

Registry No.—**4a**, 7287-82-3; **4b**, 7287-81-2; **4b** methyl ether, 34386-38-4; **4c**, 536-50-5; **4d**, 5379-19-1; **4e**, 31108-34-6; **4f**, 34386-42-0; **4g**, 13513-82-1; **4h**, 23308-82-9; **4i**, 454-91-1; **4j**, 1737-26-4; **4k**, 403-41-8; **4l**, 6939-95-3; **4m**, 3391-10-4; **4n**, 98-85-1;

4n methyl ether, 4013-34-7; **4o**, 5391-88-8; **11**, 1193-81-3; **14**, 617-94-7; **15**, 1565-71-5; **16**, 2309-47-9; potassium *tert*-butoxide, 865-47-4.

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Semipinacolic Deamination of 2-Amino-1-(2-methoxyphenyl)-1-phenylethanol¹

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To elucidate the behavior of the *o*-methoxyphenyl group in cationic rearrangements, 2-amino-1-(2-methoxyphenyl)-1-phenylethanol (**1**) has been deaminated with sodium nitrite in 50% aqueous acetic acid. This reaction produced 2-methoxydeoxybenzoin (**2**), 2'-methoxydeoxybenzoin (**3**), and 3-phenylbenzofuran (**4**), respectively, in proportions 47:12:27 at 0° and 43:13:19 at 30°. Ketones **2** and **3** were not produced in equal proportions as has previously been reported. Production of **4** demonstrates for the first time methoxy oxygen (*o*-MeO-5) involvement in deaminative rearrangements and shows that use of the ratio of **3** to **2** to determine "migratory aptitude" of *o*-methoxyphenyl is improper. A mechanism is presented to account for the observed products.

Considerable attention has been given to migratory abilities of various aryl groups in pinacol and related rearrangements. Bachmann and coworkers,² in their studies of rearrangements of symmetrical tetraaryl glycols, assigned migratory aptitudes to a series of substituted aryl groups relative to phenyl; a few examples are *p*-methoxyphenyl (500), *p*-tolyl (15.7), phenyl (1.0), and *o*-methoxyphenyl (0.3).³ With the exception of ortho-substituted phenyl groups, these relative migratory aptitudes follow the order expected from consideration of relative rates of electrophilic aromatic substitution. The low migratory abilities for the ortho-substituted phenyl groups have been ascribed to steric hindrance⁴ or "ortho effect."⁵ Matsumoto and coworkers^{5b,6,7} reinvestigated the pinacolic rearrangement of the symmetrical di-*o*-methoxyphenyldiphenyl glycol, as suggested by Pocker.^{3a} Their results, though varying with the diastereomer investigated, demonstrated a migratory aptitude of *o*-methoxyphenyl roughly in agreement with the above value. Matsumoto⁷ concluded that Pocker's suggestion^{3a} of *o*-anisyl oxygen involvement⁸ with the developing carbonium ion was not in accord with his thermodynamic data.

A number of deaminations of substituted aminoethanols (semipinacols) of the type ArPhC(OH)CH₂(NH₂)R are known in which the predicted (on the basis of relative migratory aptitudes) aryl group does not migrate to provide the majority of rearranged prod-

uct.⁹ Curtin, *et al.*,⁹ explained these results by means of a transition-state "cis effect," whereas Collins, *et al.*,¹⁰ ascribe such behavior to ground-state conformational control. In cases in which the migration terminus is primary, the migratory aptitudes of aryl groups during deamination follow the expected order, but the values are much reduced compared to the symmetrical tetraaryl glycol cases. For example, in 2-amino-1-aryl-1-phenylethanol the migratory aptitudes (phenyl = 1.0) are *p*-methoxyphenyl (1.5), *p*-tolyl (1.3), and *p*-chlorophenyl (0.9).^{9f} Rather similar results are obtained in systems lacking the hydroxyl group.¹¹

