a single spiral of 7 mm. Pyrex glass which was immersed in liquid nitrogen during operation; through a 3-way stopcock to the conventional iodine pentoxide oxidation tube (before use, the iodine pentoxide was heated at 230–240° for 12 hr. in a stream of nitrogen

(18) We gratefully acknowledge the help of Dr. L. Friedman, Brookhaven National Laboratory, Upton, N. Y. The amount of oxygen-18 in the carbinol was determined from the cracking pattern by measuring the intensities of the  $\text{C}_6\text{H}_5\text{O}^+(n)$ ,  $n + 1$  and  $n + 2$  peaks and calculating the amount of oxygen-18 after subtracting the contribution of  $2\text{C}^{18}$ ,  $\text{C}^{18}\text{D}$ ,  $2\text{D}$  and  $\text{C}^{18}\text{O}^{17}$  species from the  $n + 2$  peak.

(19) Melting points are corrected; boiling points are not. Microanalyses by the Schwarzkopf Microanalytical Laboratory, Woods 77, New York.

(20) R. A. Dinerstein and R. W. Klipp, *Anal. Chem.*, **21**, 545 (1949).

to dehydrate any periodic acid); then through a U-tube cooled in Dry Ice-acetone to condense iodine vapor; and finally through a sample trap immersed in liquid nitrogen. (The sample trap consisted of a U-tube of 7 mm. Pyrex glass fitted with a stopcock at the entrance tip and another stopcock before the mass spectrometer fitting (a  $7/32$  joint) at the other end.)

Thorough flushing with nitrogen prior to analysis was very important. The electric furnace for driving the sample into the carbon black<sup>18</sup> was replaced simply by a small flame with satisfactory results. After completion of the pyrolysis, sweeping with nitrogen was continued for 20 min. The sample trap was detached and, still cooled in liquid nitrogen, was evacuated at 1–2 mm. to remove nitrogen.

The isotope ratios were determined in a 60° Nier-type of mass spectrometer operated at an ionizing potential of 150 volts. Each day's runs were standardized by analysis of a sample of carbon dioxide from a tank and the results were then normalized using 0.204 atom %<sup>21</sup> as the normal abundance of oxygen-18.

In calculating the atom fraction of oxygen-18, the dilution which occurs in the oxidation of the carbon monoxide to carbon dioxide is taken into account. For a compound with one oxygen atom, equation (a) is used and for a compound with two, equation (b), both giving  $x$ , the atom fraction of oxygen-18, calculated as if all the excess were concentrated in one position. In each observation

$$\frac{0.99796x + 0.00204(1-x)}{0.00408(1-x)} = \frac{46/44(\text{sample})}{46/44(\text{tank CO}_2)} \quad (a)$$

$$\frac{0.99796(0.00204+x) + 0.00204(1.99796-x)}{0.00408(1.99796-x)} = \frac{46/44(\text{sample})}{46/44(\text{tank CO}_2)} \quad (b)$$

the mass numbers between 22 and 48 were examined to check for leakage of air and the presence of other contaminants.

**Exchange Experiment with Carbon Dioxide-O<sup>18</sup> and Iodine Pentoxide.**—An evacuated, 20-cc., Pyrex bulb containing 4.0 g. of iodine pentoxide was filled with carbon dioxide to a pressure of 100 mm. The 46/44 ratio was  $25.5 \times 10^{-3}$  corresponding to 1.3 atom % of oxygen-18. After being heated 2 hr. at 125–140°, the 46/44 ratio was  $25.6 \times 10^{-3}$  showing that no dilution had occurred.

**Benzophenone-O<sup>18</sup>.**—A mixture of 35 g. of diphenyldichloromethane, b.p. 131–133° at 0.6 mm., and 9.7 g. of water containing  $1.33 \pm 0.02$  atom % excess oxygen-18 (supplied by the Stuart Oxygen Co. on allocation by the Atomic Energy Commission) was stirred at 100° for 3 hr. in a two-necked flask with mercury-sealed stirrer, reflux condenser and calcium chloride drying tube. The resulting product was filtered, recrystallized once from iso-octane and twice from hexane giving 24.3 g. of benzophenone-O<sup>18</sup>, m.p. 47–48°, containing  $1.22 \pm 0.02$  atom % excess of oxygen-18 (Table I: H, I, J, K, L).

