drolyzed[9a,b] to acetone and (+)3-methylcyclohexanone with a mixture of 25 ml. of concentrated hydrochloric acid and 75 ml. of water. The acetone was removed by fractionation as it formed. After removal of the acetone the boiling point rose to 95–98° where (+)3-methylcyclohexanone steam distilled. The ketone was dried and distilled to give 13.3 g. (68.8%) of (+)3-methylcyclohexanone boiling at 166.5–168° (735 mm.), $n^{24.8}_{\mathrm{D}}$ 1.4440, α^{26}_{D} +12.01° (*l* 1 dm., neat), $[\alpha]^{25}_{\mathrm{D}}$ +14.2° (*c* 4.13, $CHCl_3$) whose infrared spectrum was identical with that of *dl*-3-methylcyclohexanone.

A 2.10-g. sample of (+)3-methylcyclohexanone was converted, in 91% yield, to (−)2,6-dibenzylidene-3-methylcyclohexanone melting at 127–129°,[10a] $[\alpha]^{26}_{\mathrm{D}}$ −42.5° (*c* 0.71, $CHCl_3$),[10b] $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 328 mμ, log ε 4.48,[10c] whose infrared and ultraviolet spectra were identical with those of *dl*-2,6-dibenzylidene-3-methylcyclohexanone, m.p. 119–120°.[10c]

A 2.00-g. sample of (−)2,6-dibenzylidene-3-methylcyclohexanone was added to 25 ml. of ethyl acetate and the suspension treated with a stream of oxygen, containing ozone at 0° until all the solid dibenzylidene derivative had dissolved and the color had faded from bright yellow to near colorless. The reaction vessel was cooled to −70° and the ozonization continued until the characteristic blue color due to the presence of excess ozone[11] was observed.

The ozonide was decomposed by dropwise addition of the reaction mixture to a cooled, well stirred mixture of 50 ml. of 30% hydrogen peroxide and 75 ml. of 10% sodium hydroxide solution. After stirring for 2 hr. the reaction mixture was heated on a steam-bath for 1 hr., cooled, acidified with concentrated hydrochloric acid to congo red. It then was extracted continuously with ether for 36 hr. The ether extract was concentrated and the residue subjected to steam distillation until all of the benzoic acid was removed. The remaining solution was evaporated to dryness under diminished pressure, extracted with hot chloroform and filtered. The chloroform solvent was evaporated to give 1.02 g. of tan crystals, m.p. 81–82°, $[\alpha]^{25}_{\mathrm{D}}$ −21.2° (*c* 0.28, $CHCl_3$), which on sublimation gave (−)α-methylglutaric acid (IIa),[3,12] m.p. 82.5–84.5°, $[\alpha]^{25}_{\mathrm{D}}$ −25.2° (*c* 6.79, $CHCl_3$), $[\alpha]^{25}_{\mathrm{D}}$ −24.7° (*c* 2.17, $CHCl_3$); neut. equiv. 73.1 (calcd. 73.1).

The infrared spectrum of IIa, in chloroform, was identical with that of II and with *dl*-α-methylglutaric acid.[2]

(+)α-Methylglutaric acid (II) as obtained from the oxidation of I showed $[\alpha]^{25}_{\mathrm{D}}$ +18° (*c* 6.87, abs. EtOH); however, II prepared from *cis*-nepetolactone[2] showed $[\alpha]^{27}_{\mathrm{D}}$ +24.2° (*c* 2.18, $CHCl_3$), $[\alpha]^{24.8}_{\mathrm{D}}$ + 22.1° (*c* 1.01, abs. EtOH).

(+)**3-Methylcyclopentanone** (IIIa).—A 11.3-g. sample of (+)pulegone (VI) was ozonized at −70° as described above. The product, 10.9 g. of tan-colored semi-solid was distilled at 180° (1 mm.) to give colorless, crystalline (+)β-methyladipic acid,[13] m.p. 85–89°, $[\alpha]^{26}_{\mathrm{D}}$ +9.6° (*c* 4.25, $CHCl_3$).

A 7.0-g. sample of (+)β-methyladipic acid was cyclized in 94.6% yield, according to the procedure of Thorpe and Kon[14] to (+)3-methylcyclopentanone[15] (IIIa), b.p. 143–143.5°, $n^{24.8}_{\mathrm{D}}$ 1.4320, α^{25}_{D} +143.70° (*l* 1 dm. neat), $[\alpha]^{25}_{\mathrm{D}}$ +154.8° (*c* 0.73, $CHCl_3$). The infrared spectrum of (+)IIIa as the pure liquid was identical with that of *dl*-3-methylcyclopentanone with the exception of a single band at 14.7 μ which was not present in the latter.