Our desire to elucidate the behavior of the *o*-methoxyphenyl group in cationic rearrangements led us to inquire into the semipinacolic deamination of 2-amino-1-(2-methoxyphenyl)-1-phenylethanol (**1**), a case in which steric hindrance in the transition state should not play an important role. Here the apparently anomalous migratory aptitude of the *o*-methoxyphenyl group, as in the symmetrical tetraaryl glycol rearrangement, should not obtain if that behavior arises from steric effects in the transition state. Indeed, Kharasch, *et al.*,¹² demonstrated that treatment of *o*-anisylidiphenylcarbinol with *tert*-butyl hydroperoxide and perchloric acid in glacial acetic acid yields mostly guaiacol and benzophenone, which arise from predominant *o*-anisyl (rather than phenyl) migration to oxygen in the ion resulting from heterolytic scission of the first-formed peroxide. Further, there should be a likely possibility of *o*-anisyl oxygen involvement with the developing ionic center (the so-called *o*-MeO-5 participation⁸) during deamination of **1**, with the resulting

(1) Taken in part from the M.S. Thesis of C. E. S., San Fernando Valley State College, 1972.

(2) W. E. Bachmann and J. W. Ferguson, *J. Amer. Chem. Soc.*, **56**, 2081 (1934); W. E. Bachmann and H. R. Sternberger, *ibid.*, **56**, 170 (1934); W. E. Bachmann, *ibid.*, **54**, 2112 (1932); W. E. Bachmann and F. H. Mosher, *ibid.*, **54**, 1124 (1932).

(3) For compilations of these and other results, see (a) Y. Pocker in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 1; (b) C. J. Collins, *Quart. Rev. Chem. Soc.*, **14**, 357 (1960).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 478.

(5) (a) C. H. Beale and H. H. Hatt, *J. Amer. Chem. Soc.*, **54**, 2405 (1932); (b) K. Matsumoto, R. Goto, A. Sera, and T. Asano, *Nippon Kagaku Zasshi*, **87**, 1076 (1967).

(6) R. Goto, K. Matsumoto, and A. Sera, *ibid.*, **87**, 93 (1966).

(7) K. Matsumoto, *Bull. Chem. Soc. Jap.*, **41**, 1356 (1968).

(8) (a) S. Winstein, *Experientia, Suppl.*, **2**, 153 (1955); see also (b) R. Heck, J. Corse, E. Grunwald, and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3278 (1957).

(9) (a) P. I. Pollack and D. Y. Curtin, *ibid.*, **72**, 961 (1950); (b) D. Y. Curtin and P. I. Pollack, *ibid.*, **73**, 992 (1951); (c) D. Y. Curtin, E. E. Harris, and P. I. Pollack, *ibid.*, **73**, 3453 (1951); (d) D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5898 (1952); (e) *ibid.*, 5905 (1952); (f) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954); (g) *ibid.*, **77**, 354 (1955).

(10) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **63**, 3654 (1961).

(11) L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952); P. S. Bailey and J. G. Burr, Jr., *ibid.*, **75**, 2951 (1953); B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4952 (1956). See also V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958), for comparison of solvolytic rearrangement of glycols and aldehydes with deamination of primary amines.

(12) M. S. Kharasch, A. Fono, W. Nudenberg, and A. C. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).

appearance of a reaction pathway unlike those in the reactions mentioned above. Tiffeneau, *et al.*,¹³ made brief mention of deamination of **1** along with several other related semipinacols. The results of these experiments seemed to be internally inconsistent, and no mention was made of any products which might have arisen from *o*-methoxy oxygen participation. In light of these facts we felt that deamination of **1** merited re-investigation.

Results

Deamination of 2-amino-1-(2-methoxyphenyl)-1-phenylethanol (**1**) was effected with sodium nitrite in 50% aqueous acetic acid at 0 and 30°, yielding the deoxybenzoins **2**¹⁴ and **3**¹⁵ and 3-phenylbenzofuran (**4**)¹⁶ (eq 1). The product compositions are recorded in

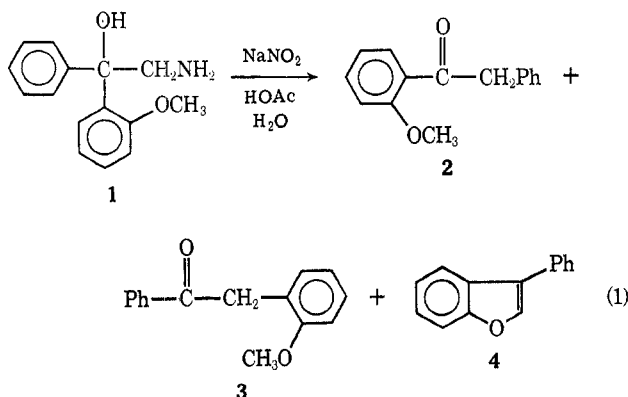


Table I. Determination of product composition was accomplished by glpc analysis of the total neutral

