TABLE I

Reduction	Substrate	Moles hydrogen absorbed in hr.		Products, %	Cleavage
		Mole	Hr.		
1	II[a] (0.01 mole) No acid added	0.011	3.5	Diphenylmethane,[b] 40	
				Benzylpiperazine,[c] 24	B
				Benzhydrylpiperazine,[d] 70	A
2	II (0.01 mole) Excess HCl added	.013	3.0	Diphenylmethane,[b] 7	B
				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 $H_3{}^+N\text{–}C_6H_4CH_2\text{–}$ is relatively more readily cleaved than the $H_3CO\text{–}C_6H_4\text{–}CH_2\text{–}$ 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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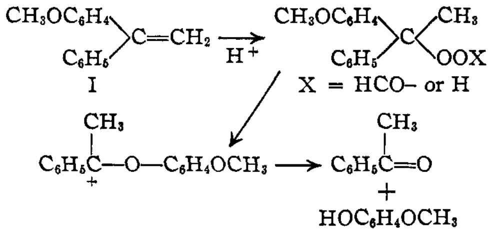
Anomalous Oxidations of 1-*p*-Anisyl-1-phenylethylene with Performic and Perbenzoic Acid[1]

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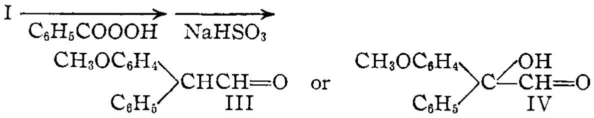
(1) Taken from the Ph.D. Dissertation presented to Columbia University in 1952 by Arthur Bradley.

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

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

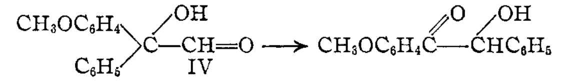
(4) M. Kharasch, A. Fone, W. Nudenberg and A. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).

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



The origin of the hydroxyaldehyde IV was not determined. Weisenborn and Taub[6] obtained a similar product from the reaction of 1-phenyl-1-*p*-xenylethylene with two moles of perbenzoic acid. They postulated that the aldehyde, phenyl-*p*-xenylacetaldehyde, first formed, enolized and that perbenzoic acid oxidation of the enol led to the hydroxyaldehyde. In the present case, however, the aldehyde III is not an intermediate in the formation of the hydroxyaldehyde IV since perbenzoic acid converts III not to IV but to *p*-methoxybenzhydrol in about 50% yield (based on unrecovered starting material).

The hydroxyaldehyde IV, when refluxed with 1 *N* potassium hydroxide, underwent rearrangement to 4-methoxybenzoin.



Although an acid-catalyzed version of this rearrangement is well known[7] we know of no previous example of such a base-catalyzed rearrangement of an hydroxyaldehyde. The reaction is analogous to known base-catalyzed rearrangements of hydroxy ketones.[8] It was found that the rearrangement of the hydroxy aldehyde IV to 4-methoxybenzoin occurred even on distillation at 12 mm. pressure. Since 4′-methoxybenzoin is known to rearrange to 4-methoxybenzoin either on treatment with base or on distillation at 1 mm. pressure,[9] it is impossible to say whether or not it, also, was initially formed in the rearrangement of IV.

Experimental[10]

1-*p*-Anisyl-1-phenylethylene (I).—This olefin was prepared in 80% yield by dehydration of the crude carbinol obtained from *p*-methoxyacetophenone and phenylmagnesium bromide by shaking in five times its volume of warm 15% sulfuric acid. The olefin solidified on cooling and was recrystallized from ether–ligroin (4/1). It had m.p. 74–75° (lit.[11] m.p. 75°).

1-*p*-Chlorophenyl-1-phenylethylene (II) (b.p. 165° (15 mm.), $n^{28}\text{D}$ 1.6115)[12] was obtained in 83% yield by distillation of the crude product obtained by the addition of phenylmagnesium bromide to *p*-chloroacetophenone.

Oxidation of I.—To 10.2 g. (0.049 mole) of 1-*p*-anisyl-1-phenylethylene (I) in 100 ml. of 90% formic acid was added with stirring 9 ml. (a 50% excess) of 30% formic acid over a period of 1 hour. The reaction was exothermic and the temperature was maintained at 40° by cooling. After the addition was completed the stirring was continued for 1 hour longer. The remaining hydrogen peroxide was decomposed with 3 g. of sodium bisulfite and the formic acid and water distilled under reduced pressure (15 mm.). Extraction with 5% sodium carbonate followed by acidification of the aqueous extracts yielded 16% of the theoretical amount of *p*-hydroxyanisole, m.p. 53–55°.[13] Distillation of the neutral fraction at 75° and 1 mm. pressure gave 4.4 g. of colorless liquid of which 55% was acetophenone as judged from the amount which could be converted to the 2,4-dinitrophenylhydrazone (m.p. 245–247° without recrystallization). The yield of acetophenone as the dinitrophenylhydrazone was thus 42%.

