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PHOTOSENSITIZED OXYGENATION OF ALKYL-SUBSTITUTED FURANS[1]

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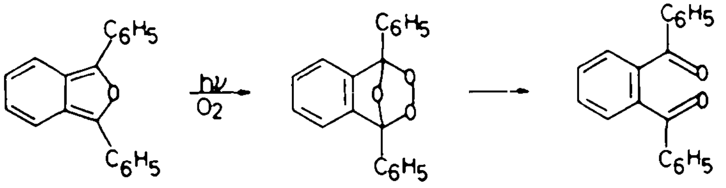
Abstract—Photooxidation in methanol of 2-methyl-, 2,5-dimethyl-, dicyclohexano- and menthofuran, sensitized by Rose Bengal, produces crystalline 2-methoxy-5-hydroperoxy-2,5-dihydrofuran derivatives by addition of solvent to intermediate ozonide-like peroxides.

THE dye-sensitized photooxygenation of furans has been the subject of extensive study.[4] The reaction is thought to proceed by way of a cyclic peroxide (a cyclobutadiene monoozonide) formed by 1,4-addition of oxygen, by analogy to the reaction with cyclic dienes.[4a] These peroxides are extremely unstable, and have been isolated in only a few cases. Diphenylisobenzofuran (I) is reported to yield a crystalline peroxide to which structure II was assigned (the furan itself is presumably the sensitizer in this reaction).[4c] The peroxide explodes over 20°, and decomposes in solution at room temperature to give III. Similarly, 2,5-diphenyl-3,4-di(*p*-bromophenyl) furan gives an unstable peroxide, which at room temperature rearranges to a mixture of products.[4f] A similar peroxide (IV) which explodes at −10° can be isolated from oxidation of



I II III

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[*] Contribution No. 1859

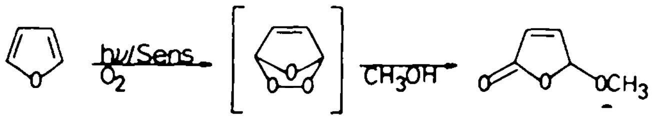
[1] Taken in part from the doctoral dissertations of K.-H. Schulte-Elte, Universität Göttingen (1960), and S. Wexler, University of California, Los Angeles (1966). Support from the National Science Foundation (Grants G-25086 and GP-3358) and from the Petroleum Research Fund (administered by the American Chemical Society) is gratefully acknowledged.

[2] Alfred P. Sloan Research Fellow. Part of this work was carried out under a Fulbright Scholarship, 1957–58, at the University of Göttingen, Germany.

[3] National Science Foundation Undergraduate Research Participant.

[4a] G. O. Schenck, *Angew. Chem.* **57**, 101 (1944); *Chem. Ber.* **80**, 289 (1947); *Angew. Chem.* **60**, 244 (1948); **64**, 12 (1952); **69**, 579 (1957); [b] *Liebigs Ann.* **584**, 156 (1953); [c] C. Dufraisse and S. Ecary, *C.R. Acad. Sci., Paris.* **223**, 735 (1946); [d] H. H. Wasserman and A. Liberles, *J. Am. Chem. Soc.* **82**, 2086 (1960); [e] H. H. Wasserman and A. R. Doumaux, Jr., *Ibid.* **84**, 4611 (1962); [f] R. K. Lutz, W. J. Welstead, Jr., R. G. Bass and J. I. Dale, *J. Org. Chem.* **27**, 1111 (1962); [g] J. Martel, *C.R. Acad. Sci., Paris.* **244**, 626 (1957).

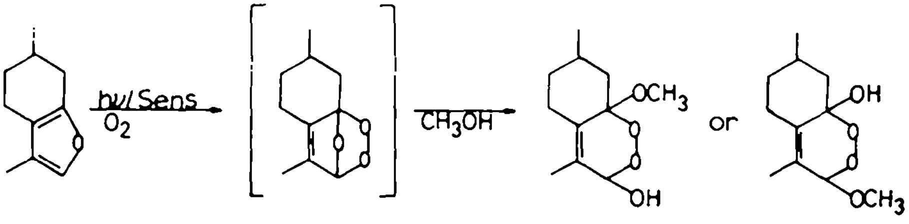
furan itself at −100°; the peroxide polymerizes slowly even at −80°, and rearranges in methanol above −20° to give pseudoester V as the only isolable product.[5,6]



IV V

Monomeric ozonide-like peroxides have been isolated only in the few cases described above; in most cases non-peroxidic products are formed from the intermediate peroxides by hydrolysis, rearrangement, or oxidation-reduction processes. Dimethylfuran was reported to give only polymeric peroxidic products.[4b]

Menthofuran (VI) reacts by an unusual course in methanol to give a relatively stable, monomeric, crystalline peroxide, which incorporates a mole of solvent and presumably arises from solvolysis of the intermediate peroxide VII; structure VIII was tentatively assigned to this compound.[7]



VI VII VIII

In order to test the generality of this reaction, and in the hope of finding a compound analogous to VIII which would readily yield to structure determination, the photosensitized oxygenation of some substituted furans was investigated.