2,5-Dibenzylidene-3-methylcyclopentanone (IVa).—This compound was prepared in quantitative yield from IIIa; m.p. 150.5–152.5°, $[\alpha]^{26.0}_{\mathrm{D}}$ −53.5° (*c* 0.98, $CHCl_3$), and $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 350 mμ, log ε 4.59, agreed with literature values of the enantiomorph IV[2] and the racemate.[2,10c] The infrared spectra of IV and IVa in chloroform were identical.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.46; H, 6.64.

Methylsuccinic Acids (V and Va).—A 0.427-g. sample of crude IV[2] was ozonized to give 0.194 g. (94%) of (−)-methylsuccinic acid[16] (V), m.p. 111–113°, $[\alpha]^{24.2}_{\mathrm{D}}$ −15.0° (*c* 1.89, abs. EtOH), neut. equiv. 65.2 (calcd. 66.0).

A 2.80-g. sample of crude IVa, m.p. 148.5–150°, $[\alpha]^{26}_{\mathrm{D}}$ −52.2° (*c* 1.15, $CHCl_3$) was ozonized to yield 1.28 g. (95%) of (+)methylsuccinic acid[16] (Va), which melted at 113–115° after sublimation, $[\alpha]^{25.5}_{\mathrm{D}}$ +15.5° (*c* 2.82 abs. EtOH), neut. equiv. 65.8 (66.0). In a similar manner a 1.70-g. sample of IVa, m.p. 150.5–152.5°, $[\alpha]^{26}_{\mathrm{D}}$ −53.2° (*c* 1.14, $CHCl_3$), after four recrystallizations from 95% ethanol, gave (+) methylsuccinic acid[4,16] Va, m.p. 113–114°, $[\alpha]^{25.5}_{\mathrm{D}}$ +15.5° (*c* 2.71 abs. EtOH), neut. equiv. 66.4 (calcd. 66.0).

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[9] (a) O. Wallach, *Ann.*, **289**, 337 (1896); (b) R. Adams, *et al.*, THIS JOURNAL, **64**, 2087 (1942).

[10] (a) O. Wallach, *Ber.*, **29**, 1596 (1896); (b) F. Nerdel and C. Kresse, *Z. Elektrochem.*, **56**, 234 (1952); (c) H. S. French and L. Wiley, THIS JOURNAL, **71**, 3702 (1949).

[11] E. R. H. Jones, *et al.*, *J. Chem. Soc.*, 4890 (1952).

[12] I. Scheer, R. B. Kostic and E. Mosettig, THIS JOURNAL, **75**, 4871 (1953).

[13] This acid, m.p. 86–88°, $[\alpha]^{26}_{\mathrm{D}}$ +11.5° (*c* 9.38, $CHCl_3$) was also prepared, in low yield and less conveniently, by oxidizing menthone according to the method of W. Semmler, *Ber.*, **25**, 3513 (1892); the menthone was obtained by the oxidation of (−)menthol according to the method of E. R. H. Jones, *et al.* (*J. Chem. Soc.*, 2548 (1953)).

[14] J. F. Thorpe and G. A. R. Kon, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 192.

[15] G. H. Stempel, *et al.*, THIS JOURNAL, **67**, 344 (1945).

[16] A. Fredga, *Arkiv. Kemi, Mineral., Geol.*, **15B**, No. 23 (1942).

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Coupling Reaction of Phenols and Phenol Alcohols with Diazonium Compounds

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The reaction of phenol alcohols with like species to form resins is of considerable interest and commercial significance. Because of its apparent parallelism, the reaction of diazonium compounds with phenol alcohols (methylolphenols) has been widely studied in an effort to determine the relative reactivities of various resin intermediates and the relative reactivities of the several positions in the phenolic nucleus.

