In Table IV are compared the effects upon the critical oxidation potential produced by introduction of different substituents on the side chain carbon atom.

TABLE IV

EFFECT OF SIDE CHAIN SUBSTITUTION ON CRITICAL OXIDATION POTENTIAL

State of substitution in side chain	ΔE_c	State of substitution in side chain	ΔE_c
$—CN$	+0.308	$—CH=N—R$	+0.040
$—COOH$	+ .040	$—CH_2—CH=CH_2$	− .068[a]
$—CONH_2$	+ .260	$—CH=CH—CH_3$	.00[a]
$—C(OR)NH_2$	+ .306	$—CH_3$	.00[a]
$—CHO$	+ .255		

[a] Based on E_c values from Fieser.

Complete hydrogen substitution is taken as the reference point, creosol the reference compound. Only substitution of a vinyl group (isoeugenol) lowers the potential; substituents in all of the other compounds examined raise the E_c values. Comparison between the potential for vanillin and the rate data of Vanon and Montheard suggests, though by no means proves, that vanillonitrile, vanillic acid amide, vanillic acid esters[14] and vanillic acid amido ester salts should undergo class B reactions at retarded rates. Assuming the rate dependent steps in the reactions concerned to be attack by nucleophilic reagents, these increased potentials, indicating as they do a decreased electrophilic character for the side chain carbon atom, explain the failure to obtain vanillic acid amide by careful hydrolysis of vanillonitrile and by ammonolysis of methyl vanillate.[10]

Addition of an aromatic amine to the carbonyl group in vanillin lowers E_c sufficiently to place the values for the azomethines in the range of potentials requisite for antioxidant activity.

Absence of an effect by the carboxyl group in vanillic acid is worthy of note. The same group in 1-naphthol-2-carboxylic acid raises E_c 0.267 v. from the value for α-napthol,[1] while in anthroquinone 2-carboxylic acid the increase in E_0 caused by the carboxyl group is 0.067 v.[15]

Acknowledgment.—The author wishes to thank Dr. V. Sivertz and Dr. E. C. Lingafelter for loan of much of the equipment with which this investigation was carried out.

Summary

The critical oxidation potentials have been determined for several compounds derived from vanillin.

The normal oxidation-reduction potential of vanillal *p*-hydroxyaniline has been determined by discontinuous electrometric titration.

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[14] Vanillic acid esters were not examined but their potentials should be close to those for vanillic acid amide.

[15] Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924).

SEATTLE 5, WASHINGTON RECEIVED JUNE 10, 1946

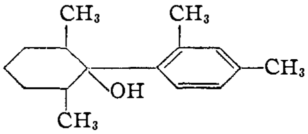
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER AND OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

The Dehydration of a Hindered Tertiary Alcohol

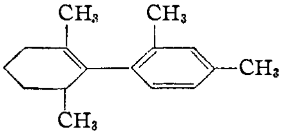
BY ROBERT B. CARLIN AND DOROTHY ANN CONSTANTINE

It has been reported[1] that 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexanol (I) is not dehydrated by the action either of potassium acid sulfate at 190–200° or of boiling acetic anhydride. It is the purpose of this paper to describe the conditions under which the dehydration has been successfully accomplished and to indicate some properties of the dehydration product.

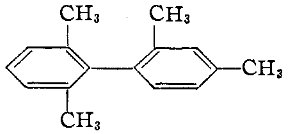
Dehydration was accomplished in 88% yield by heating I at 200–220° with anhydrous oxalic acid for one hour. The comparative resistance of I to dehydration was indicated by its stability toward anhydrous oxalic acid at 130°, a temperature at which Zelinsky and Zelikow[2] were able to bring about the dehydration of a number of open-chain and cyclic secondary and tertiary alcohols with the same reagent.



