N hydrochloric acid afforded a tan powder which was redissolved in dilute sodium hydroxide; the basic solution was treated with charcoal, boiled, filtered and reacidified. In this way there was obtained 53.0 g. (96%) of II, melting at 251–255° dec. After two crystallizations from methanol, the melting point was constant at 262–265° dec.

Anal. Calcd. for $C_{13}H_8O_2Se$: C, 56.06; H, 2.92; neut. equiv., 275.2. Found: C, 56.49; H, 2.99; neut. equiv., 278.

Ultraviolet Absorption Spectra.—The ultraviolet spectrum of 4-carboxydibenzoselenophene displayed maxima at 288 mμ, log ε 3.81; 296 mμ, log ε 3.76; 342 mμ, log ε 3.46. The spectrum of the sulfur analog, 4-carboxydibenzothiophene, showed maxima in mμ at 282, log ε 3.85; 340, log ε 3.51. In the region of the spectra investigated (260–350 mμ) 2-carboxydibenzothiophene had no maxima.

4-Valeryldibenzoselenophene.—When carbonation was effected in the reverse order, by adding powdered carbon dioxide to the mixture containing the lithium salt, no acidic fraction was obtained. When the ether layer was stripped of solvent, the residue was crystallized from methanol. Yellow crystals (37.2 g., 59%), which are presumed to be 4-valeryldibenzoselenophene were thus obtained, melting at 102–108°. After one recrystallization from the same solvent, the melting point was constant at 107–108°.

Anal. Calcd. for $C_{17}H_{16}SeO$: C, 64.76; H, 5.12. Found: C, 64.96; H, 5.21.

A 2,4-dinitrophenylhydrazone, prepared in ethanol and recrystallized from ethanol–acetone, was constant melting at 245–255° dec.

Anal. Calcd. for $C_{23}H_{20}N_4O_4Se$: C, 55.75; H, 4.07. Found: C, 55.68; H, 4.11.

4-Methyldibenzoselenophene.—From 46.2 g. (0.2 mole) of dibenzoselenophene, 0.8 mole of *n*-butyllithium and 25.2 g. (0.2 mole) of dimethyl sulfate, according to a previously described procedure,[3] there was obtained 39.2 g. (80%) of 4-methyldibenzoselenophene. The crude pink crystals melted at 75–80°; after two recrystallizations from low-boiling petroleum ether, the melting point was constant at 83–84°.

Anal. Calcd. for $C_{13}H_{10}Se$: C, 63.68; H, 4.11. Found: C, 63.86; H, 4.14.

4-Iododibenzoselenophene.—Using the method of Gilman and Summers,[12] from 0.2 mole of I and 0.8 mole of *n*-butyllithium, there was obtained 36.4 g. (51%) of white crystals, melting at 96–100°. After one recrystallization from ethanol, the material was constant melting at 99–100°.

Anal. Calcd. for $C_{12}H_7ISe$: C, 40.36; H, 1.97. Found: C, 40.87; H, 2.03.

4-Carboxydibenzoselenophene-5-oxide (III).—The method of McCullough, *et al.*,[11] afforded a quantitative yield of the oxide from 5.5 g. (0.02 mole) of the acid II. The material decomposed at 192–194° (with the evolution of oxygen), and then melted at 260–265° with decomposition (the melting point of (II)).

Anal. Calcd. for $C_{13}H_8O_3Se$: C, 53.62; H, 2.76; iodometric equiv. wt., 291.2. Found: C, 53.44; H, 2.82; iodometric equiv. wt., 292.

Salts.—The strychnine salt of III was prepared by dissolving equimolar quantities of the acid and alkaloid in a small volume of 95% ethanol, boiling for 10 minutes, filtering, adding ether to incipient cloudiness and chilling for an hour. The white crystals were obtained in quantitative yield, decomposing at 170–177°. One crystallization from the same solvent changed the decomposition point to 169–171°, $[\alpha]^{23}D$ 0.00° in the concentration range of 0.2 to 2.0%, in 95% ethanol. Further purification failed to change the melting point or the specific rotation.

Anal. Calcd. for $C_{34}H_{30}N_2O_6Se$: C, 65.28; H, 4.83; N, 4.47. Found: C, 65.19; H, 4.89; N, 4.71.

In an attempt to obtain the free acid, the salt was treated with 10% sodium hydroxide solution, stirred and filtered to remove the liberated strychnine; when the filtrate was acidified with 10% aqueous sulfuric acid, the material recovered, in quantitative yield, was the reduced acid II. Its identity was established by a mixed melting point with an authentic sample.

