TABLE II
REDUCTIONS IN DIFFERENT HYDROCARBON SOLVENTS AT 65°

Compound reduced	Solvent: Benzene BH_4^{-a}	Benzene Time (hr.)	Benzene Yield (%)	Hexane BH_4^{-a}	Hexane Time (hr.)	Hexane Yield (%)	Mineral oil BH_4^{-a}	Mineral oil Time (hr.)	Mineral oil Yield (%)
2-Ethylhexaldehyde	A	4	86	B	4	88	B	4	100
p-Nitrobenzoyl chloride	A	2	133	B	2	138	B	2	144
Benzoyl peroxide	A	3[b]	65	B	3	93	B	3	88

[a] A = cetyl trimethyl ammonium, B = tripicryl methyl ammonium. [b] At 25°.

compounds, containing functional groups known to be reduced by boronhydrides, were tried using one or both of the new quaternary ammonium borohydrides in hydrocarbon solvents, principally benzene. For comparison with the usual solvents for borohydride reductions, similar reductions were tried in isopropyl alcohol and water. Reductions were tested at room temperature or 65° or both. The results are summarized in Table I in terms of yield obtained in the specified time intervals.

The general utility of the long-chain quaternary ammonium borohydrides in various hydrocarbon solvents is indicated by several reductions listed in Table II, in which hexane and mineral oil were used as reaction solvents.

From Table I, it can be seen that there is no essential difference in reducing power between the two borohydrides used. A comparison of the results obtained in benzene shows that, as would be expected, aldehydes are reduced readily; ketones, only very slowly, even at elevated temperatures; and esters, not at all at room temperature and only slowly at higher temperatures. Peroxides and acid halides are readily reduced, while nitriles are not.

The exceptions to these generalizations are aromatic derivatives containing the *p*-nitro group. No reduction occurs at room temperature, regardless of solvent, and the *p*-nitro analog is also not reduced under these conditions. At 65°, however, ethyl *p*-nitrobenzoate and *p*-nitrobenzoyl chloride are reduced rapidly, regardless of solvent, while the unnitrated analog is either not reduced or only slowly. Furthermore, incomplete reduction of the nitro group itself is indicated in several of the runs in hydrocarbons, as shown by yields of 135–145%. The values are beyond experimental error, and are reproducible, as shown by the results with *p*-nitrobenzoyl chloride in benzene. Additional proof of this side reaction is provided by the fact that nitrobenzene itself comsumes hydridic hydrogen when treated with the quaternary ammonium borohydrides at 65° in benzene. In six hours, reaction amounts to 31%, based on 1:1 stoichiometry. Additional work is planned to clarify the nature of this side reaction.

A comparison of solvents shows that specific reductions occur most easily in water, less so in an alcohol, and slowest in the hydrocarbons. Such a comparison must be made cautiously, however, for variations in solubility of a particular compound among the different solvents undoubtedly also contribute to the ease of reduction observed. The results in Table II indicate no difference among the three hydrocarbon solvents tested.

Experimental

Materials.—The cetyl trimethylammonium borohydride used was 93% pure, based on hydrogen evolution on acid hydrolysis; the tricapryl methyl ammonium borohydride, 90%. The principal contaminants were quaternary ammonium halide, and small amounts of free amine and amineborane.

Commercial organic reagents and solvents were used without further purification.

Reductions were carried out in conventional glass equipment on a 0.1–0.2 mole scale, using 50 to 100% excess borohydride (corrected for purity). Yields were calculated, based on the known stoichiometry of the reactions, from the volume of hydrogen evolved upon acid hydrolysis of unreacted borohydride at the end of each run. The known quantity of borohydride added permitted calculation of the amount of hydrogen consumed by the reaction after correction to STP, and thence the per cent yield.

The extent of experimental error in this rapid survey resulting from the limited quantities and techniques used, is estimated at a maximum of 15%.

A New Constituent of *Daucus carota* L.: 2,4,5-Trimethoxybenzaldehyde

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Several attempts at the isolation of bitter principles from the roots, seeds, and leaves of carrots have been described in the literature prior to 1958[1] but they led to the separation of only amorphous uncharacterized products, apparently of glycosidic nature. A few years ago, a crystalline compound was isolated from bitter carrots[2] and it was proven to be 3-methyl-6-methoxy-8-hydroxy-3′,4′-dihydroisocoumarin.[3] However, this sub-

(1) E. Reeb, *J. pharm. Alsace Lorraine*, **50**, 13 (1923); F. V. Gizycki and H. Herrmanns, *Arch. Pharmazie*, **284**, 8 (1951); S. L. Agarval, P. C. Dandja, and V. N. Sharma, *Indian Pharmacist*, **8**, 291 (1953).

(2) A. Dodson, H. N. Fukui, C. D. Ball, R. L. Carolus, and H. M. Sell, *Science*, **124**, 984 (1956).

(3) E. Sondheimer, *J. Am. Chem. Soc.*, **79**, 5036 (1957).

stance, which is related to fungi metabolites, could have been produced by the action of microorganisms. The problem of the nature of the original bitter principles of carrots, and in particular, of carrot seeds, remained open[4] until the isolation of the bitter crystalline "Gazarin" from the seeds of *D. carota* var. *boissieri* Schweinf. was reported.[5] This new compound melted at 113° and was assigned the molecular formula $C_{15}H_{18}O_6$. Its structure was not elucidated.