I



II



III

Although the composition of the product of dehydration of I is in accord with the structure 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexene (II), it was recognized that the action of oxalic acid at comparatively high temperatures on I might produce isomers of II. However, the occurrence of carbon skeleton rearrangements during the dehydration of I appeared unlikely in view of the fact that the product was dehydrogenated to 2,2′,4,6′-tetramethylbiphenyl (III) by the application of the same conditions under which I has been shown[1] to be directly converted to III. Had a rearrangement of the hydroaromatic

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[1] Carlin, THIS JOURNAL, **67**, 928 (1945).

[2] Zelinsky and Zelikow, *Ber.*, **34**, 3249 (1901).

ring in I occurred during dehydration, it is most improbable that the rearrangement product could have rearranged again to the original carbon skeleton during dehydrogenation.[3]

The ultraviolet absorption spectrum of the dehydration product of I failed to permit a distinction to be made between the structure II and isomers having the double bond in other positions in the hydroaromatic ring. It might be expected that the spectrum of a compound of structure (II) would be very similar to those of 1-phenyl-1-cyclohexene[4] and some of its analogs,[5] and to that of styrene.[4,6] However, the spectrum of the dehydration product did not show a maximum in the region 240–250 mμ, which characterizes the spectra of 1-phenyl-1-cyclohexene and styrene; indeed, the spectrum of the dehydration product is somewhat similar to that of the carbinol from which it was formed (Fig. 1) and to those of cannabidiol dimethyl ether and dihydrocannabidiol dimethyl ether, which have been shown to be substituted phenylcyclohexenes in which the double bond in the hydroaromatic ring is not conjugated with the benzene ring.[5] Nevertheless, the conclusion that the absorption spectrum of the dehydration product of I eliminates the structure II from consideration would be unjustified. Rodebush and Feldman[6] have demonstrated that strong absorption bands, which may be attributed to resonance interaction between the aliphatic double bond and the benzene ring in substituted phenylethylenes, appear only if the ring can assume a position coplanar with the atoms directly attached to the ethylenic linkage. Therefore, the spectrum of a compound having the structure II could not show the absorption maximum which characterizes the spectra of 1-phenyl-1-cyclohexene and styrene unless the rings can be coplanar. Since studies of the spectra of substituted biphenyls[6-10] have demonstrated the effects of mechanical interference between methyl groups in the *ortho* positions in both rings, there can be no doubt that a similar effect should be encountered in the spectrum of a compound of structure II. The three methyl groups in *ortho* positions should prevent ring coplanarity, and the absorption caused by resonance interaction between the benzene ring and the double bond in the hydroaromatic ring should be greatly weakened. Thus, the structure II for the dehydration product of I is compatible with the spectrum of the compound, and, in the light of evidence previously cited, II appears to be the most probable structure. Inasmuch as various fractions obtained by distillation of the dehydration product of I gave the same absorption curve, it is unlikely that the product was a mixture.

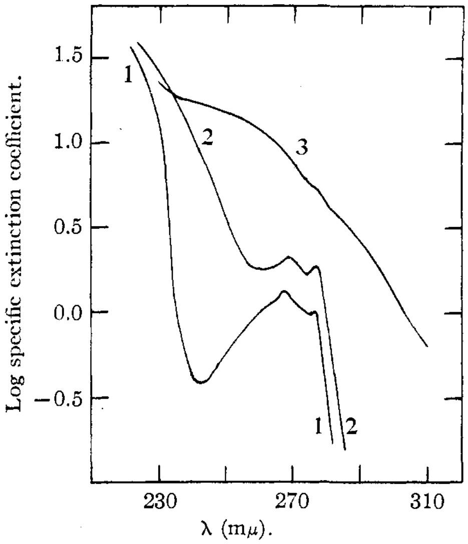

Fig. 1.—The ultraviolet absorption spectra of: 1-(2,4-dimethylphenyl)-2,6-dimethylcyclohexanol (I), curve 1; 1-(2,4-dimethylphenyl)-2,6-dimethylcyclohexene (II), curve 2; and product of II after standing in a stoppered vessel for four months, curve 3.