TABLE I
PRODUCT COMPOSITION IN DEAMINATION OF SEMIPINACOL 1

Product	Yield, %	
	0°	30°
2	47.1	42.5
3	11.6	12.6
4	26.7	18.8

product (freed of polymer by filtration through alumina) to determine the ratio of **4** to the mixture of **2** and **3**, followed by nmr spectral analysis to determine the ratio of **2** to **3** (see Experimental Section). Compounds **2**, **3**, and **4** were synthesized independently and known mixtures were prepared to standardize the analyses.

Since a mechanism can be drawn for further reaction *via o*-methoxy oxygen attack on the protonated keto group, control experiments were performed to demonstrate that **3** was in fact stable to the deamination conditions. Ketones similar to **2** are known⁹ to be stable to these conditions. The furan **4** would not be expected to decompose under these conditions, although vigorous conditions (polyphosphoric acid at 132° for 2 hr) cause a clean isomerization to 2-phenylbenzofuran

(13) M. Tiffeneau, A. Oryékhoff, and M. Roger, *Bull. Soc. Chim. Fr.*, **49**, 1757 (1931). It should be noted that *Chem. Abstr.*, **26**, 2423 (1932), contains errors in the translation of this article, substituting twice *m*- for *o*-MeOC₆H₄ and once *p*- for *m*-MeOC₆H₄ at critical points.

(14) M. O. Farooq, W. Rahman, M. Ilyas, and S. Jehan, *Chem. Ber.*, **94**, 1996 (1961).

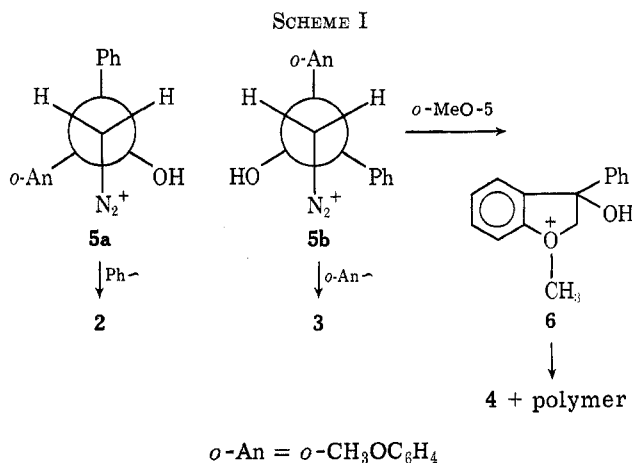
(15) Å. Spetz, *Acta Chem. Scand.*, **10**, 1422 (1956).

(16) W. Davies and S. Middleton, *J. Chem. Soc.*, 822 (1958).

(80%);¹⁶ furthermore, **4** is largely insoluble in the reaction medium, as are **2** and **3**.

Discussion

Examination of the data in Table I shows that the *apparent* migratory aptitude of *o*-methoxyphenyl relative to phenyl (the ratio **3/2**) is 0.25 at 0° and 0.30 at 30°. This would appear to be in agreement with the results obtained from the rearrangement of the symmetrical di-*o*-anisyl-diphenyl glycol.^{2,5b,6,7} However, the presence of **4** in the product mixture demonstrates that *o*-MeO-5 involvement⁸ is important and must arise from the rotamer which should otherwise lead to *o*-methoxyphenyl migration (see Scheme I). Thus it is



apparent that the term "migratory aptitude" should not be applied in cases of this sort, since it does not reflect a proper comparison of total product formation. This is the first case in which *o*-MeO-5 involvement has been demonstrated in deaminative rearrangement.¹⁷ Further, the relative proportions of **2** and **3** are considerably different from those previously reported (1:1).¹³

Scheme I portrays what we believe to be the best explanation of the observed results of deamination of semipinacol **1**. We represent the reactive intermediates as diazonium ions in which aryl migration and/or methoxy oxygen involvement take place in an anti relationship with the leaving group. Such a mechanism is generally accepted in reactions of this type, particularly in primary amines.^{9,18-22} In an elegant stereo- and radiochemical study, Benjamin, Schaeffer, and Collins²³ showed that the deamination of optically active and radiolabeled 2-amino-1,1-diphenyl-1-propanol proceeded with 12% retention of configuration at the migration terminus. This result was interpreted in terms of classical carbonium ions as the active intermediates, with phenyl migration occurring in accord

(17) Oxygen involvement of a different type is known, as, for example, carbonyl participation in deamination of glutamine: A. T. Austin and J. Howard, *Chem. Ind. (London)*, 1413 (1959).