Oxidation of 1-*p*-Chlorophenyl-1-phenylethylene (II) **with Performic Acid.**—This oxidation was carried out in the same way as the oxidation of I, above. However in this case the neutral fraction of the product from 30 g. (0.14 mole) of II was extracted with 20% benzene in petroleum ether, evaporation of which left an oil (36 g.) which, when scratched with a glass rod under petroleum ether, crystallized to yield 25 g. of white solid. Recrystallization from a mixture of chloroform and petroleum ether gave 12.5 g. (0.045 mole, 32%) of a **monoformate ester of 1-*p*-chlorophenyl-1-phenylethanediol,** m.p. 85°.

Anal. Calcd. for $C_{15}H_{13}ClO_3$: C, 65.2; H, 4.7; Cl, 12.9. Found: C, 65.3; H, 4.8; Cl, 12.7.

Hydrolysis of the formate ester (0.85 g.) by treatment with 100 ml. of 1 *N* sodium hydroxide under reflux for 10 minutes yielded 0.46 g. (60%) of **1-*p*-chlorophenyl-1-phenylethanediol,** m.p. 89–90° (mixed m.p. with formate ester 67–69°) after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{14}H_{13}ClO_2$: C, 67.6; H, 5.2; Cl, 14.3. Found: C, 67.7; H, 5.1; Cl, 14.1.

Reaction of I with Perbenzoic Acid. (a) **At −10° to Give *p*-Anisylphenylacetaldehyde** (III).—To 36 g. (0.17 mole) of I in 100 ml. of dry chloroform at −10° was added 0.19 mole of perbenzoic acid in a titrated chloroform solution[14] over a period of 1 hour. Titration indicated that the theoretical amount of peracid reacted almost immediately. The cold solution was extracted with 10% sodium carbonate and the solvent removed under reduced pressure. Sodium metabisulfate (45 g.) in 75 cc. of water was added and the mixture shaken vigorously for 20 minutes. The mixture was allowed to stand for 24 hours during which time the bisulfite addition compound with warm sodium carbonate solution yielded III which after distillation at 8–10 mm. (b.p. 180–192°) amounted to 16 g. (0.07 mole, 40%). A center cut, b.p. 189–190° (10 mm.), had $n^{25}\text{D}$ 1.5886.

The semicarbazone after recrystallization from a methanol–water mixture melted at 128° in agreement with the report of Tiffeneau and Levy.[15]

(b) **At 5°.**—The reaction was carried out as above except that it was conducted at 0–5° (with 21 g., 0.01 mole, of I) and, when completed, was allowed to warm to room temperature before extraction with sodium carbonate. The sodium bisulfite treatment was carried out as above. Decomposition of the bisulfate addition fraction, however, gave a solid and an oil. The solid was separated by crystallization and was shown to be **α-hydroxy-*p*-anisyl phenyl acetaldehyde (IV)** which after recrystallization from benzene–petroleum ether had m.p. 73–74°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.8. Found: C, 74.7; H, 6.0.

The yield was 30%, but in another experiment in which the perbenzoic acid was added rapidly to the olefin with a subsequent vigorous exothermic reaction the yield of the hydroxyaldehyde was 50%.

The oily aldehyde fraction above, upon distillation, gave 5.0 g. (0.020 mole, 20%) of III, b.p. 190–200° (12 mm.), identified by conversion to the semicarbazone, and 4.5 g. (20%) of 4-methoxybenzoin, b.p. 215–225° (12 mm.), m.p. 106–107° (lit.[16] 106°) after recrystallization from benzene. A mixed m.p. with authentic 4-methoxybenzoin showed no depression.

From the benzene used to wash the bisulfite addition fraction was isolated a 5% yield of a **monobenzoate of 1-*p*-anisyl-1-phenylethanediol,** m.p. 142° after recrystallization from chloroform–petroleum ether.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.9; H, 5.7. Found: C, 75.7; H, 5.8.

Saponification with refluxing 1 *N* potassium hydroxide for

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[6] F. Weisenborn and D. Taub, This Journal, **74**, 1329 (1952).