Ziegler and Zigeuner[1] have conducted the most complete studies of this reaction, although several others have been cited by Hultzsch.[2] Their method involved isolation, identification and measurement of yield of azo compound formed when the coupling reagent reacted with a methylolphenol. They found it possible to replace a methylol group in either the *ortho* or *para* position. The reaction also is analogous to the replacement of the substituent group in phenol aldehydes, phenolcarboxylic acids and phenolsulfonic acids.[2]

When the *para* position is not blocked by halogen or alkyl, reaction occurs preferentially in the *para* position. When a choice exists between replacement of an *o*-hydrogen atom or an *o*-methylol group in the same molecule, the methylol group is displaced, formaldehyde being eliminated in the reaction. From these experiments it has sometimes been concluded, logically but incorrectly, that the order of ease of replacement is *p*-methylol, *p*-hydrogen, *o*-methylol, *o*-hydrogen atom.[3] However, the experiments of Ziegler and Zigeuner did not include any examples of competition between displacement of a methylol group and displacement of

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[1] (a) E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 42 (1948); (b) **79**, 89 (1948); (c) **79**, 358, 363 (1948).

[2] K. Hultzsch, "Chemie der Phenolharze," Springer, Berlin, 1950, p. 35.

[3] G. Sprengling, paper presented before Division of Paint, Varnish and Plastics Chemistry, 118th Meeting, Am. Chem. Soc., Chicago, Ill., 1950.

a similarly placed hydrogen atom in a different molecule, particularly when the position in question was the *para* position.

It is not safe to assume, therefore, that because replacement of methylol groups in preference to hydrogen atoms in the same molecule occurred in the *ortho* position, a similar preferred replacement of methylol groups over hydrogen atoms will occur in the *para* position where, of necessity, the competition must be between substituents in different molecules. In fact, we have found that such a preference does not exist in the *para* position.

The methylol group when present in the *para* position has been shown to exert a deactivating effect upon the phenol molecule.[4] The removal of the methylol substituent also might be expected to require more energy than simple displacement of a proton since hydroxybenzyl alcohols are formed initially by substitution of the methylol moiety for hydrogen. It therefore is surprising to find the methylol group ranked ahead of hydrogen in ease of replaceability. Our experiments were intended to check the accuracy of this conclusion and have shown it to be incorrect with respect to the *para* position.

In the case of the *o*-methylol isomer, there is an additional factor to be considered: namely, the chelation of the methylol group with the phenolic oxygen atom. Chelation in *o*-methylolphenol anions has been discussed by Freeman and Lewis[4] who also have reported the effect of an *o*-methylol group in increasing the reactivity of a phenolic nucleus. As a result of the effects of this chelation, the order of replacement given by Ziegler and Zigeuner is correct with respect to the *ortho* substituent and is confirmed by our results.

For our experiments a series of competitive reactions was designed to compare the reactivity of the hydrogen atom and the methylol group at various locations in the phenolic nucleus. One equivalent of each of the two compounds to be compared (methylol compound and parent phenol) was allowed to compete in the same homogeneous solution for a single equivalent of the diazonium reagent. After conclusion of the reaction, the solutions were analyzed for unreacted methylolphenol compounds by the quantitative paper chromatographic technique.[5] Completeness of reaction was checked by drying and weighing the precipitate of azo compound formed. The coupling reagent was *p*-nitrobenzenediazonium fluoroborate, chosen because of its stability in crystal form, reactivity, and the water insolubility of the azo compounds prepared from it.

The results are summarized in Table I. An amount greater than 50% reacted indicates that a methylol compound was more reactive than the corresponding phenol having a hydrogen atom instead of the methylol group. Since the compounds were compared each with its parent phenol and not to a common standard, it should be noted that comparisons of relative reactivity cannot be drawn between members in the table except in those cases where the same parent phenol was common to several members.

Experimental

The *p*-nitrobenzenediazonium fluoborate was prepared as previously indicated.[6] However, since this procedure was not intended to yield analytical reagent grade product, an additional purification was necessary. Despite poor solubility properties of the diazonium salt, recrystallization from methanol (100 ml. per g. of solute) was found to yield the purest product. The temperature during recrystallization was maintained below 50° to prevent decomposition of the diazonium salt. Small yellow needles were recovered in 50% yield. The substance does not melt, but decomposes sharply when immersed in capillary tubes for 30 seconds at 164.5°. Analysis for carbon and hydrogen was complicated by interference effects attributed to both boron and fluorine.

Anal.[7] Calcd. for $C_6H_4N_3O_2BF_4$: B, 4.57; F, 32.1. Found: B, 4.55; F, 32.5.

As Siggia[8] has indicated, sodium carbonate solution is preferred to sodium hydroxide as the coupling medium. Under identical conditions, and coupling with the methylol of *p*-cresol, yields of azo product averaging 96% were obtained with sodium carbonate, with sodium hydroxide 88%. These results also indicate the diazonium salt to be of high purity, the error being no greater than expected from manipulative and solubility losses.

