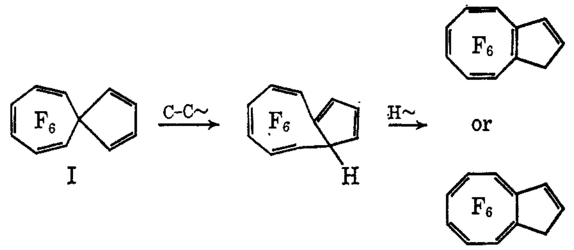
a triplet at τ 6.67.[15] The fluorine nmr spectrum of III shows peaks for six different fluorines grouped roughly in pairs at 107, 113, 120, 122, 131, and 133 ppm upfield from internal fluorotrichloromethane.

These chemical shifts seem inconsistent with any structure containing the valence–tautomeric bicyclo-[4.2.0] system[11] and III is preferred, although the structure cannot be regarded as unequivocably proved.



I

III

A mechanism for the conversion of I into III can be constructed and involves a carbon–carbon bond shift (possibly in the norcaradiene form II) followed by a hydrogen shift. These steps have rather good analogy, albeit in much more simple systems.[16-18]

Experimental Section

Spiro[4.6]-6,7,8,9,10,11-hexafluoroundeca-1,3,6,8,10-pentaene (I).—A solution of 1 ml of diazocyclopentadiene[19,20] in 122 g of hexafluorobenzene was irradiated through a Pyrex filter with a 450-W Hanovia medium-pressure mercury arc for 14 hr. The hexafluorobenzene was removed by distillation at 0.1 mm leaving a dark brown, thick oil. This was distilled in a bulb-to-bulb apparatus at room temperature and 0.025 mm to yield 500 mg of a yellow oil. Spectral analysis revealed this to be I contaminated with traces of dicyclopentadiene.

Anal.[21] Calcd for $C_{11}H_4F_6$: C, 52.82; H, 1.61. Found: C, 53.01; H, 1.72.

Pyrolysis of I. A. Flow System.—A solution of 10 mg of I in 0.5 ml of cyclohexane was dropped slowly into a 12-in. Pyrex tube packed with glass helices under nitrogen at 220°. Residence time was *ca.* 1 sec. Under these conditions I is converted into a mixture of 40% I and 60% III with *ca.* 90% recovery. Increasing the temperature to 255° resulted in 90–95% conversion into III with somewhat reduced recovery.

B. Gas Chromatography.—Compound I is easily converted into III in the injector or detector–collector of a gas chromatograph. The peak corresponding to I is simply collected and reinjected. Injection on a 5-ft SE 30 silicone oil column operated at 95° (injector, 130°, and detector, 210°) with a flow rate of 100 cc of helium/min results, as revealed by reinjection, in *ca.* 25% I (retention time 22 min) and 75% III (retention time 42 min, mp 50–52°).

Anal. Found: C, 52.71; H, 1.66.

Registry No.—I, 16033-88-8; III, 16021-17-3; diazocyclopentadiene, 1192-27-4; hexafluorobenzene, 392-56-3.

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[15] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Varian NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, No. 227.

[16] J. W. De Haan and H. Kloosterziel, *Rec. Trav. Chim. Pays-Bas*, **84**, 1594 (1965), and references therein.

[17] W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

[18] S. McLean and R. Haynes, *ibid.*, 2385 (1964).

[19] W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

[20] T. Weil, *J. Org. Chem.*, **28**, 2472 (1963).

[21] Although acceptable carbon and hydrogen analyses could be obtained on I, fluorine analysis was poor. We do not know the precise cause of this but can point out that I is most unstable. Exposure to air results in rapid darkening and eventual deposition of a brown-black solid.

Electron-Transfer Polymers. XXXIII. Compounds Related to Tocopherol

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Redox polymers[1a] have been prepared by polycondensation of 2,5-disubstituted benzoquinones.[1b] In the resulting linear polymers the redox group is part of the chain. In this paper we report the preparation of redox monomer from a quinonyl glycol. In this polymer the redox groups are pendant from the chain.[2] In the course of preparing this monomer several interesting new compounds, analogs of tocopherol derivatives, were prepared, and new behaviors were observed.

