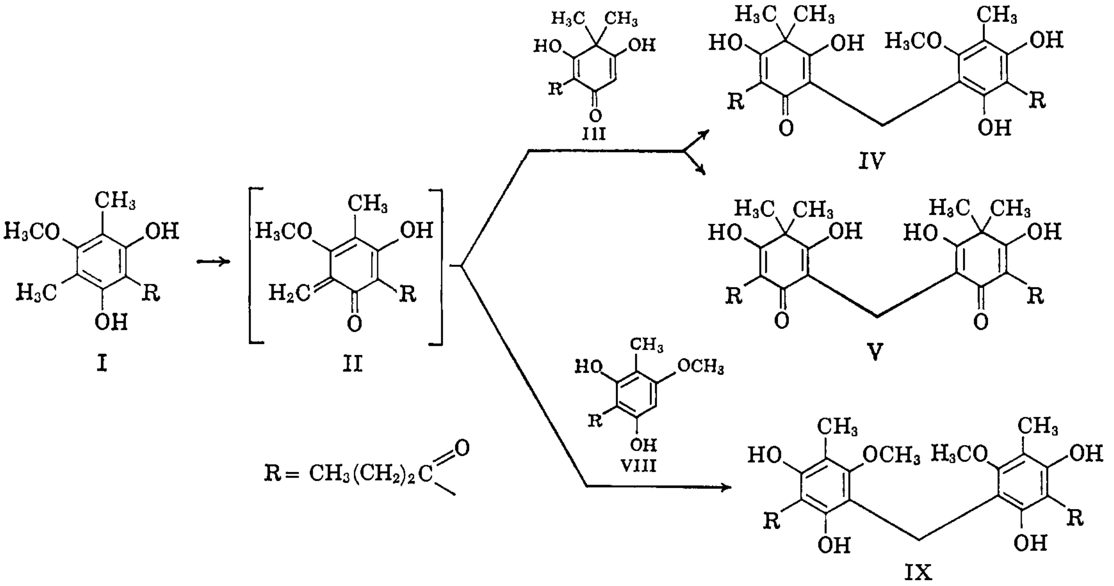
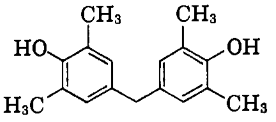
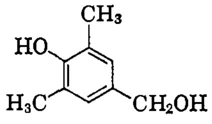
filicinic acid (III). Because of the similarity of this process to the chemical coupling of mesitol to VII,[2] as well as the horseradish peroxidase induced oxidation of mesitol to VII,[3] we were led to study the action of this enzyme upon an equimolar mixture of I and III in phosphate buffer at pH 7.8.[4] A fair yield (~30%) of a mixture of *p*-aspidin (IV) and albaspidin (V) was obtained and the products were identified by paper chromatography[5] and mass spectra.[6] The albaspidin (V) resulted from the further reaction of *p*-aspidin with III, since a mixture of III and IV at pH 7.8 without enzyme was shown to form albaspidin (V) with the liberation of a corresponding amount of aspidinol (VIII); *cf.* "rottleron change."[7]





VI



VII

In an analogous example, methylaspidinol (I) was combined with an equimolar quantity of aspidinol (VIII) and, after a few minutes incubation with peroxidase, methylenebisaspidinol (IX) was obtained in crystalline form and identified by comparison of melting point (190–191°) and infrared spectrum with authentic material.[8] Both I and VIII were required; incubation of either I or VIII alone gave rise to no discernible dimeric species.[9]

The facility with which these reactions proceed led us to look for peroxidase activity within the plant. Highest activity is usually found in the roots;[10] in contrast no activity was found in *Dryopteris* rhizomes while the leaves gave a highly positive test. This suggests that the dimerization, and presumably the main biosynthetic activity, is taking place in the leaves while the rhizomes are a storage location for the dimeric compounds.