**Perbenzoic Acid Oxidation of Benzophenone-O<sup>18</sup> to Phenylbenzoate-carbonyl-O<sup>18</sup>.**—A solution of 35 g. of perbenzoic acid in 1100 cc. of benzene to which 20.0 g. of benzophenone-O<sup>18</sup> had been added was allowed to react in the dark for 10 days. After being washed once with aqueous sodium carbonate and then three times with water, the benzene solution was concentrated. The residue was fractionally crystallized from iso-octane to yield 1.0 g. of benzophenone, m.p. 40–44°, and 18.0 g. of phenylbenzoate, m.p. 61–66°. Recrystallization from ethanol raised the m.p. to 68–69.5°. The phenylbenzoate contained  $1.19 \pm 0.02$  atom % excess of oxygen-18 (Table I: M, N, O).

**Anal.** Calcd. for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ : C, 78.8; H, 5.1. Found: C, 78.9; H, 5.1.

**Reduction of Phenylbenzoate-carbonyl-O<sup>18</sup> with Lithium Aluminum Hydride.**—To 600 cc. of anhydrous ether in a 1-l. 3-necked flask equipped with mercury-sealed stirrer, reflux condenser, drying tube and dropping funnel, 4.0 g. of lithium aluminum hydride was added. After 30 minutes' stirring, 7.0 g. of phenylbenzoate-carbonyl-O<sup>18</sup> in 150 cc. of dry ether was added over a period of 10 min. After stirring for 5 hr. and standing for an additional 12 hr., water was added gradually precipitating material which was filtered and washed with ether.

(21) A. O. Nier, *Phys. Rev.*, **77**, 789 (1950).

The filtrate and washings were extracted with 700 cc. of 5% sodium hydroxide solution in 100-cc. portions and then with 300 cc. of water in 100-cc. portions. No phenol was present in the alkaline washings. The ether solution, dried over magnesium sulfate was concentrated to a residue which was distilled giving 3.0 g. of benzyl alcohol-O<sup>18</sup>, b.p. 49° at 1 mm. Evaporative distillation at 5 mm. gave material  $n_D^{20}$  1.5372, containing  $1.13 \pm 0.02$  atom % excess oxygen-18 (Table I: J).

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>O: C, 77.8; H, 7.5. Found: C, 77.5; H, 7.2.

The precipitate obtained above was dissolved in 10% aqueous sulfuric acid and extracted with 450 cc. of ether. The ether extract was washed with 50 cc. of water and ex-

tracted with 100 cc. of 5% sodium hydroxide. This solution was washed with ether, acidified and extracted with 160 cc. of ether in four portions. The ether extract was washed successively with 40 cc. of water and with 40 cc. of saturated sodium bicarbonate solution and then was concentrated. The residue was distilled at 1 mm. collecting all volatile material in a Dry Ice trap. Redistillation under nitrogen gave 2.0 g. of phenol; b.p. 175–180° at 770 mm.; m.p. 38–39°. The phenol contained  $0.001 \pm 0.005$  atom % excess of oxygen-18 (Table I: P).

*Anal.* Calcd. for C<sub>6</sub>H<sub>6</sub>O: C, 76.6; H, 6.2. Found: C, 76.8; H, 6.4.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

### Catalytic Debenzylation. III. The Influence of $\alpha$ -Substitution on the Ease of Hydrogenolysis<sup>1</sup>

BY RICHARD BALTZLY AND PETER B. RUSSELL

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The effect on the ease of hydrogenolysis of  $\alpha$ -substitution in benzyl groups has been investigated. A methyl group in the  $\alpha$ -position lessens the ease of cleavage to about the same extent as one in the ring. Benzyl and phenyl groups have a smaller influence. The block against hydrogenolysis exerted by certain groups ( $-\text{COOR}$  and  $-\text{CH}_2\text{NR}_3^+$ ) attached to the benzylic carbon atom is removed by interpolation of one methylene radical.