With cinchonine, quinine and brucine there were obtained oils or non-purifiable mixtures.

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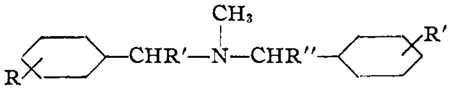
Catalytic Debenzylation. IV. The Competitive Hydrogenolysis of Benzyl-like Groups Attached to Different Nitrogen Atoms

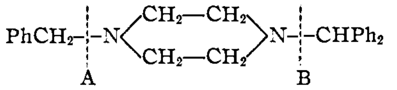
BY RICHARD BALTZLY AND PETER B. RUSSELL

RECEIVED MAY 13, 1954

In previous papers in this series[1–3] the effect of substitution, both in the aromatic nuclei and on the α-positions, on the relative ease of cleavage of the benzyl groups in a dibenzylmethylamine (I) by hydrogenolysis has been studied. The results are open to objection on the grounds that the substitution in one nucleus might have an effect on the ease of cleavage of the other.[4] Indeed that some such effect does in fact operate is quite obvious since the over-all rate of hydrogenolysis is a function of the total substitution in I rather than the substitution of the benzyl group removed.[2]



I



II

The present communication presents a brief series of experiments which show clearly that the *relative* ease of cleavage of a benzyl group from I is a function of the substitution *in that group alone* and not in I as a whole.

The first experiments were carried out with N-benzyl-N′-benzhydrylpiperazine (II). Here although both benzyl-like groups are in the same molecule they are attached to different isolated nitrogen atoms and presumably the above objections no longer apply. Hydrogenolysis of II under the usual conditions[1–3] in the absence of added acid (redn. 1) gave predominately the cleavage A (*ca.* 70%) with some cleavage B (30–40%). In acid solution (redn. 2), however, the cleavage was almost unilateral in the direction A.

Similar results were obtained when a mixture of N-benzhydryl-N′-methyl- and N-benzyl-N′-methylpiperazines was hydrogenated. Under acid conditions (redn. 4) the benzhydryl group was cleaved to a less extent than in the absence of acid (redn. 3) (19:35).

These results are in accord, qualitatively at

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[12] H. Gilman and L. Summers, THIS JOURNAL, **72**, 2767 (1950).

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

[2] R. Baltzly and P. B. Russell, *ibid.*, **72**, 3410 (1950).

[3] *Idem*, *ibid.*, **75**, 5598 (1953).

[4] H. Dahn, P. Zoller and V. Solms, *Helv. Chim. Acta*, **37**, 565 (1954).

TABLE I

Reduction	Substrate	Moles hydrogen absorbed in hr.		Products, %	Cleavage
		Mole	Hr.		
1	II[a] (0.01 mole)	0.011	3.5	Diphenylmethane,[b] 40	
	No acid added			Benzylpiperazine,[c] 24	B
				Benzhydrylpiperazine,[d] 70	A
2	II (0.01 mole)	.013	3.0	Diphenylmethane,[b] 7	B
	Excess HCl added			Benzhydrylpiperazine,[d] 90	A
3	Benzyl-(0.01 mole) and benzhydryl-(0.01 mole) methylpiperazines; no acid added	.012	1.0	Diphenylmethane,[b] 35	
4	As above with added acid	.012	5.5	Diphenylmethane,[b] 19	
5	p-Aminobenzyldimethylamine[e] (0.01 mole) and p-methoxybenzyldimethylamine[f] (0.01 mole) acid added	.009	8	p-Methoxytoluene, 10	
				p-Toluidine,[g] 65	

[a] H. Morren, S. Trobin, R. Denayer, E. Grivsky and J. Marcia, *Bull. soc. chim. Belg.*, **60**, 282 (1951). [b] Estimated as tetranitrodiphenylmethane.[3] [c] M.p. of hydrochloride 253° (R. Baltzly, *et al.*, THIS JOURNAL, **66**, 263 (1944)). [d] M.p. 70–72° (K. E. Hamlin, A. W. Weston, F. E. Fischer and R. J. Michaels, *ibid.*, **71**, 2731 (1947)). [e] Prepared by *in situ* reduction of the nitro compound (Bennett and Willis, *J. Chem. Soc.*, 264 (1929)), with a platinized charcoal catalyst. [f] For hydrochloride see Tiffeneau, *Bull. soc. chim.*, **9**, 825 (1911). [g] Isolated as p-acetamidotoluene.

least, with the previously recorded observations[3,5] that in basic solution I ($R = R' = R''' = H$; $R'' = Ph$) on hydrogenolysis gives only about 10–15% of benzhydrylmethylamine whereas in acid solution a 75% yield of this base was isolated. This reversal in direction of cleavage on acidification arises then from properties inherent in the benzyl-N- and benzhydryl-N systems themselves, and is not peculiar to the benzyl-N-benzhydryl combination.

