Calculation of Rate Constants.—With the exception of the nitrophenyl and nitrobenzyl ethyl carbonates, first-order rate constants were obtained from the slopes of the plots of log ($P_\infty - P_t$) or log ($E_\infty - E_t$) against time. The nitro compounds showed secondary decomposition, and their first-order rate constants were obtained from the initial slopes of plots of dE/dt against E.[1] The phenyl ethyl carbonates were all pyrolyzed several times, and the mean values of the rate constants are given in Table I. Average deviations from the mean were within ±1% except for the *p*-methoxy compound (±1.5%). The precision in the pyrolysis of benzyl ethyl carbonates was *ca.* ±2%. Rate constants are given in Table II.

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Autoxidation of Galvinoxyl[1]

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The hindered phenoxyl radical galvinoxyl,[2] G·, [derived from 2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-hydroxybenzal)cyclohexadienone] is finding increasing use as a radical scavenger.[3] The original reports[2] indicated that it was stable to oxygen both in the solid phase and in solution. We wish to call attention to the instability of solutions of galvinoxyl and to the interesting feature of its consumption *via* an autocatalytic path: A freshly prepared solution of galvinoxyl (10^{-3} M) in undegassed benzene at 25° was observed to undergo almost no change in optical density for many minutes, after which induction period the concentration of galvinoxyl rapidly fell. This behavior also took place in the dark but did not occur in degassed solvent. When a solution of galvinoxyl was shaken in an atmosphere of oxygen, the rate of disappearance of galvinoxyl (followed spectrophotometrically) closely paralleled the rate of uptake of oxygen (Fig. 1). Oxygen consumption was 1.4 moles per mole of galvinoxyl. Among the oxidation products were 2,6-di-*t*-butyl-1,4-benzoquinone (20%) and 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (4%). No other discrete products were isolated from the residual tar.

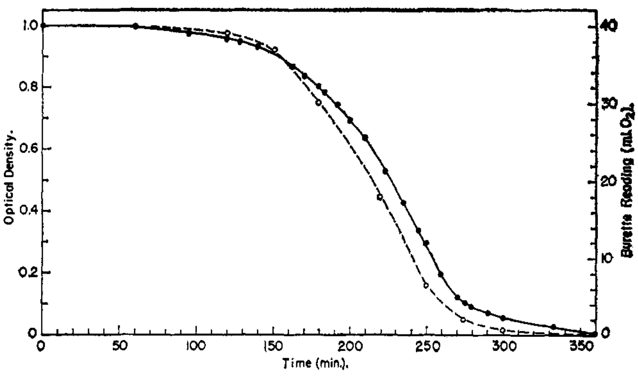
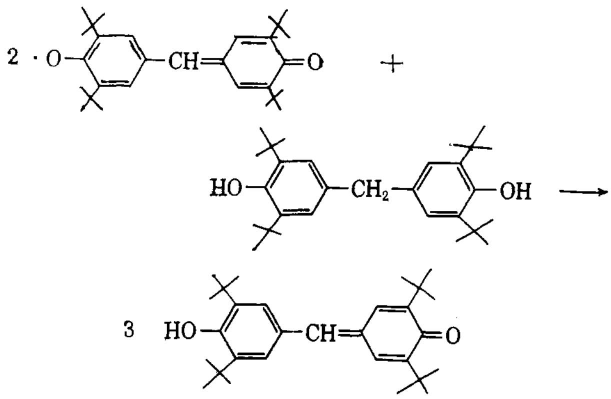


Fig. 1.—Autoxidation of galvinoxyl (0.02 M) in benzene by shaking in an oxygen atmosphere at room temperature: solid circles, consumption of oxygen; open circles, consumption of galvinoxyl followed spectrophotometrically at 530 mμ.

A number of experiments were effected to ascertain the basis of the inhibition period. Autocatalysis by products of the autoxidation reaction was excluded in that the addition of fresh galvinoxyl to an already oxidized solution exhibited a similar induction period. In view of the general effectiveness of phenols as inhibitors of autoxidation, a small sample of the bisphenol trihydrogalvinoxyl, GH_3 (3,5,3′,5′-tetra-*t*-butyl-4,4′-dihydroxydiphenylmethane), was added to a solution of galvinoxyl in benzene. An inmediate reaction occurred, and the remaining galvinoxyl *was markedly stabilized towards oxygen* (Fig. 2). The stoichiometry of the galvinoxyl-*tri*hydrogalvinoxyl reaction[4] is 2:1, producing hydrogalvinoxyl, GH, in high yield.