Samples of the phenolic pairs investigated constituting 0.001 mole each were weighed on the analytical balance and dissolved together in 5 ml. of 5% sodium carbonate solution. The diazonium compound (0.001 mole) was weighed, dissolved in 10 ml. of distilled water, and added quantitatively to the alkaline phenolic solution. After 15 minutes, 1 ml. of 50% acetic acid was added to neutralize the alkali, causing the azo product to precipitate. At the end of another 15 minutes, the insoluble azo compound was separated by gravity filtration the filtrate being collected quantitatively in a 25-ml. volumetric flask. The precipitate was washed with distilled water until the volumetric flask was diluted to mark. The precipitate was dried at 110° for two hours and weighed. In those cases where there is one common

TABLE I

COUPLING OF DIAZONIUM SALTS WITH METHYLOLPHENOLS AND CORRESPONDING PHENOLS[a]

Methylol compound	Phenol	Over-all coupling prod., %[c]	Methylol compound reacted, %
2-Hydroxy 3-methyl 5-*t*-butylbenzyl alcohol[9]	2-Methyl-4-*t*-butylphenol	82[b]	>96
2-Hydroxy 5-methylbenzyl alcohol[10]	4-Methylphenol	100	76
2-Hydroxy 3,5-dimethylbenzyl alcohol[11]	2,4-Dimethylphenol	82[b]	60
2,6-Dimethylolphenol[12]	Phenol	84	53
2-Hydroxybenzyl alcohol[6]	Phenol	98	52
2,4,6-Trimethylolphenol[12]	Phenol	76	52
2,6-Dimethylolphenol	Trimethylolphenol	85	52
2,4,6-Trimethylolphenol	2,6-Dimethylolphenol	85	46
4-Hydroxybenzyl alcohol[6]	Phenol	95	45
4-Methylolsalicylaldehyde[13]	Salicylaldehyde	88	42
3-Hydroxybenzyl alcohol[6]	Phenol	93	41
4-Hydroxy 3,5-dimethylbenzyl alcohol[14]	2,6-Dimethylphenol	86[b]	41
4-Hydroxybenzoic acid	Phenol	97	12

[a] If methylol compound is equally reactive with parent phenol, 50% reacted will be observed. [b] Sodium carbonate solution not sufficiently strong to solubilize compounds; sodium hydroxide used. [c] In those cases where more than one product results, a theoretical yield was calculated based on the analysis.

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(5) J. H. Freeman, *Anal. Chem.*, **24**, 2001 (1952).

(6) J. H. Freeman, *ibid.*, **24**, 955 (1952).

(7) Analysis by Mr. J. F. Reed.

(8) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 297.

(9) G. Sprengling, S. Beatty and K. Adams, THIS JOURNAL, **72**, 4314 (1950).

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(11) H. v. Euler, *Arkiv. Kemi, Mineral. Geol.*, **14A** [10], 17 (1940).

(12) J. H. Freeman, THIS JOURNAL, **74**, 6257 (1952).

(13) R. Stoermer and K. Behn, *Ber.*, **34**, 2456 (1901).

(14) E. Adler, *Arkiv. Kemi, Mineral. Geol.*, **15A** [7], 12 (1941).

coupling product, the percentage yield of dried precipitate is a check on the completeness of reaction. The phenols used were analytical reagent grade. The methylolphenols were prepared in accordance with the references listed in Table I.

The analyses for unreacted methylolphenols in the filtrate were made by the paper chromatographic method using spot weights as a measure of concentration.[5]

Conclusions

Several conclusions may be drawn from the experimental data in Table I.

In all examples studied, a *p*-methylol group is more difficult to replace than a *p*-hydrogen atom. A similar result also was obtained in the case of the *p*-carboxylic acid. Diazonium coupling is known to be of the electrophilic aromatic substitution type.[15a,b] The inductive effect of a *p*-methylol substituent is to withdraw electrons and hence to deactivate the ring to electrophilic substitution. In a competitive reaction, therefore, the unsubstituted parent phenol should be more reactive than a *p*-methylol substituted phenol. Our results agree with this conclusion. A similar effect was reported for the case of formaldehyde adding to the phenolic nucleus.[4]