Trimethylhydroquinone (1,3,4-trimethyl-2,5-dihydroxybenzene) was converted into 3-hydroxy-6-methoxy-2,4,5-trimethylbenzyl chloride (I).[3] Treatment with sodioethyl malonate produced ethyl(3-hydroxy-6-methoxy-2,4,5-trimethylbenzyl)malonate (II). Reduction of II with lithium aluminum hydride yielded 2-(3′-hydroxy-6′-methoxy-2′,4′-5′-trimethylbenzyl)propane-1,3-diol (III). (See Chart I.) Oxidative cleavage of the methoxy group in III with lead tetraacetate suspended in 50% aqueous tetrahydrofuran (THF) produces the desired monomer, 2-(duroquinonyl)propane-1,3-diol (V), as yellow crystalline material. If, however, III is oxidized with lead tetraacetate suspended in dry THF there is produced a white, crystalline material with a carbonyl band at 1683 cm^{-1}, and no hydroxyl band in the ir spectrum and λ_{max} at 244 mμ (ϵ 1.09×10^4) in the uv spectrum. The uv spectrum closely resembles that of 9-substituted α-tocopherol.[4] This new substance appeared to be 8a,3-epoxymethano-5,7,8-trimethyl-6H,8aH-dihydrochroman-6-one (IV). Then IV, shaken with cation exchange resin in the acid form in 50% aqueous THF, gives V in good yield. Reduction of IV in the presence of palladium charcoal yields 3-hydroxymethyl-5,7,8-trimethylchroman-6-ol (VII) quantitatively. Reoxidation of VII produces IV by using ceric ammonium nitrate or silver oxide in dry THF quantitatively. When yellow V is reduced in an attempt to obtain 2-(durohydroquinyl)propane-1,3-diol (VI), a white crystalline material could be isolated but in air it quickly oxidizes to red (quinhydrone!) then yellow quinone V. If the reduction is carried out in acid, there is obtained stable VII, presumably *via* VI. When the methoxy group of III is cleaved with HCl, there is formed VII, presumably *via* the VI pathway (Chart I). These behaviors bear strong analogy to those of the tocopherols. Structure VII differs from α-tocopherol only in the substituents on the oxygen ring. When the corresponding ring is opened there is

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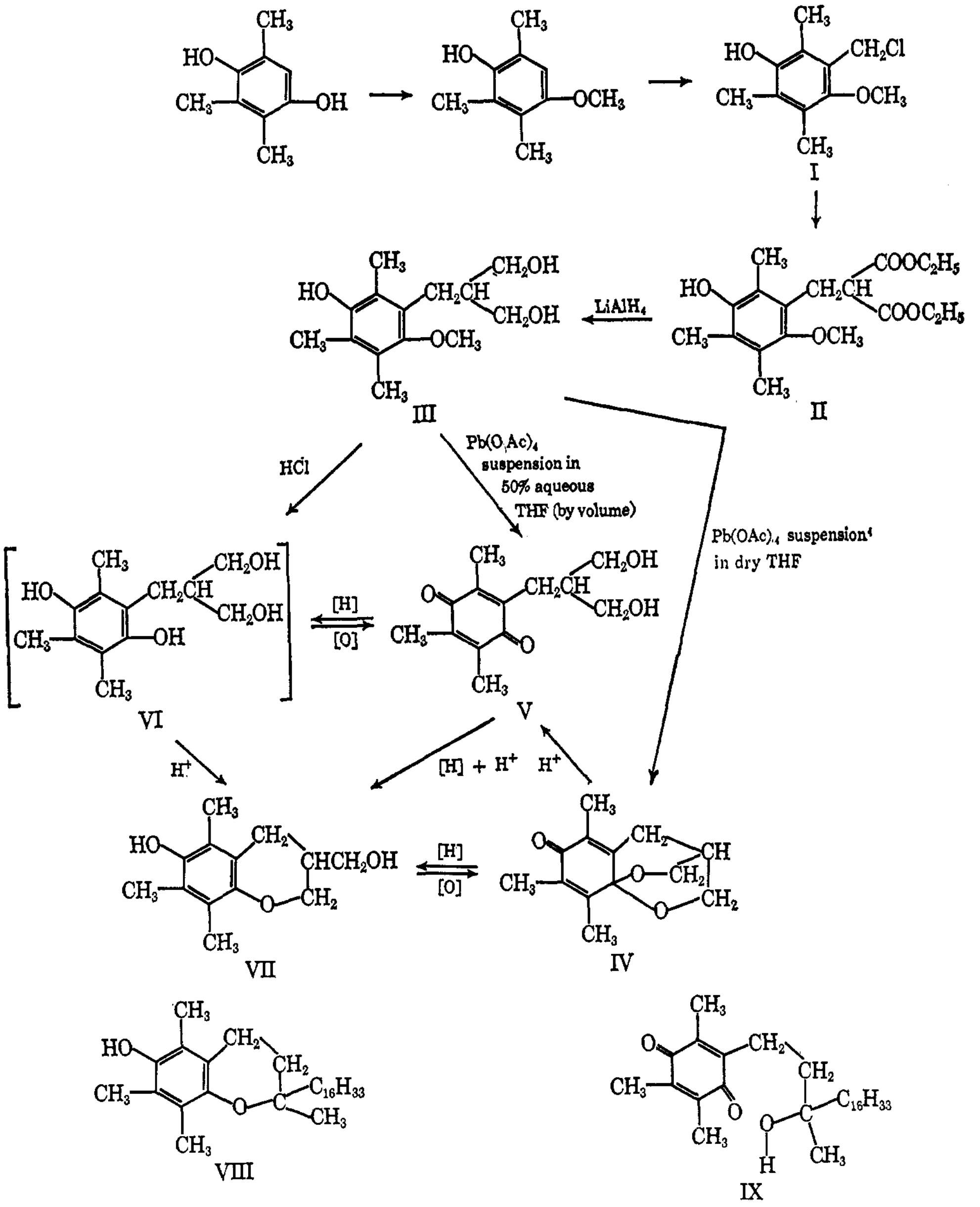
[1] (a) H. G. Cassidy and K. A. Kun, "Oxidation–Reduction Polymers," Interscience Publishers, Inc., New York, N. Y., 1965; (b) G. Wegner, N. Nakabayashi, and H. G. Cassidy, *J. Org. Chem.*, **32**, 3155 (1967).