If the difficulty with which I was dehydrated to II may be ascribed to mechanical interference, by the methyl groups surrounding the carbinol group, with the approach of the attacking reagent, then the difficulty with which other hindered 1-phenyl-1-cyclohexanols are dehydrated should parallel the deviations of the absorption spectra of the resulting substituted 1-phenyl-1-cyclohexenes from that of the parent, unsubstituted compound. Efforts are now being made to discover whether such a relationship exists.

Experimental[11]

1-(2,4-Dimethylphenyl)-2,6-dimethyl-1-cyclohexene (II).—A mixture of 5.5 g. of 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexanol (I)[1] and 3.5 g. of anhydrous oxalic acid[12] was heated in a bath maintained at 200–220° for one hour. After the first half-hour, 1 g. of fresh anhydrous oxalic acid was added. The cooled mixture was dissolved in ether, and the ether solution was washed three times with 5% aqueous sodium bicarbonate and once with water. After the solution was dried over "Drierite," the ether was removed and the residue was distilled under diminished pressure. The distillate (4.1 g., 81%) was a colorless, viscous liquid, b. p. 102–103° (3 mm.), $n^{20}{}_{D}$ 1.5340.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.67; H, 10.33. Found: C, 89.60; H, 10.25.

The compound decolorized 3% alcoholic bromine solution without evolution of hydrogen bromide, but it reacted very slowly with potassium permanganate in acetone. A specimen from which the analytical sample was withdrawn became viscous and slightly colored on standing in a stoppered vessel in the laboratory for four months. The

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[3] *Cf.* Plattner, *Die Chemie*, **55**, 131, 154 (1942).

[4] Pestemer and Willigut, *Monatsh.*, **66**, 119 (1935).

[5] Adams, Wolff, Cain and Clark, THIS JOURNAL, **62**, 2215 (1940).

[6] Rodebush and Feldman, *ibid.*, **68**, 896 (1946).

[7] Pickett, Walter and France, *ibid.*, **58**, 2296 (1936).

[8] Calvin, *J. Org. Chem.*, **4**, 256 (1939).

[9] O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940).

[10] Williamson and Rodebush, *ibid.*, **63**, 3018 (1941).

[11] Melting points are corrected. Microanalysis by Dr. Carl Tiedcke, Laboratory of Microchemistry, New York, N. Y.

[12] Bowden, "Organic Syntheses," Coll. Vol. I, 2nd ed., 42 (1941).

ultraviolet absorption spectrum of the material (Fig. 1) indicated an appreciable change had occurred. The viscous material was soluble in ethanol. Although it was not examined further, it appeared likely that the change had occurred as a result of polymerization, or autooxidation, or both, of II.

Ultraviolet absorption spectra were determined by means of a Beckman Quartz Spectrophotometer.

2,2',4,6'-Tetramethylbiphenyl (III) was prepared from (II) by means of the same procedure which converted the carbinol I to III.[1] The crude yellow liquid product (1.5 g., 23%) from 6.5 g. of II, which contained some sulfur, had n^{20}_{D} 1.5635. The liquid was not purified, but was identified with III by converting it to its **tetranitro derivative**.[1] From 0.5 g. of crude III, 0.1 g. of the crude tetranitro derivative, m. p. 210–217°, was obtained. This impure material was dissolved in a mixture of 100 cc. of benzene and 100 cc. of petroleum ether (b. p. 40–60°), and the solution was allowed to trickle through a column (1.2 × 25 cm.) of chromatographic alumina. The column was developed with 100 cc. of benzene. When the washings were concentrated to 2 cc., the tetranitro derivative crystallized from the solution. Three recrystallizations from petroleum ether (b. p. 65–110°) containing a little benzene gave pale yellow needles, m. p. 235–237°, alone or when mixed with an authentic specimen.

Summary

1. 1-(2,4-Dimethylphenyl)-2,6-dimethyl-1-cyclohexanol (I) has been dehydrated to 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexene (II) by heating I at 200–220° with anhydrous oxalic acid.

2. A comparison of the ultraviolet absorption spectra of I and II with those of compounds of similar structure indicates that a relationship may exist between the difficulty with which hindered carbinols, such as I, are dehydrated and the absorption spectra of their dehydration products.