(18) D. J. Cram and J. E. McCarty, *J. Amer. Chem. Soc.*, **79**, 2866 (1957).

(19) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957), and references cited therein.

(20) D. V. Banthorpe in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, London, 1968, Chapter 10.

(21) R. D. Guthrie, *J. Amer. Chem. Soc.*, **89**, 6718 (1967).

(22) M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966).

(23) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Amer. Chem. Soc.*, **79**, 6160 (1957).

with the "cis effect,"^{20,21} a later interpretation was based on ground-state conformational control.¹⁰ Nevertheless, in the present case a primary carbonium ion would be necessary in order to parallel the mechanism of Collins and coworkers,²³ and we believe that Scheme I is a better choice here.

Two comments on the details of Scheme I are in order. First, the high proportion of the apparently less sterically favorable ion **5a** (see Table I) might be influenced by a high population of the ground-state conformation leading to **5a** because of more favorable hydrogen bonding between methoxy and amino groups (not possible in the ground-state conformation leading to **5b**) as well as between amino and hydroxyl groups. Matsumoto, *et al.*,²⁴ have presented evidence for the importance of RO...HO bonding in *o*-alkoxy glycols, and molecular models indicate that this might be a favorable arrangement in the present instance; the nmr spectrum of **1** shows shielding of the methoxy group compared with precursors which lack the amino group, but we do not regard this as definitive. This argument assumes that migration is competitive with central C-C bond rotation.^{19,23} Second, we feel that the products **3** and **4** do not completely reflect the amount of starting material reacting through ion **5b**; we believe that "polymer" (*i.e.*, yellow material lost by filtration of the reaction products through alumina) is formed mainly, though not exclusively, through ion **6** in Scheme I. Our reasoning is as follows. Curtin and Crew^{9f} showed that, in the *p*-methoxy analog of **1** and in related semipinacols, ketones were recovered in 97–100% of the theoretical yield. (See Results section for comments on the stabilities of our products to the reaction conditions.) Thus it appears that, in the absence of oxygen involvement of the type depicted in **6**, deamination proceeds cleanly to ketonic (and monomeric) products. Furthermore, comparison of the results at 30° with those at 0° appears to reinforce this argument. At the higher temperature the proportion of phenyl migration (**5a** → **2**) decreases, *o*-methoxyphenyl migration (**5b** → **3**) increases slightly, and production of **4** decreases substantially while "polymer" formation increases markedly; these results are in general agreement with expectations of increased polymer formation at higher temperature. The nature of this polymeric material has not been explored, but several possibilities for diversion of **6** to products other than **4** can be envisaged; for example, capture of **6** by water or acetic acid could give either glycol or hydroxy acetate which could undergo various acid-catalyzed decompositions.

We are presently conducting further experiments which we hope will shed more light on the role of the *o*-methoxyphenyl group in rearrangements of a nature similar to that reported here.

Experimental Section

All melting points were determined in open capillary tubes in a Thomas-Hoover melting-point apparatus and are uncorrected. Infrared (ir) spectra were recorded on Beckman IR-8 and Perkin-Elmer 700 spectrophotometers. Nuclear magnetic resonance (nmr) spectra were recorded on a Hitachi Perkin-Elmer R-20 60-MHz spectrometer. Ultraviolet (uv) spectra were recorded on a

Perkin-Elmer 202 spectrophotometer in solvent ethanol. Gas-liquid partition chromatography (glpc) was performed on a 6 ft × 0.25 in. SE-30 column at 209° in a Loenco 2400 gas chromatograph with a helium carrier gas flow rate of about 60 cm³/min.

2-Bromo-2'-methoxyacetophenone.—The procedure of Buckman, *et al.*,²⁵ was followed. The yield of bromo ketone was 80%: bp 130° (1 mm); ir (neat) 1680 cm⁻¹ (C=O); nmr (CCl₄) δ 7.3 (4 H, m, ArH), 4.39 (2 H, s, CH₂Br), and 3.96 (3 H, s, OCH₃).