Although a wide variety of materials (anilines, phenols, dyes, etc.) have been used as hydrogen donors with peroxidase, this appears to be one of the few examples[11] of the formation of a natural product with the aid of this versatile enzyme.

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(2) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 1726 (195).

(3) H. Booth and B. C. Saunders, *ibid.*, 940 (1956).

(4) Compounds I and III (3 μmoles each) were stirred with 0.6 ml of phosphate buffer (pH 7.8), 0.75 ml of hydrogen peroxide (0.015%), and 0.06 mg of crystalline horseradish peroxidase (Boehringer) for 15 min.

(5) A. Penttila and J. Sundman, *J. Pharm. Pharmacol.*, **13**, 531 (1961).

(6) Mass spectra were obtained by slowly volatilizing the crude reaction mixture from the end of a probe inserted in the ion source of an Associated Electrical Industries MS-9 double-focussing mass spectrometer. The monomers I and III (or I and VIII) volatilized at <100° showing the parent ions at *m/e* 238 (I) and 224 (III and VIII). Complete evaporation left the dimers IV and V, or IX, which volatilized at ~170°, showing a parent ion at *m/e* 460 in each case as well as characteristic fragment ions.

(7) T. Backhouse, A. McGookin, J. Matchett, A. Robertson, and E. Tittensor, *J. Chem. Soc.*, 113 (1948).

(8) R. Boehm, *Ann.*, **329**, 269 (1903).

(9) Unless demethylation of I occurs, only VIII could oxidize to a dimer; however the former process has been observed; *cf.* ref 2.

(10) K. Wachholder, *Biochem. Z.*, **213**, 394 (1942).

(11) For example, pyrogallol → purpurogallin: R. Willstätter and J. Weiss, *Ann.*, **433**, 17 (1923).

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A New Hydrogen-Abstracting Reaction with Diethyl Azodicarboxylate

Sir:

Azo-disubstituted compounds would be expected to be strong electron acceptors when their substituents are electron-attracting groups such as alkoxycarbonyl, acyl, nitrile, and so on. The treatment of these compounds with Hückel MO theory indicates that they show the special case of possessing a vacant bonding orbital.[1] For example, the energies of the vacant bonding orbitals of dimethyl azodicarboxylate, diethyl azodicarboxylate, azodiacetyl, and Δ^1-1,2,4-triazoline-3,5-dione[2] showed +0.369, +0.369, +0.357, and

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(1) Recently, F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **87**, 1819 (1965), reported that molecular orbital calculation on azodicarbonitrile indicated an unfilled bonding orbital was present at $+0.42\beta$.

(2) Although this compound is unknown, the 4-phenyl derivative was synthesized already (R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 615 (1962)).

Table I. Nonphotochemical Hydrogen Abstraction Using Diethyl Azodicarboxylate

Starting material	Procedure	Time, hr	Product	Yield, %
Ethanol	A	72	Acetaldehyde[a]	62
Isopropyl alcohol	A	48	Acetone[a]	84
Cyclohexanol	A	72	Cyclohexanone[a]	55
Benzyl alcohol	B	5	Benzaldehyde[a]	60
p-Nitrobenzyl alcohol	B	5	*p*-Nitrobenzaldehyde	57
α-Methylbenzyl alcohol	B	10	Acetophenone	87
Benzhydrol	B	10	Benzophenone	70
Hydrazobenzene	B	0.5	Azobenzene	98
Anisidine	B	5	4,4′-Azodianisole	28
Ethanethiol	A	48	Ethyl disulfide	90
2-Propanethiol	A	72	Isopropyl disulfide	70
2-Propene-1-thiol	A	0.5	Allyl disulfide	90
1-Dodecanethiol	B	5	Dodecyl disulfide	95
t-Dodecyl mercaptan	B	10	*t*-Dodecyl disulfide	70
Benzenethiol	A	24	Phenyl disulfide	90
p-Nitrobenzenethiol	D[b]	8	*p*-Nitrophenyl disulfide	Not measured
o-Aminobenzenethiol	B	4	*o*-Aminophenyl disulfide	67
2-Naphthalenethiol	C	5	2-Naphthyl disulfide	87
2-Mercaptobenzothiazole	B	0.5	2,2′-Dithiobisbenzothiazole	95

[a] Isolated as the semicarbazone. [b] Ethanol was used as solvent.