[7] S. Danilow, *Ber.*, **60**, 2390 (1927).

[8] D. Y. Curtin and S. Leskowitz, This Journal, **73**, 2633 (1951); D. B. Sharp and E. L. Miller, *ibid.*, **74**, 5643 (1952); R. B. Turner, *ibid.*, **75**, 3484 (1953).

[9] J. Buck and W. Ide, *ibid.*, **55**, 855 (1933).

[10] All melting points are corrected. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, N. Y.

[11] R. Stoermer and M. Simon, *Ber.*, **37**, 4163 (1904).

[12] E. Bergmann and A. Bondi, *ibid.*, **64**, 1468 (1931).

[13] R. Robinson and J. C. Smith, *J. Chem. Soc.*, 392 (1926).

[14] G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

[15] M. Tiffeneau and J. Levy, *Bull. soc. chim.*, **39**, 782 (1926).

[16] S. Jenkins, This Journal, **56**, 682 (1934).

1 hour gave 1-*p*-anisyl-1-phenylethanediol (V), m.p. 103–104 after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.6. Found: C, 73.3; H, 6.9.

Reduction of α-Hydroxy-1-*p*-anisyl-1-phenylacetaldehyde to 1-*p*-Anisyl-1-phenylethanediol (V).—The hydroxyaldehyde IV (0.5 g.) was reduced with lithium aluminum hydride in ether[17] to give 0.45 g. of solid, which after recrystallization from benzene–petroleum ether melted at 104–105°. The m.p. of a mixture with the sample obtained above showed no depression.

This glycol did not react with sodium bisulfite solution under conditions even more rigorous than those which caused the corresponding epoxide to rearrange.

Rearrangement of IV in Base.—A solution of 0.53 g. (0.0022 mole) of IV in 40 cc. of 50% aqueous methanol containing 1.0 g. of potassium hydroxide was heated under reflux for 1 hour. After the addition of 40 cc. of water and cooling a precipitate appeared, which after being filtered and dried, weighed 0.48 g., m.p. 85–100°. After two recrystallizations from chloroform–petroleum ether 0.25 g. (0.0010 mole, 46%) of 4-methoxybenzoin, m.p. 104–105°, was obtained.

Reaction of *p*-Anisylphenylacetaldehyde (III) with Perbenzoic Acid.—Redistilled III (2.0 g., 0.0089 mole) was allowed to stand for 12 hours with 30 ml. of chloroform containing 1.6 g. (0.0116 mole) of perbenzoic acid. The isolation procedure used above for the reaction of II with perbenzoic acid yielded an oil which did not crystallize and was then chromatographed on alumina. The column was eluted successively with benzene–petroleum ether ($^1/_4$) (200 ml.), pure benzene (200 ml.), and ether–petroleum ether ($^1/_1$) (250 ml.). The first 200-ml. fraction contained 0.70 g. (35%) of recovered starting material, n^{27}_D 1.5860. The third fraction yielded a solid (0.59 g., 31%) which after recrystallization from benzene–petroleum ether was shown to be *p*-methoxybenzhydrol (0.42 g., 0.0020 mole, 23%), m.p. 68°. A mixed m.p. with authentic material showed no depression.

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[17] W. G. Brown, in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 489.

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p-*t*-Butylstyrene and its Polymers

By L. L. Ferstandig, J. C. Butler and A. E. Straus

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The commercial use of polystyrene is often limited by its relatively low heat distortion point. Some success has been attained in overcoming this difficulty, while retaining other desirable properties, by introducing substituents on the benzene ring. Work done in this Laboratory has shown that the new polymer made from *p*-*t*-butylstyrene has the highest heat distortion point (117.8° at 264 p.s.i. fiber stress) yet reported for alkyl-substituted polystyrenes.

p-*t*-Butylstyrene was synthesized by acetylation of *t*-butylbenzene, reduction of the *p*-*t*-butylacetophenone with lithium aluminum hydride to methyl-*p*-*t*-butylphenylcarbinol, and dehydration of the carbinol with potassium bisulfate. The reduction of the ketone with lithium aluminum hydride is an improvement, with respect to yields and simplicity, over those previously reported.[1,2]

p-*t*-Butylstyrene was polymerized in bulk, both thermally and with the aid of peroxide catalyst, to yield hard, clear and colorless polymers with high molecular weight and low methanol solubilities.[3] Some of the polymers were made from spectroscopically pure *p*-*t*-butylstyrene which had been purified by distillation and crystallization. The monomer prepared without the benefit of crystallization had about 2% of the *meta* isomer present. This material yielded a polymer of essentially the same properties as that of the pure *para* isomer.