2-Azido-2'-methoxyacetophenone.—A solution of sodium azide (0.975 g, 15.0 mmol) in water (3 ml) was added at once with stirring to the above bromo ketone (3.00 g, 13.1 mmol) dissolved in ethanol (7.5 ml). Within 30 min there appeared a suspension of pale yellow oil which solidified on cooling. The solid was filtered and washed repeatedly with water until a silver nitrate test for bromide ion in the wash water was negative. After drying, 2.24 g (89%) of crude azide was recovered. It was recrystallized to constant melting point from methanol: mp 45–46°; ir (Nujol) 2130 (strong, N₃), 2210 (weak, N₃), and 1675 cm⁻¹ (C=O); nmr (CCl₄) δ 7.3 (4 H, m, ArH), 4.32 (2 H, s, CH₂N₃), and 3.95 (3 H, s, OCH₃).

Anal. Calcd for C₉H₉N₃O₂: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.82; H, 4.93; N, 21.96 (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.).

2-Amino-2'-methoxyacetophenone Hydrochloride.—A suspension of 5% palladium on charcoal (0.375 g) in absolute ethanol (2 ml) was stirred under hydrogen at 1 atm pressure and room temperature for 10 min. A solution of the above azido ketone (1.00 g) in acidified ethanol (2.6 ml of 36% hydrochloric acid in 7.8 ml of absolute ethanol) was admitted into the catalyst-ethanol mixture and allowed to react for 29 hr. The mixture was filtered, the catalyst was washed with three small portions of absolute ethanol, and the solution was concentrated on a rotary evaporator. Absolute ether was added until moderate precipitation of product occurred. After 9 days of refrigeration the solid was collected, washed with absolute ether, and dried to yield 0.763 g (72%) of the white, crystalline salt: mp (methanol-benzene) 165.0–165.6° dec; ir (CCl₄) 2700 (NH₃⁺), 2580 (NH₃⁺), and 1665 cm⁻¹ (C=O); nmr (DMSO-*d*₆) δ 8.62 (3 H, s, NH₃⁺), 7.4 (4 H, m, ArH), 4.35 (2 H, s, COCH₂), and 3.56 (3 H, s, OCH₃).

2-Amino-1-(2-methoxyphenyl)-1-phenylethanol (1).—The Grignard reagent was prepared in flame-dried apparatus, and these procedures were carried out under an atmosphere of dry nitrogen. Phenylmagnesium bromide was prepared by reaction of dry bromobenzene (1.87 g, 11.9 mmol) with magnesium turnings (0.29 g, 12.1 mmol) in absolute ether (5 ml). The finely powdered amine salt from the previous procedure (0.402 g, 2.0 mmol) was added in small portions with stirring over 65 min, and the mixture was allowed to reflux gently in an oil bath for 4.5 hr. The reaction mixture was then poured into a solution of ammonium chloride (0.5 g) in water (10 ml plus one drop of concentrated ammonium hydroxide). After hydrolysis was complete, the layers were separated, the aqueous layer was extracted twice with ether, and the ether extracts were pooled with the original organic phase. After drying (MgSO₄), the solution was filtered, diluted with absolute ether (40 ml), and acidified with gaseous hydrogen chloride. A white precipitate formed at once, and after prolonged addition of hydrogen chloride a pink solid began to appear. At this point addition of the gas was stopped and the flask was refrigerated for 2 days. The product was then filtered, washed with ether, and allowed to dry, yield 0.298 g (53%), mp 168–169° (lit.¹³ mp 175–176°).

The free amine **1** was obtained by dissolving the hydrochloride (0.500 g) in water (5 ml) and adding 1 *M* sodium hydroxide (*ca.* 2 ml) dropwise. The resulting suspension was extracted with chloroform and the organic phase was dried (MgSO₄) and solvent was removed on a rotary evaporator. After recrystallization to constant melting point from chloroform-ether, the amine was obtained as white crystals: mp 104–106° (lit.¹³ mp 107–108°); ir (CDCl₃) 3485 cm⁻¹ (NH₂); nmr (CDCl₃) δ 7.0 (9 H, m, ArH), 3.48 (3 H, s, OCH₃), 3.37 (1 H, d, *J* = 13 Hz, CHNH₂), 3.09 (1 H, d, *J* = 13 Hz, CHNH₂), and 2.0 (3 H, s, broad, NH₂ and OH).