In agreement with Ziegler and Zigeuner, it was observed that an *o*-methylol group is replaced more easily than an *o*-hydrogen atom. The presence of an *o*-methylol group also enhances the reactivity of the molecule toward diazonium coupling. This effect likewise has a parallel in the formaldehyde addition reaction.[4] The two latter conclusions do not appear to be amenable to the type of explanation accorded the *p*-methylol substituent. The factor which apparently differentiates the *o*-methylol compound from either the *para* or *meta* isomer is the possibility of chelation or hydrogen bonding between the *ortho* substituent and the phenolic hydroxyl group. Such internal hydrogen bonds are known to exist in *ortho* methylolphenols[16] and are believed to account for certain observed anomalies.[17]

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Cleavage of Some Organosilicon Compounds by Formic Acid

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When tri-(2-biphenylyl)-silanol was refluxed for 24 hours with 98–100% formic acid in an attempt to prepare hexa-(2-biphenylyl)-disiloxane, the only pure product isolated so far was biphenyl. The extension of the reflux period to 48 hours resulted in a 76.5% yield of biphenyl based upon the cleavage of all three biphenylyl groups. A quantitative yield of hexaphenyldisiloxane (m.p. 220–222°) has been obtained when triphenylsilanol was refluxed for 16 hours with 98% formic acid.[1]

$$(2\text{-}C_6H_5C_6H_4)_3SiOH + HCOOH \longrightarrow C_6H_5C_6H_5$$
$$(C_6H_5)_3SiOH + HCOOH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3$$

A similar treatment of tris-(*p*-chlorophenyl)-ethoxysilane with formic acid gave hexakis-(*p*-chlorophenyl)-disiloxane.[2]

The above results suggested the possibility that the cleavage reaction is characteristic of sterically hindered aryl silanols, while the condensation to disiloxane is characteristic of non-sterically hindered silanols. The isolation of naphthalene from the tri-(1-naphthyl)-silanol reaction and of hexa-(*p*-tolyl)-disiloxane from the attempt to cleave tri-(*p*-tolyl)-silanol supported the conjecture. The cleavage of 2-biphenylyltriphenylsilane and of tri-(2-biphenylyl)-silane, however, demonstrated that the cleavage reaction was not limited to silanols. The failure of tri-(2-biphenylyl)-chlorosilane to undergo cleavage and the isolation of benzene from the reaction of triphenylsilane and formic acid stress the importance of factors other than steric hindrance. It is also interesting to note that the yield of benzene from triphenylsilane was practically identical with the yield of biphenyl from tri-(2-biphenylyl)-silane.

In the cleavage of triphenylsilanol in glacial acetic acid with hydrogen chloride[3] hexaphenyldisiloxane is probably an intermediate since under milder condition (10% hydrochloric acid in acetic acid) hexaphenyldisiloxane was obtained.[4] The lack of reaction between hexaphenyldisiloxane and formic acid indicates that formic acid is a weaker cleaving agent than the hydrogen chloride–glacial acetic acid combination. This weakness also is substantiated by the failure of formic acid to cleave tetraphenylsilane which has been cleaved by hydrogen chloride.[4]

Experimental[5]

General Procedure.—Into a dry, round-bottomed flask containing the organosilicon compound and some boiling chips was added 10–15 ml. of 98–100% formic acid per gram of the compound to be cleaved. Nitrogen under slight pressure was introduced through the top of the reflux condenser and the flask was heated with a heating mantle. The reaction mixture was refluxed gently for 48 hours, cooled, filtered, then washed with 98–100% formic acid. The product obtained was purified, then identified by a mixed melting point with an authentic sample. The filtrate was distilled and the fraction distilling at the boiling point of the product sought or at the boiling point of its azeotropic mixture with formic acid was neutralized and redistilled. The residue from the first distillation was neutralized and the resulting precipitate was filtered, then purified and identified in the manner previously described.

Tri-(2-biphenylyl)-silanol.[6]—The filtration of the product from the reaction of 4 g. (0.0074 mole) of tri-(2-biphenylyl)-silanol and 50 ml. of formic acid yielded 1.76 g. of biphenyl melting at 70–70.5°. The mixed melting point with an authentic sample of biphenyl was not depressed. The filtrate was diluted with 50 ml. of water, neutralized with sodium carbonate and filtered. The crude product when recrystallized from a mixture of petroleum ether (b.p. 77–115°) and ethanol weighed 0.42 g. and melted at 67.5–69.5°. The crude material recovered from the filtrate was chromatographed on alumina with benzene as the solvent and eluent. The two biphenyl fractions obtained were 0.16 g. (m.p. 69–70°) and 0.27 g. (m.p. 66--68°). The total yield of the biphenyl isolated was 2.61 g. (76.5%).

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(1) H. W. Melvin, unpublished studies.

(2) H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 968 (1951).

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