We have now isolated "Gazarin" by the published method[6] and proved its identity with 2,4,5-trimethoxybenzaldehyde (asaronaldehyde), already known as a natural constituent of the essential oil of *Asarum europaeum* L.[7,8]

Molecular weight determination (isopiestic method) and analysis, including methoxyl determination, made us revise the formula of "Gazarin" to $C_{10}H_{12}O_4$ or $C_7H_3O(OCH_3)_3$. The infrared spectrum suggested an aromatic carbonyl compound $C_6H_2(OCH_3)_3CHO$. The nuclear magnetic resonance spectrum[9] revealed three adjacent singlet peaks with τ-values: 6.20, 6.15, and 6.09 p.p.m. of equal area and in the correct region for methoxyl aromatic), two singlet peaks with τ-values: 3.57 and 2.78 p.p.m. (indicative of two non-adjacent protons on the benzene ring), and one peak with $\tau = -0.18$ p.p.m. (indicative of aldehyde). This pattern was closely parallel to that shown by anisaldehyde, 3,4-dimethoxybenzaldehyde, and 5,7-dimethoxy-6-formyl-2-methylchromone. The fact that the ring protons could not be adjacent and that the compound was not symmetrical restricted the choice to only two possibilities: 2,4,5- and 2,3,5-trimethoxybenzaldehydes. The latter melts at 71°[10], and therefore, "Gazarin" is 2,4,5-trimethoxybenzaldehyde (reported m.p., 114°[7]). Further confirmation was afforded by the identity of the melting points of two simple carbonyl derivatives of these two substances.

Experimental

Crushed seeds of *D. carota* L. var. *boissieri* Schweinf. were extracted by the method of D. Y. Haddad, *et al.*,[5] to give the natural product as colorless crystals, m.p. 113–114° (uncor.), soluble in hot water, and cold ethanol, ether, chloroform, and benzene. It gave a violet-blue spot (under ultraviolet light) of R_f 0.62 when chromatographed on Whatman No. 1 paper (temp., 27°, water used as eluent, ascending technique). Characteristic infrared bands were found at 6.01, 6.19, and 11.63 mμ. *p*-Nitrophenylhydrazone, m.p. 233–234° (reported m.p.: 234°[7]); semicarbazone, m.p. 209–210° (reported m.p. 208°[11]).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17; three OCH_3, 47.49; mol. wt., 196.20. Found: C, 61.52; H, 6.30; OCH_3, 45.33. mol. wt., 198 (modified isopiestic method with a Mechrolab Model 301 thermoelectric osmometer).

Acknowledgment.—The author is indebted to Dr. Jerry P. Heeschen for helpful advice.

(4) Comp. F. Korte, H. Barkemeyer, and I. Korte, *Fortschr. Chem. Org. Naturstoffe*, **17**, 124 (1959).

(5) D. Y. Haddad, S. M. Khafagy, and N. Nazmi, *Egypt. Pharm. Bull., Sci. Ed.*, **40**, 81 (1958).

(6) As extraction involved use of hot water, the possibility that 2,4,5-trimethoxybenzaldehyde exists in the intact seed as an easily hydrolysable complex with some other substances is not excluded.

(7) J. V. Alphen, *Rec. trav. chim.*, **46**, 195 (1927).

(8) I. Gerö, *Chem. Folyoirat.* **34**, 103, 115 (1928); *Chem. Abstr.*, **23**, 4943.

(9) N.m.r. spectra were recorded in deuterochloroform using tetramethylsilane as internal reference at +10 p.p.m. with a Varian Associates Model A-60 analytical n.m.r. spectrometer.

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Structure of the Alleged Diels–Alder Adduct from 2,3-Dimethylquinoxaline and Quinone[1]

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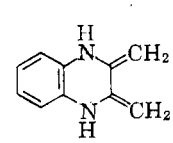
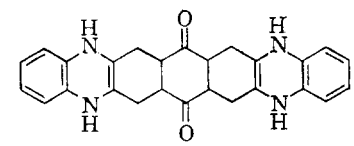
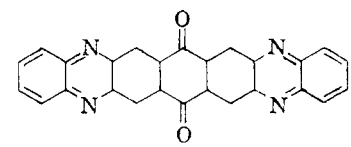
In discussions of quinoxalines, reference[2] is frequently made to the "Diels–Alder" reaction of 2,3-dimethylquinoxaline and *p*-benzoquinone in which the former compound is thought to react in its tautomeric form I. Schönberg and Mustafa,[3] who first reported this reaction, proposed structures II or III for the product on the basis of the finding that quinoxalines not capable of forming a diene system do not undergo this reaction. It



I



II



III

appeared to us that the dihydroquinoxaline systems present in either structure should be exceedingly sensitive towards air oxidation (which is apparently not the case) and that the structure of the "adduct" was therefore suspect. We have found that this alleged "Diels–Alder" product is in fact a complex

(1) This investigation was supported by a grant (CY-2551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) (a) E. H. Rodd, ed., "Chemistry of Carbon Compounds," Vol. IVB, Elsevier Publishing Co., Amsterdam, 1959, p. 1349; (b) J. C. E. Simpson, "The Chemistry of Heterocyclic Compounds: Condensed Pyridazine and Pyrazine Rings," Interscience Publishers, Inc., New York, 1953, p. 278; (c) R. C. Elderfield, ed., "Heterocyclic Compounds," Vol. VI, John Wiley and Sons, Inc., New York, 1957, p. 480.