Earlier papers in this series<sup>2,3</sup> have dealt mainly with the effect of substitution in the aromatic nucleus on the stability of benzyl groups toward hydrogenolysis. The present paper extends the observations made in Part I<sup>2</sup> on the effect of  $\alpha$ -substitution in the benzyl radical. There it was shown that the groups  $-\text{COOH}$ ,  $-\text{CONH}_2$ ,  $-\text{COOR}$  or  $-\text{CH}_2\text{NR}_3^+$  in the  $\alpha$ -position prevented debenzylolation under our standard conditions. Using more stringent conditions the debenzylolation of mandelic acids and phenylethanolamines has been achieved.<sup>4,5</sup>

The hydrogenolysis of a number of derivatives homologous with the first series was carried out with a view to finding out how far these groups could be removed without losing their effect. Ethyl benzoylacetate in methanol containing a palladized charcoal catalyst absorbed two mols of hydrogen. The reaction slowed after the absorption of slightly more than one mol of hydrogen (reduction of the ketone to an alcohol) and the final mol of hydrogen (debenzylation) was absorbed at about one-tenth the rate of the reduction of benzyl alcohol. Ethyl nicotinoylacetate on reduction also lost the  $\beta$ -oxygen but at a rather slow rate. It should be noted that in this instance the substituted benzyl residue of the (unisolated) ethyl  $\beta$ -phenyl- $\beta$ -hydroxypropionate is replaced by a substituted 3-pyridylmethyl group.  $\beta$ -Dimethylaminopropiophenone hydrochloride<sup>6</sup> was reduced smoothly to  $\gamma$ -phenylpropyldimethylamine hydrochloride. It

is thus apparent that the interpolation of one methylene group between the benzylic hydroxyl and the interfering  $\alpha$ -group in both mandelic acid and phenylethanolamine compounds permits debenzylolation to proceed although with somewhat diminished ease.

The previous papers in this series<sup>2,3</sup> have utilized the competitive debenzylolation of dibenzylmethylamines, usually as the hydrochlorides, with a different substituent in each of the benzyl radicals to demonstrate the effects of these substituents. The same method was turned to a study of the effects of  $\alpha$ -substitution. In the series of experiments, the results of which are reported in Table I, the tertiary amine hydrochlorides in dilute solution in methanol (0.01–0.02 mole in 50 ml. of methanol) were shaken with hydrogen at about 2 atm. over-pressure in the presence of palladized charcoal. The mixture of products was analyzed usually by crystallization of the hydrochlorides of the secondary bases.

The almost unilateral cleavage of  $\alpha$ -phenethylbenzylmethylamine hydrochloride to  $\alpha$ -phenethylmethylamine hydrochloride (reduction 1, Table I) indicates that the presence of a methyl substituent in the  $\alpha$ -position stabilizes the C–N bond. The reduction of  $\alpha$ -phenethyl-*p*-methylbenzylmethylamine hydrochloride to an inseparable mixture of  $\alpha$ -phenethylmethylamine and *p*-methylbenzylmethylamine hydrochlorides (reduction 2) indicates that the effect of a methyl group in the  $\alpha$ -position is very similar to the effect of the same group in the *p*-position. This is confirmed by the observations that the stabilizing effect of an  $\alpha$ -methyl group is less than that of a *p*-methoxyl (reduction 3) and greater than that of a *p*-amino group (reduction 4). In the previous papers of this series<sup>2,3</sup> it was demonstrated that the order of *p*-substituents in stabilizing the C–N bond is: Class I ( $-\text{OMe}$ ,  $-\text{OH}$ ,  $-\text{NH}$

(1) Presented in part before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1952.

(2) R. Baltzly and J. S. Buck, *THIS JOURNAL*, **65**, 1984 (1943).

(3) R. Baltzly and P. B. Russell, *ibid.*, **72**, 3410 (1950).

(4) K. Kindler, *et al.*, *Ann.*, **554**, 9 (1943); *Ber.*, **74**, 315 (1941); **76**, 1211 (1943); **77**, 585 (1944).

(5) K. W. Rosenmund and E. Karg, *ibid.*, **75**, 1850 (1942).

(6) We wish to thank Dr. D. W. Adamson (Wellcome Research Laboratories, Chemical Division, Beckenham, Kent, England) for this substance.