It is interesting to note that copolymers made of styrene and *p*-*t*-butylstyrene show a straight-line relationship of heat distortion point and mole percentage composition; for example, a copolymer having the composition of 39 mole % *p*-*t*-butylstyrene and 61 mole % styrene has a heat distortion point of 100.6°.

Experimental

Methyl-*p*-*t*-butylphenylcarbinol.—About 400 ml. of absolute ether was added to 11.4 g. (0.3 mole) of lithium aluminum hydride in a nitrogen-filled flask. The mixture was stirred for about 15 minutes and then *p*-*t*-butylacetophenone[4] (176.0 g., 1.00 mole) was added over a period of 1.5 hours. Water was then added slowly until no more gas was evolved. The mixture was poured onto 200 g. of ice and water, and 700 ml. of 10% sulfuric acid was added. The ether layer was separated, and the aqueous layer was extracted twice with 200-ml. portions of ether. The combined ether layers were dried over anhydrous potassium carbonate and concentrated, leaving 178.1 g. of a white crystalline solid, m.p. 62–64° (100 weight % yield). The crude carbinol was recrystallized from mixed hexanes, yielding 164.0 g. (92.0 mole %) of methyl-*p*-*t*-butylphenylcarbinol, m.p. 66.6–67.4° (cor.).

***p*-*t*-Butylstyrene.**[5]—Potassium bisulfate (6.4 g.) was fused in a 1-l. three-necked, round-bottomed flask equipped with a thermometer and a 9-inch long, 1-inch diameter, Vigreux column. Hydroquinone (2.0 g.), *t*-butylcatechol (1.0 g.) and the carbinol (188.1 g., 1.06 moles) were added. The system was evacuated to 100 mm. pressure. The pot was heated as rapidly as possible while still keeping the foaming under control. The reaction was completed in one hour and ten minutes with a maximum pot temperature of 195° and a maximum vapor temperature of 150°. The two-phase distillate was separated yielding 157.5 g. (93.2 weight %) of the dried crude *p*-*t*-butylstyrene and 17.6 g. of water.

The crude *p*-*t*-butylstyrene was mixed with 5 g. of *p*-*t*-butylcatechol and distilled at a 10:1 reflux ratio in a 0.75-inch by 32 inch column packed with McMahon saddles.[6] The yield of pure *p*-*t*-butylstyrene [b.p. 91.5° (9.0 mm.), n^{20}_D 1.5270 and d^{20}_4 0.8883] was 123.0 g. (0.768 mole), or 72.5 mole % based on carbinol.

A portion of the *p*-*t*-butylstyrene was purified by low temperature crystallization in which the f.p. was raised from 37.2° (cor.) to a constant −36.9° (cor.).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.06. Found: C, 89.79, 89.78; H, 9.94, 9.95.

Polymerization.—The inhibitor was removed by alkaline washing, and the monomer was flash-distilled before each polymerization. Five-ml. samples of the monomer were placed in cleaned 10-ml. ampoules, cooled in a Dry Ice–acetone mixture, and the air was removed by evacuation to less than 1 mm. followed by flushing with nitrogen, repeating the cycle five times, ending with vacuum. The ampoules were sealed off and subjected to a varying heat cycle with or without added peroxides. In a typical catalytic run, the monomer and 0.02 to 0.04 weight % of di-*t*-

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[1] C. G. Overberger, C. Frazier, J. Mandelman and H. F. Smith, This Journal, **75**, 3326 (1953).

[2] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, *ibid.*, **68**, 1105 (1946).

[3] The poly-*p*-*t*-butylstyrene samples, even those fractionated to remove low molecular weight polymer, have an unexplained tendency to adhere to the fingers after handling. However, this is not due to ordinary tackiness, because the polymer does not adhere to paper nor to other samples of the same polymer, and its tack temperature [A. D. McLaren, T. T. Li, R. Rager and H. Mark, *J. Polymer Sci.*, **7**, 463 (1951)] is 174° compared to 106° for polystyrene.

[4] J. C. Butler, L. L. Ferstandig and R. D. Clark. This Journal, **76**, 1906 (1954).

[5] C. S. Marvel and G. L. Schertz, *ibid.*, **65**, 2054 (1943).

[6] R. T. Struck and C. R. Kinney, *Ind. Eng. Chem.*, **42**, 77 (1950)