+0.408, respectively, in units of β, and from this fact it would be predicted that they might have a high tendency to abstract hydrogen atoms from hydrogen donors.

Schenck and Formaneck[3] first reported the photochemical dehydrogenation with diethyl azodicarboxylate (**1**); they found that photochemical reaction of **1** with isopropyl alcohol gave pinacol and tetraethyl tetrazanetetracarboxylate, and acetaldehyde and **1** gave diacetyl and diethyl hydrazodicarboxylate (**2**). Recently, and concurrently with the present work, Cookson, *et al.*,[4] reported the photochemical oxidation of ethanol and cyclohexanol with **1** to give acetaldehyde and cyclohexanone. We have extended the usefulness of this reagent in a dehydrogenation reaction which may serve as a basis for preparative procedures. It has now been found that **1** is a useful oxidizing agent involving hydrogen abstraction from hydrogen donors, with good agreement with the quantum chemical prediction stated above. In this communication we wish to describe a new nonphotochemical hydrogen-abstracting oxidation using diethyl azodicarboxylate (**1**).

Compound **1** reacts smoothly with a wide variety of primary or secondary alcohols, mercaptans, anilines, and hydrazobenzenes to form aldehydes or ketones, disulfides, azobenzenes, and azobenzenes, respectively, while it itself undergoes hydrogenation to diethyl hydrazodicarboxylate (**2**). The reaction can be performed either by keeping the thoroughly mixed starting materials with 1 equiv of **1** in the dark at room temperature for 1 to 3 days (procedure A), or by refluxing the starting material with 1 equiv of **1** in anhydrous benzene for 0.5 to 10 hr (procedure B). Chloroform can be employed as the solvent (procedure C), and potentially other solvents may be used. The completion of the reaction is characterized by a change in color from orange red to pale yellow. Representative (not optimum) examples are listed in Table I.

The reaction of hydrazobenzene with **1** proceeds remarkably rapidly even in cold benzene to give azobenzene and **2** in almost quantitative yield. This would be connected with the strong electron-donating property of hydrazobenzene, and in fact the latter has an occupied antibonding orbital (-0.495β) according to Hückel MO method.

We consider this hydrogen-abstracting reaction as possessing considerable potential synthetic utility because of the mildness of the conditions employed and the good yields obtained. Moreover, it is noteworthy that **1** has no oxygen atoms which are available for oxidation; accordingly, this reaction does not proceed further after abstraction of hydrogen.

An investigation of the mechanism of these reactions and the reaction of other azo-disubstituted derivatives such as azodicarbonitrile, azodiacetyl, and 4-phenyl-Δ^1-1,2,4-triazoline-3,5-dione[2] with electron donors is in progress.

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(3) G. O. Schenck and H. Formaneck, *Angew. Chem.*, **70**, 505 (1958).

(4) R. C. Cookson, I. D. R. Stevens, and C. T. Watt, *Chem. Commun.*, 259 (1965). They also found that the reaction of cyclohexanol and **1** to give cyclohexanone and **2** proceeds in the dark, although in poor yield.

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A New General Structural Category of Heteropolyelectrolytes. Unusual Magnetic and Thermal Contraction Phenomena[1]

Sir:

This is to report an extensive investigation which establishes a new general structural category of heteropolyelectrolytes. The formula of the anions is

$$[H_hM^{+m}O_6X^{+x}O_4W_{11}O_{30}]^{-(14-m-x-h)}$$

Some of the salts have unusual physical properties.

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