PITTSBURGH, PENNSYLVANIA

RECEIVED SEPTEMBER 5, 1946

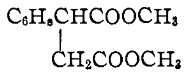
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Polymers. XXIV. The Reaction of Benzoyl Peroxide and Maleic Ester[1]

BY C. S. MARVEL, E. J. PRILL[2] AND D. F. DETAR[3]

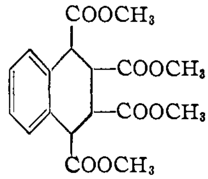
Earlier work in this Laboratory[4] has indicated that *l*-menthyl maleate reacts in the presence of benzoyl peroxide, even though maleic esters do not form high polymers under these conditions. A continuation of this study with dimethyl and diethyl maleate has shown that maleic esters do unite with themselves to a limited extent to yield crystalline products containing peroxide and solvent residues. Since the start of this work, which was interrupted by the war and only recently resumed, several articles have appeared reporting the presence of chemically-bound fragments of peroxides[5,6] and solvents[7] in polymers, and reporting the addition[8] of compounds such as benzene diazonium chloride and carbon tetrachloride to double bonds in the presence of peroxides.

The reaction of two moles of dimethyl maleate with one mole of benzoyl peroxide yields a complex mixture from which there may be isolated unchanged ester (about 15%), a small amount (5% based on the maleic ester) of dimethyl phenylsuccinate (I), larger amounts (25%) of two crystalline esters, $C_{18}H_{20}O_8$ (IIA, m.p. 149°; IIB, m.p. 95°), and a considerable amount of non-volatile material (30–40%) containing more than two maleic ester residues. Compounds IIA and IIB are probably stereoisomeric forms of either tetramethyl 1,2,3,4-tetralintetracarboxylate (III) or tetramethyl 1-methylhydrindenetetracarboxylate (IV). It may be noted that the tetraline derivative (III) can exist in four racemic and two meso forms, and the hydrindene derivative (IV) in four racemic forms.

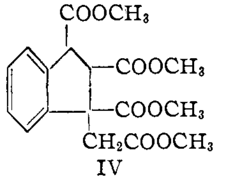


$$\begin{array}{l}\mathrm{C_6H_5CHCOOCH_3}\\ \quad\;|\\ \quad\mathrm{CH_2COOCH_3}\end{array}$$

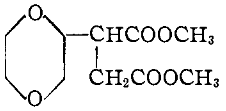
I



III



IV



V

When the above reaction is carried out in dioxane solution, the same products are formed, and additional products containing the dioxane group, such as dimethyl dioxanylsuccinate (V), are formed.

The elementary analyses of the higher boiling fractions also indicate the presence of dioxane-containing compounds of which VI is a possible

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[1] For the twenty-third communication see THIS JOURNAL, **68**, 1088 (1946).

[2] du Pont Post-doctorate Research Assistant, University of Illinois, 1941–1942. Present address: General Laboratories, United States Rubber Company, Passaic, New Jersey.

[3] Present address: Department of Chemistry, Cornell University, Ithaca, New York.

[4] Marvel and Frank, THIS JOURNAL, **64**, 1675 (1942).

[5] Price, Kell and Krebs, *ibid.*, **64**, 1103 (1942); Price and Durham, *ibid.*, **64**, 2508 (1942); Price and Tate, *ibid.*, **65**, 517 (1943); Pfann, Salley and Mark, *ibid.*, **66**, 983 (1944).

[6] Bartlett and Cohen, *ibid.*, **65**, 543 (1943).

[7] Springer, *Kautschuk*, 14, 159, 197, 212 (1938); *C. A.*, **33**, 3629 (1939); Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

[8] Koelsch, THIS JOURNAL, **65**, 57 (1943); Koelsch and Boekelheide, *ibid.*, **66**, 412 (1944); Kharasch, Urry and Jensen, *ibid.*, **67**, 1626 (1945); *Science*, **102**, 128 (1945).