Dimethylfuran (XI) was photooxidized in methanol, using a water-cooled immersion irradiation apparatus with Rose Bengal as sensitizer. Oxygen uptake was quantitative and extremely rapid, and a crystalline product (m.p. 75–77°) with properties very similar to those of the menthofuran peroxide[7] was isolated in 88% yield. The chemical and physical properties of this compound (described below) rule out a structure analogous to VIII, and are consistent only with structure XI.[8]

Compound XI was found to have the molecular formula $C_7H_{12}O_4$, which corresponds to the composition dimethylfuran·O_2·CH_3OH. It liberated iodine strongly from potassium iodide-acetic acid solutions, in accord with the presence of an O—O bond. With $Pb(OAc)_4$, gas was evolved, as is characteristic of compounds containing the OOH-group.[9] No CO absorption was present in the IR spectrum, but a single

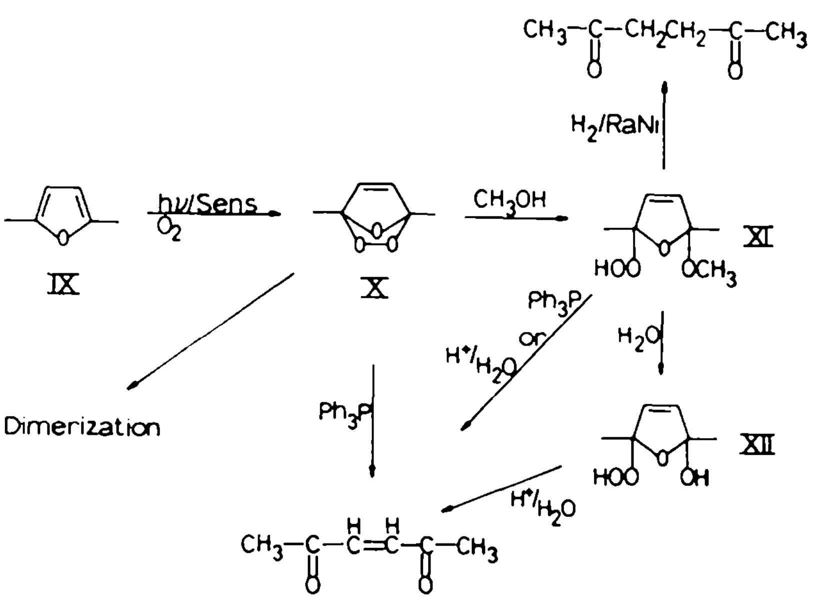
[5] S. H. Schroeter, R. Appel, R. Brammer and G. O. Schenck, *Liebigs Ann.* **692**, 42 (1966); similar results for 3-methylfuran have recently been reported: J. P. van der Merve and C. F. Garbers, *J. South African Inst.* **17**, 149 (1964); *Chem. Abstr.* **62**, 9088e (1965).

[6] E. Koch and G. O. Schenck, *Chem. Ber.* **99**, 1984 (1966).

[7] G. O. Schenck and Ch. S. Foote, *Angew. Chem.* **70**, 505 (1958).

[8] The same compound is produced by oxidation with $NaOCl-H_2O_2$: C. S. Foote and S. Wexler, *J. Am. Chem. Soc.* **86**, 3879 (1964).

[9] R. Criegee, H. Pilz and H. Flygare, *Chem. Ber.* **72**, 1799 (1939).



band appeared in the OH region at high dilution. The frequency of this peak was measured accurately under high resolution and found to be 2·848 μ, which corresponds to hydroperoxyl rather than OH absorption.[10,11]

The *p*-nitrobenzoate (prepared by the procedure of Brewster and Ciotti[12]) had a C=O band (in $CHCl_3$) at 5·64 μ (perester), confirming the presence of a hydroperoxyl group in XI.[13,14] The NMR spectrum of XI had a one-proton singlet at 0·78 τ, assigned to OOH absorption.[15] In addition, two olefinic protons (two-proton singlet at 3·98 τ), one OMe group (3-proton singlet at 6·64 τ and quantitative Zeisel determination), and two C–Me groups (3-proton singlets at 8·42 and 8·47 τ), were present. The compound readily gave the *bis*-2,4-dinitrophenylhydrazone of *trans*-1,2-diacetylethylene[16a] (XIII), identical to that produced from 2,5-dimethoxy-2,5-dimethyldihydrofuran.[16b] Compound XI could be reduced with triphenylphosphine in ether[17] to 1,2-diacetylethylene (XIII), (the *trans*-form was isolated),[18] or with Raney Nickel and hydrogen (2 moles) to 2,5-hexanedione.