2-Methoxydeoxybenzoin (2).—The reaction of 2-methoxybenzamide with benzylmagnesium bromide was carried out according to the procedure of Farooq, *et al.*¹⁴ Purification of the product was effected by application of 15 g of the crude product to a column of 575 g of silica gel and elution with ether-pentane (1:4): ir (neat) 1675 cm⁻¹ (C=O); nmr (CDCl₃) δ 7.2 (9 H, m, ArH),

(24) K. Matsumoto, R. Goto, T. Asano, and H. Wada, *Nippon Kagaku Zasshi*, **88**, 92 (1967).

(25) S. J. Buckman, J. D. Pera, and F. W. Raths, German Patent 1,174,017 (1964); *Chem. Abstr.*, **61**, 9987d (1964).

4.27 (2 H, s, COCH₂), 3.83 (3 H, s, OCH₃); uv $\lambda_{\text{max}}^{\text{EtOH}}$ 207, 247, 313 nm.

2-Methoxybenzil.—By the procedure of Farooq, *et al.*,¹⁴ 2-methoxydeoxybenzoin (2) (3.930 g, 17.39 mmol) was oxidized with selenium dioxide (2.12 g, 19.13 mmol) in acetic anhydride (35 ml). Chromatography of the resulting oil on silica gel with petroleum ether (bp 30–60°)—chloroform (1:1) provided 2.867 g (69%) of nearly pure 2-methoxybenzil as a yellow oil which slowly crystallized, mp 67–69°, plus ca. 0.6 g of impure material.

The material prepared as above was identical with another sample prepared by benzoin condensation between 2-methoxybenzaldehyde and benzaldehyde, followed by oxidation of the product with potassium permanganate, as described by Brass, *et al.*:²⁶ mp 70.1–7° (lit.²⁶ mp 71–72°); ir (CCl₄) 1655 and 1676 cm⁻¹ (C=O); nmr (CCl₄) δ 7.4 (9 H, m, ArH) and 3.45 (3 H, s, OCH₃).

2-Hydroxybenzil.—By the procedure of Somin and Kuznetsov,²⁷ 2-methoxybenzil was fused with several times its volume of freshly prepared pyridine hydrochloride under nitrogen at 180° for 2 hr. 2-Hydroxybenzil was obtained as an amber oil (64%) which was only slightly impure as judged by thin layer chromatographic analysis on silica gel: ir (neat) 3350 (OH, very broad), 1720, 1675, 1630 cm⁻¹ (C=O); nmr (CDCl₃) δ 12.4 (1 H, broad s, ArOH) and 7.6 (9 H, m, ArH).

2'-Hydroxydeoxybenzoin.—2-Hydroxybenzil was reduced by the procedure of Spetz¹⁵ to give 2'-hydroxydeoxybenzoin as a yellow solid (60%). This was crystallized from ethanol-water to give tan flakes: mp 126–130° (lit.¹⁵ mp 110–120° dec); ir (CCl₄) 3490 (OH) and 1675 cm⁻¹ (C=O); nmr (acetone-*d*₆) δ 8.6 (1 H, broad s, OH), 7.5 (9 H, m, ArH), and 4.33 (2 H, s, CH₂).

2'-Methoxydeoxybenzoin (3).—2'-Hydroxydeoxybenzoin was methylated by the procedure of Spetz¹⁵ to provide 3 as a light yellow, crystalline solid (94%): mp 56–58° [crystallization from a small volume of methanol raised the melting point to 58.5–59.5°; successive crystallizations of a portion of the solid from small quantities of methanol gave mp 60–61° (lit.¹⁵ mp 61.5–62°)]; ir (CCl₄) 1683 cm⁻¹ (C=O); nmr (CDCl₃) δ 7.4 (9 H, m, ArH), 4.27 (2 H, s, CH₂), and 3.74 (3 H, s, OCH₃); uv $\lambda_{\text{max}}^{\text{EtOH}}$ 204, 243 nm.

3-Phenylbenzofuran (4).—The procedure of Davies and Middleton¹⁶ was followed: bp 115° (1 mm) [lit.¹⁶ bp 110° (0.3 mm)]; n_{D}^{25} 1.6308 (lit.²⁸ n_{D}^{25} 1.6296); ir (neat) 860 cm⁻¹ (furan band²⁹); nmr δ 7.4 (m); uv $\lambda_{\text{max}}^{\text{EtOH}}$ 205, 270 nm.