The data of Fig. 2 are suggestive that the inhibition period, Fig. 1, is due to the presence of hydrogalvinoxyl, an impurity difficult to remove in the preparation of galvinoxyl. The addition of hydrogalvinoxyl to a solution of galvinoxyl revealed a close relationship between the amount added and the length of the inhibition period (Table I). These data are suggestive of the presence of a few per cent of hydrogalvinoxyl in the galvinoxyl (in accord with the value of 97 ± 1% purity determined by the titrimetric method) and carry the further implication that a completely pure sample of galvinoxyl in solution might undergo rapid autoxidation.

The inhibition period is also markedly dependent on concentration. A 10^{-3} M solution of galvinoxyl in benzene was 50% consumed in 1 hr.; a 4×10^{-6} M solution was only 10% destroyed in 24 hr. The sta-

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(1) This work was supported by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the U. S. Government.

(2) (a) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957); (b) M. S. Kharasch and B. S. Yoshi, *J. Org. Chem.*, **22**, 1435 (1957).

(3) (a) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962); (b) P. D. Bartlett, B. H. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962); (c) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(4) The reaction kinetics is complex. It is hoped that a full account of the G-GH_3 reaction can be presented at a later date.

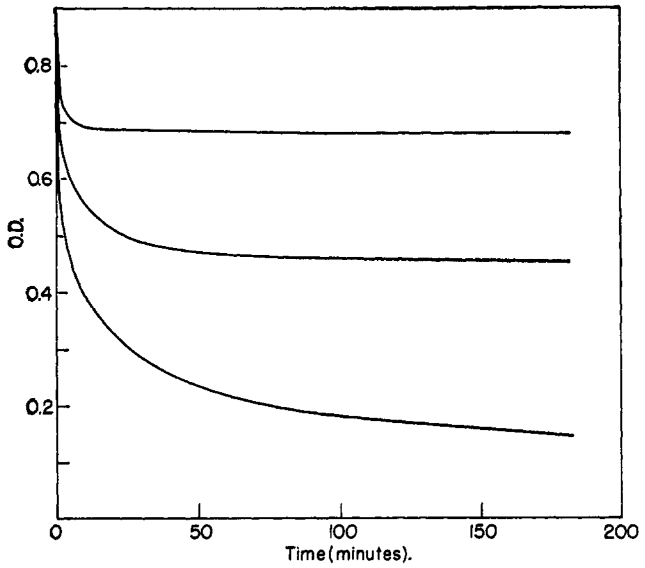

Fig. 2.—Reaction of galvinoxyl with trihydrogalvinoxyl in benzene at 25°; initial concentration of galvinoxyl, $10^{-3} M$ (O.D., 0.90). Initial concentration of trihydrogalvinoxyl: upper curve, $1.25 \times 10^{-4} M$; middle curve, $2.50 \times 10^{-4} M$; lower curve, $5 \times 10^{-4} M$.

Table I

Inhibition of the Autoxidation of Galvinoxyl by Hydrogalvinoxyl in Benzene at 30°

Hydrogalvinoxyl, % added	Inhibition time, min.	Δt
0	59	59
4	117	58
8	171	54
12	277	56

bility of solutions of galvinoxyl with varying solvents has not been investigated. Qualitatively, the results of Fig. 1 are observed with both benzene and carbon tetrachloride.[5]

It is of interest that this hindered phenoxyl radical, galvinoxyl, a type of compound usually considered as an inhibitor of autoxidation, is itself susceptible to autoxidative destruction.[6]

Experimental

Galvinoxyl was prepared by the procedure of G. M. Coppinger.[2a] The method of Greene, Adam, and Cantrill[3c] was used for its purification and titrimetric analysis.