[2] Syntheses and properties of the polymers will be published elsewhere.

[3] W. John and F. H. Rathmann, *Ber.*, **74**, 890 (1941).

[4] W. H. Harrison, J. E. Gander, E. R. Blakley, and P. D. Boyer, *Biochim. Biophys. Acta*, **21**, 150 (1956).

Chart I



obtained the unstable hydroquinone which is readily oxidized to α-tocopherolquinone (IX).[5,6]

The intriguing correspondence of IV, V, VI, and VII to 9-substituted-α-tocopherone, α-tocopherolquinone (IX), α-tocopherolhydroquinone, and α-tocopherol (VIII)[4,6] leads us to point out the important role of the γ-hydroxyl. The redox potential of durohydroquinone is low; the hydroquinone form is very easily oxidized. By building into the molecule a suitably placed hydroxyl we provide automatic stabilization of the reduced form (VII) through ring closure.

Experimental Section

Preparation of II.—To a sodium ethylate solution [6.10 g (0.265 g-atom) of sodium in 135 ml absolute ethanol] was added 23.2 g (0.145 mol) of ethyl malonate in 40 ml of absolute ethanol, dropwise with cooling. After 15 min, 28.2 g (0.131 mol) of I in 100 ml of dry THF was added slowly. The reaction mixture was refluxed 1.5 hr. Refluxing longer than 2 hr decreased the yield. After neutralization with acetic acid, the solvent was removed and the residue was suspended in water and extracted with ether. The ether solution was dried with magnesium sulfate, the solvent was removed, and the residue was crystallized from carbon tetrachloride (refrigerator) to yield 13.9 g (31.4%) of white crystals: mp 118–119°; ir spectrum, OH (3475), C=O (1750, 1725), -CO- (1250 cm^{-1}); nmr,[7] CH_3 (ring) and CH at τ 7.90 and 7.84 (10) and α-CH_2 at 6.80 (2), C_2H_5 (ester) at 8.81 (6) and 5.88 (4) CH_3-O- at 6.38 (3).

Anal. Calcd for $C_{18}H_{26}O_6$: C, 63.88; H, 7.75. Found: C, 63.90; H, 7.68.

When the synthesis was carried out with 1.20 g (0.052 g-atom) of sodium, 8.0 g (0.050 mol) of ethyl malonate, and 10.7 g (0.050 mol) of I, a yield of 5.3 g (31%) of II was obtained.