A mixture of equimolecular quantities of p-aminobenzyl- and p-methoxybenzyldimethylamines in acid solution was also hydrogenated (redn. 5) (0.01 mole each). The uptake of hydrogen was slow. From the products 0.001 mole of p-methoxytoluene and 0.006 mole of p-acetamidotoluene were isolated. This indicates that the $H_3{}^+N–C_6H_4CH_2–$ is relatively more readily cleaved than the $H_3CO–C_6H_4–CH_2–$ in accordance with previous experiments on[2] I ($R' = R'' = H'$; $R = p\text{-}\overset{+}{N}H_3$; $R''' = p\text{-}OCH_3$).

Experimental

The methods of hydrogenolysis employed have been described in detail in earlier papers.[1–3] The reductions carried out are given in Table I.

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(5) H. Dahn, V. Solms and P. Zoller, *Helv. Chim. Acta*, **35**, 2117 (1952).

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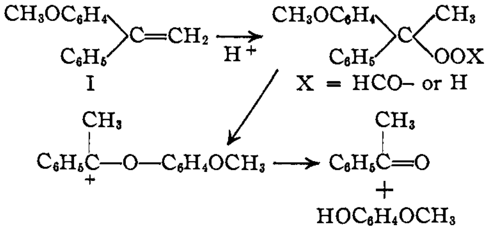
Anomalous Oxidations of 1-p-Anisyl-1-phenylethylene with Performic and Perbenzoic Acid[1]

BY DAVID Y. CURTIN[2] AND ARTHUR BRADLEY

RECEIVED JUNE 23, 1954

It has been found that 1-p-anisyl-1-phenylethylene (I) reacts with hydrogen peroxide in formic acid to give not the expected hydroxyformate but, instead, p-hydroxyanisole (isolated in 16% yield) together with acetophenone in 40% yield. p-Chloro-1,1-diphenylethylene (II), on the other hand, was converted to the hydroxyformate which could be isolated in 30% yield and hydrolyzed to the corresponding glycol in 60% yield.

It appears likely that the reaction of the anisyl olefin I involves the addition to the olefinic double bond of either hydrogen peroxide or performic acid followed by the rearrangement of the intermediate hydroperoxide or perester. Such rearrangements of hydroperoxides and their esters are well known. The migration of the p-anisyl rather than the phenyl ring is in accord with previous studies[3] of this rearrangement. Thus the addition catalyzed by perchloric acid of hydrogen peroxide to the olefin I has been reported to yield the same products obtained above.[4]



The olefin I reacted rapidly with perbenzoic acid at −10° to give what was presumably the corresponding epoxide. The epoxide was not isolated, however, but treated with sodium bisulfite solution, a procedure which has been shown to convert 1,1-diphenylethylene oxide to diphenylacetaldehyde[5] and which in the present case gave 1-p-anisyl-1-phenylacetaldehyde bisulfite addition compound from which the aldehyde III was isolated in a yield of 40%. At temperatures above 0° the yield of alhyde III fell markedly and when the oxidation was carried out at room temperature by adding the perbenzoic acid rapidly to the olefin a vigorous exothermic reaction ensued and instead of III, a new aldehyde, α-hydroxy-p-anisyl-phenylacetaldehyde (IV), was formed in 50% yield after decomposition of the sodium bisulfate adduct. The hydroxyaldehyde IV was characterized by reduction with lithium aluminum hydride to 1-p-anisyl-1-phenyl-1,2-ethanediol (V). The glycol V was also obtained in small yield as its monobenzoate from the original perbenzoic acid oxidation.

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(1) Taken from the Ph.D. Dissertation presented to Columbia University in 1952 by Arthur Bradley.

(2) Department of Chemistry, University of Illinois, Urbana, Ill.

(3) See E. G. E. Hawkins, *Quart. Revs.*, **4**, 269 (1950).

(4) M. Kharasch, A. Fone, W. Nudenberg and A. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).

(5) A. Klages and J. Kessler, *Ber.*, **39**, 1754 (1906).