Autoxidation of Galvinoxyl.—A stream of oxygen was passed through a solution of 1 g. (2.37 mmoles) of galvinoxyl in 500 ml. of carbon tetrachloride. After 24 hr. the initial dark reddish brown solution decolorized to a pale reddish orange solution. The solvent was removed under reduced pressure and the residue chromatographed on an alumina column, eluting with *n*-pentane. The first ten fractions contained an intensely yellow solid, 2,6-di-*t*-butyl-1,4-benzoquinone, 0.2613 g., m.p. 64.5–65.5° (lit.[7] m.p. 65–66°), identical in infrared spectrum with that reported in the literature[7]; mol. wt.: calcd., 220; found, 214 (Rast). The next compound eluted from the column was a white solid, 41 mg., m.p. 185–186°. Two recrystallizations from an ether–pentane mixture afforded 3,5-di-*t*-butyl-4-hydroxybenzaldehyde, m.p. 186–188° (lit.[8] m.p. 187–188°), m.m.p. 186–188°, and identical in ultraviolet and infrared spectra with an authentic sample. No other discrete compound could be isolated from the alumina column. An autoxidation in benzene gave similar results.

Reaction of Galvinoxyl with Trihydrogalvinoxyl.—To a dry constricted test tube, flushed with nitrogen, was added 0.844 g. (2 mmoles) of galvinoxyl and 0.425 g. (1.0 mmole) of trihydrogalvinoxyl, followed by 30 ml. of freshly distilled benzene (deaerated with nitrogen). The solution was degassed, sealed, and left for 3 days at 25°. The ultraviolet absorption of the resulting solution at 385 mμ showed an ϵ of 32,000; for pure hydrogalvinoxyl at λ 385 mμ, ϵ is 33,800. Removal of solvent afforded material identical in infrared spectrum with hydrogalvinoxyl. Several recrystallizations of the product from methanol–water afforded pure hydrogalvinoxyl, m.p. 158–159° (lit.[2] m.p. 158–159°).

Spectrophotometric and Volumetric Determination of the Rate of Autoxidation of Galvinoxyl.—For the spectrophotometric rate a 0.001 M solution of galvinoxyl in benzene (reagent grade, distilled from sodium) was prepared. Readings of optical density *vs.* time were made at 530 mμ in a stoppered quartz cell in a Beckman DU spectrophotometer.

The rate of oxygen absorption was measured by the procedures normally employed in catalytic hydrogenations. Concurrent changes in optical density were followed by periodic removal of a sample by a syringe inserted through a rubber stopple. Representative data are summarized in Fig. 1.

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[5] A ~$10^{-4} M$ solution of galvinoxyl in undegassed isooctane (spectral grade) in quartz showed no change in the intensity of the electron spin resonance signal (the normal 10-line spectrum of galvinoxyl is changed to a broad band in the presence of oxygen) over a period of hours (private communication from G. M. Coppinger).

[6] A number of chain branching steps may be envisioned to describe the autocatalysis. Some of these are outlined in the Ph.D. thesis of W. Adam; M. I. T., February, 1961.

[7] E. Müller and K. Ley, *Ber.*, **88**, 601 (1955).

[8] G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

Hydroboration in the Sugar Series[1a]

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Brown and Subba Rao[2] observed that terminal olefins were smoothly converted into trialkylboranes in the presence of a solution of aluminum chloride and sodium borohydride in bis(2-methoxyethyl) ether (diglyme). These trialkylboranes were readily converted into the corresponding alcohols by subsequent oxidation with hydrogen peroxide. The procedure has been improved[3] by the use of different solvents, hydrides, and Lewis acids. It was of interest to apply this hydroxylation reaction to the sugar series. An available terminal olefin is I which may be designated 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose. This substance is obtainable from 1,2-*O*-isopropylidene-α-D-glucofuranose by treatment of its 5,6-di-*O*-*p*-toluenesulfonate with sodium iodide.[4]

Three possible products could be obtained from the hydroboration of I: 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose, the C-5 epimeric 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose, and 5-deoxy-1,2-*O*-iso-

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[1] (a) Supported in part by Grant No. CY-3232 from the Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health (Research Foundation Project 759). Preliminary communication: Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 2D. (b) National Science Foundation Cooperative Graduate Fellow, 1961–1964. (c) Socony-Mobil Fellow, Department of Chemistry, 1959–1960.

[2] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

[3] H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *ibid.*, **82**, 4233 (1960).

[4] H. Ohle and E. Dickhäuser, *Ber.*, **58**, 2593 (1925); J. K. N. Jones and J. L. Thompson, *Can. J. Chem.*, **35**, 955 (1957); L. D. Hall, L. Hough, and R. A. Pritchard, *J. Chem. Soc.*, 1537 (1961).