Preparation of III.—To a stirred suspension of 1.2 g of lithium aluminum hydride in 50 ml of dry THF, cooled in ice, was added dropwise 50 ml of THF containing 5.5 g (0.0162 mol) of II. After the vigorous reaction had subsided the mixture was refluxed for 2 hr. Excess hydride was removed by careful addition of water, and the mixture was neutralized with acetic acid. Saturated aqueous ammonium chloride solution was added, and the upper, organic layer was decanted. The water layer was washed with ether, and the washings and organic layer were combined and dried with magnesium sulfate. The solvent was removed by evaporation from the dried mixture, and the residue

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(5) J. Bunyan, D. McHale, and J. Green, *Brit. J. Nutr.*, **17**, 391 (1963).

(6) J. Green and D. McHale in "Biochemistry of Quinones," R. A. Morton, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 8.

(7) Nmr data were obtained with a Varian Associates Model A-60 spectrometer. The chemical shifts are given in τ values; the numbers within parentheses indicate the number of protons.

was recrystallized from methanol to give 2.55 g (61.5%) of white crystals: mp 173–175°; ir, OH (3415, 3308), -C-O (1240, 1167, and 1036 cm^{-1}); nmr,[7] CH_3 (ring) and CH at τ 8.03, 7.88, 7.71 (total 10), α-CH_2 at 7.23 (2), CH_3O at 6.63 (3), $-CH_2O-$ at 6.17 (4).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.72; H, 8.57.

Preparation of IV and V. A.—To a stirred solution of 0.62 g (0.0024 mol) of III in 20 ml of dry THF was added 1.2 g (0.0027 mol) of lead tetraacetate. The suspension was refluxed 15 min. Aqueous sodium hydroxide was added and the mixture was extracted with ether. On evaporation of the solvent from the dried ether solution there was obtained a red-yellow oily residue. This was dissolved in a small amount of acetonitrile and refrigerated. White plates crystallized in a yield of 0.15 g (28%), mp 159–160°. From the mother liquor, by recrystallization from THF-*n*-heptane a further yield of 0.13 g (23%) of white crystals, mp 159–160°, was obtained, and 0.07 g (12%) of yellow crystals melting at 79–79.5° were also obtained. The white crystalline material is IV and the yellow is V.

Anal. Calcd for $C_{13}H_{16}O_3$ (IV): C, 70.89; H, 7.32. Found: C, 71.02; H, 7.28.

Calcd for $C_{13}H_{18}O_4$ (V): C, 65.53; H, 7.61. Found: C, 65.46; H, 7.58.

The ir spectrum of IV showed C=O at 1683, 1644, and 1633 (C=C) and -C-O- at 1260, 1197, 1099, and 1040. That for V showed -OH at 3285; C=O (quinone) at 1630; and -CO- at 1303, 1260, and 1070 cm^{-1}. The nmr spectra[7] of IV showed CH_3 (ring) and CH_2 at 8.00 (3), 8.14 (6), and 7.77 (1); α-CH_2 at 7.24 (2); $-CH_2-O$ at 6.06, 5.91, 5.72, and 5.58 (total 4).

B.—To 22.0 g (0.0866 mol) of III in 700 ml of THF was added 700 ml of water, then 44.0 g (0.995 mol) of lead tetraacetate. The suspension was stirred and refluxed for 30 min. After addition of sodium hydroxide, extraction with ether, and drying and evaporation of the ether, there was obtained a red-yellow residue. This was dissolved in a small amount of THF, and *n*-heptane was added. Compound V crystallized. The crude material was recrystallized from THF-*n*-heptane to yield 11.0 g (63.4%), mp 79.0–79.5°. From the mother liquor there was obtained 2.0 g (10.5%) of IV.

Preparation of VII. A.—A suspension of 1.0 g (0.0039 mol) of III in 30 ml of water and 30 ml of concentrated hydrochloric acid was refluxed, with stirring, for 9.5 hr. On cooling, the product crystallized. Recrystallization from acetonitrile gave 0.62 g (72%) of VII as white crystals: mp 171–172°; ir spectrum, OH [3300, 3150, (chromanol, 1610)] and -C-O- (1255, 1241, 1125 cm^{-1}); nmr,[7] CH_3 (ring) and CH at 8.29, 8.25, 8.17, (total 10), CH_2 at 7.92 (2), $-CH_2O-$ at 6.69 (2), and 6.43 (2).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.16. Found: C, 70.06; H, 8.09.