The ir spectrum of this authentic 3-phenylbenzofuran was identical with that of the deamination product 4; its retention time on glpc, which was the same as that of 4 (6.3 min), was unchanged on admixture with 4.

Deamination of 1.—The aminoethanol 1 (199.6 mg) was dissolved in 50% aqueous acetic acid and the solution was placed in an ice bath. A solution of sodium nitrite (284 mg, a fivefold excess) in water (2 ml) was added dropwise with stirring over 5 min, and the mixture was allowed to stir for 24 hr at 0°. At the end of this period, the reaction was quenched by adding a 10% aqueous sulfamic acid solution dropwise until the solution no longer gave a positive test with starch-iodide paper. The reaction mixture was transferred to a continuous extractor, diluted with water (21 ml), and subjected to continuous extraction with petroleum ether for approximately 8 hr. The extract was stirred with anhydrous potassium carbonate until the solution was neutral; then it was filtered and the potassium carbonate residue was dissolved in water and extracted with chloroform. These extracts were dried (MgSO₄) and combined with the original organic phase. After removal of the solvent on a rotary evaporator,

the crude product weighed 160.5 mg. This mixture was dissolved in 5 ml of ether and filtered through 2 g of neutral alumina. The nonpolymeric products were readily eluted with ca. 20 ml of ether; removal of solvent left 151.6 mg of an oil. This mixture was subjected to the analysis described below; results are recorded in Table I.

A similar run was carried out with 200.2 mg of 1 in an oil bath at 30 ± 1° for 4 hr. After continuous extraction the crude product weighed 162.4 mg; after elution through alumina, 133.0 mg of mixture was recovered. This was subjected to the analysis described below; results are recorded in Table I. Repeat runs gave similar results.

The 3-phenylbenzofuran could be separated from the deoxybenzoin by chromatography on silica gel (100–200 mesh). Product 4 was eluted with ether-petroleum ether (2:98), and 2 and 3 were eluted with ether.

Determination of the Ratio of 4 to 2 + 3 in Deamination Products.—A mixture of known composition was prepared from 4 and the deoxybenzoin separated on column chromatography; this was dissolved in ether and analyzed by glpc to determine detector response to each of the two peaks in the chromatogram. The retention time for 4 was 6.3 min, and that of the deoxybenzoin mixture was 12.1 min. Then the product mixtures from the deamination runs were analyzed by glpc with appropriate detector-response corrections applied to the measured peak areas (planimeter).

Determination of Proportions of 2 and 3 in Deamination Products.—Standard mixtures of the two deoxybenzoin 2 and 3 were prepared such that each mixture weighed ca. 50 mg. These mixtures were 75.8, 79.6, and 83.6% in 2. Each of these deoxybenzoin mixtures was dissolved in 0.3 ml of CDCl₃ and its nmr spectrum was recorded. The methoxy proton peaks of the two compounds differ in chemical shift by 6.4 Hz in this solvent and at this concentration, and expansion of the sweep to 120 Hz separates the two signals. The integrations of the expanded methoxy peaks of the standards were used for comparison with those of the deamination samples. Peak-height ratios of these signals in the standard mixtures, determined at both 600- and 120-Hz sweep widths, were also determined and plotted against composition. The ratio of 2 to 3 in the alumina-filtered deamination mixture was determined by the nmr integration and by comparison with the peak-height ratio plots. Agreement between the values determined by these methods was within ±1%. It was demonstrated that presence of 4 in the deamination samples had no effect on this analysis.

Control Experiment.—Compound 3 (50 mg) was subjected to the deamination conditions described above. Similar work-up followed by continuous extraction recovered 44 mg of crystalline material; this was filtered through alumina and then analyzed by glpc. The material was indicated to be pure 3.

Registry No.—1, 34589-94-1; 2, 33470-10-9; 3, 27356-33-8; 4, 1839-72-1; 2-bromo-2'-methoxyacetophenone, 31949-21-0; 2-azido-2'-methoxyacetophenone, 34635-38-6; 2-amino-2'-methoxyacetophenone HCl, 34589-97-4; 2-methoxybenzil, 34082-43-4; 2-hydroxybenzil, 34589-99-6; 2'-hydroxydeoxybenzoin, 2491-31-8.

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