B.—A solution of 0.50 g (0.0023 mol) of IV in 20 ml of THF was shaken in an atmosphere of hydrogen with a catalytic amount of 10% palladium charcoal at room temperature. Within 10 min 60 cc of hydrogen was absorbed (theory, 51 cc; probably the excess went to the solvent.) From the filtered solution there was obtained a pale yellow powder which on recrystallization from acetonitrile, yielded 0.40 g (80%) of white crytals, mp 171–172°. No depression was observed in mixture melting point with VII.

C.—A solution of 0.5 g (0.0021 mol) of V in 5 ml of glacial acetic acid and 15 ml of water was refluxed with 0.5 g of zinc powder for 0.5 hr. The mixture was neutralized with sodium hydroxide, extracted with ether, and the extract was dried and evaporated. The reddish residue was recrystallized from acetonitrile to give 0.28 g (60%) of VII, mp 171–172°.

Oxidative titration of VII with ceric ammonium nitrate in 90% aqueous acetic acid at 25° gave an equivalent weight of 114.5 (calcd, 111). The midpoint potential was about 0.657 V.

Ultraviolet Spectra.—The solvent, λ_{max} in mμ, and the molar extinction coefficient are given in that order: IV (CH_2Cl_2, 244, 1.09×10^4); V (CH_2Cl_2, 272, 1.65×10^4; CH_3OH, 269, 1.99×10^4); VI (CH_3OH, 289, 3.9×10^3); VII (CH_2Cl_2, 296, 2.29×10^3).

Registry No.—II, 16526-47-9; III, 16526-48-0; IV, 16526-49-1; V, 16526-50-4; VII, 16526-51-5; VIII, 16526-52-6.

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Reaction of Pseudoxazolones and Hydrazoic Acid

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The reaction of 4-arylidene-5-oxazolones with hydrazoic acid was reported by Awad, *et al.*[1,2] to produce tetrazolylacrylic acid derivatives in good yields. In examining the reactivity of 2-isopropylidene-4-methyl-3-oxazolin-5-one[3] (Ia, pseudooxazolone) with more than 2 mol of hydrazoic acid, we obtained white crystalline materials in 38% yield by their reaction condition as shown in Table I.

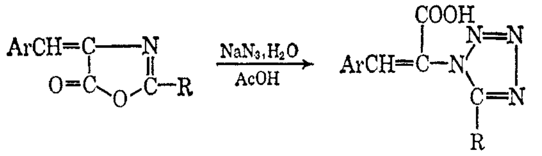

TABLE I

ELEMENTAL ANALYSES OF IV

R	Mp, °C	Crude yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Me	210[a]	38	42.40	6.56	38.10	42.77	6.61	37.81
i-Pr	216[a]	71	48.10	7.60	33.00	48.59	7.55	32.18
i-Bu	216[a]	96	50.50	8.01	30.90	50.71	7.94	30.95

[a] Melted with decomposition.

That this product was a urea derivative was established by several spectral methods. The infrared spectrum showed strong absorptions at 3310, 2140,[4] and 1660 cm^{-1} arising from amide and urea N–H stretching, azide asymmetric stretching, and amide and urea carbonyl stretching vibrations, respectively. The nmr spectrum of the product displayed a 12-proton singlet at δ 1.44 due to four *gem*-methyl groups, a 6-proton doublet centered at 1.47; a 2-proton quartet centered at 5.65 (J = 6 cps); and a broad NH proton singlet at 3.66 in pyridine.

Mass spectra of IV offered a good indication of the presence of azide linkages and of the structure of IV. Each peak corresponded well to fragments formed from the molecular ion peak by cleavage at positions as shown in Chart I. In addition, elimination of methyl and isobutyl radicals gave rise to *m/e* 353 and 395 in IVa and IVc, respectively.

The first step in this transformation is postulated to be 1,4 addition of hydrazoic acid to I forming a satu-

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[1] W. I. Awad, A. F. M. Fahmy, and A. M. A. Sammour, *J. Org. Chem.*, **30**, 2222 (1965).

[2] H. Behringer and W. Grimme, *Chem. Ber.*, **92**, 2967 (1959).

[3] Y. Iwakura, F. Toda, and Y. Torii, *Tetrahedron*, **23**, 3363 (1967).

[4] C. N. R. Rao, T. S. Chao, and C. W. W. Hoffman, *Anal. Chem.*, **29**, 916 (1957).