On very mild hydrolysis, XI gave (in 50% yield) a new crystalline compound,

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[10] A Perkin–Elmer Model 421 grating spectrophotometer was used for these measurements. Spectra were taken of 0·005M solutions in CCl_4, using a narrow slit, slow sweep, and expanded scale by Messrs. D. Steele and M. Haugh.

[11] Alcohols absorb at 2·760 ± 0·01 μ, whereas alkyl hydroperoxides absorb at 2·820 ± 0·01 μ in dilute CCl_4 solution: R. F. Goddu, *Near Infrared Spectroscopy*, in *Advances in Analytical Chemistry and Instrumentation* (Edited by C. N. Reilly) vol 1; p. 347. Interscience, New York (1960).

[12] J. H. Brewster and C. J. Ciotti, Jr., *J. Am. Chem. Soc.* **77**, 6214 (1955).

[13] A very similar *p*-nitroperbenzoate has C=O absorption at 5·66 5·68 μ: N. A. Milas and A. Golubovic, *J. Org. Chem.* **27**, 4319 (1962).

[14] W. H. T. Davison, *J. Chem. Soc.* 2456 (1951).

[15] Several similar hydroperoxides absorb near 0·5 τ[18]; *t*-butyl hydroperoxide absorbs at 1·08 τ

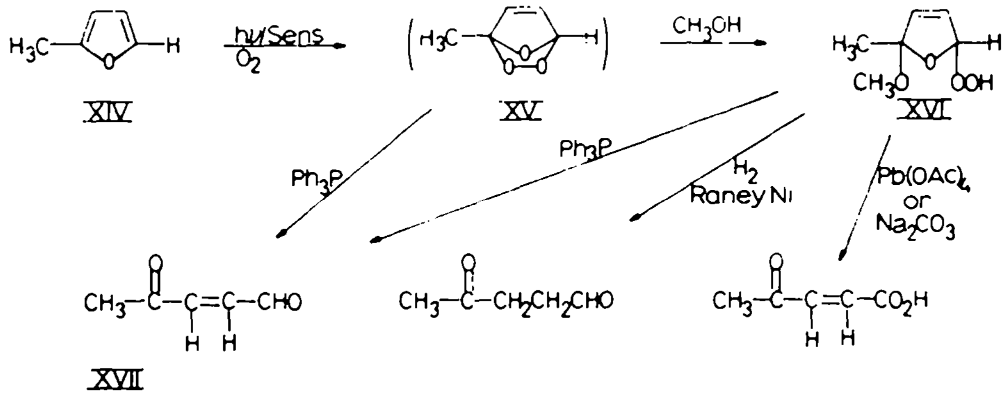
[16a] This is presumably formed by isomerization of the initially formed *cis*-compound; [b] J. Levisalles, *Bull. Soc. Chim. Fr.* 997 (1957); G. O. Schenck, *Chem. Ber.* **77**, 661 (1944).

[17] L. Horner and W. Jurgeleit, *Liebigs Ann.* **591**, 138 (1955); J. I. G. Cadogan, *Quart. Rev.* **16**, 208 (1962).

m.p. 134–136°, whose structure was shown to be XII. The analysis of this compound corresponded to $C_6H_{10}O_4$; like XI, the compound freed iodine strongly from potassium iodide–acetic acid solution. No C=O absorption was present in the IR, but two bands were found in the OH region, with frequencies measured to be 2·835 (OOH) and 2·750 μ (OH).[10,11] The NMR spectrum (in dioxane) showed the presence of two olefinic protons (2-proton singlet at 4·05 τ), OH and OOH groups (2-proton singlet at 4·72 τ),[18] and two C—CH_3 groups (6-proton singlet at 8·60 τ). Compound XII also gave the 2,4-dinitrophenylhydrazone of *trans*-1,2-diacetylethylene.[16]

That the ozonide X is intermediate in the production of XI could be demonstrated by carrying out the photooxidation of IX in benzene-petroleum ether at −25° (dinaphthylenethiophene as sensitizer). Treatment of the cold solution with methanol produced the methoxyhydroperoxide (XI) in fair yield, while reduction of the crude photooxidation mixture with triphenylphosphine[17] gave *trans*-1,2-diacetylethylene.[16] If the solution was left 2 hrs at room temperature, addition of methanol no longer gave XI, but only a dimeric peroxide could be isolated.

In a similar manner, photooxidation of 2-methylfuran (XIV) in methanol gave a product with properties consistent with structure XVI.



The compound was found to have the molecular formula $C_6H_{10}O_4$, and was rather unstable, exploding over 100°, and decomposing after a few days at room temperature. No C=O or OH absorption was present in the IR, but absorptions characteristic of an OOH group appeared at 2·86 and 1·45 μ.[11] The compound was reduced with triphenylphosphine[17] to β-acetylacrolein (XVII), and with hydrogen on Raney Nickel to β-acetylpropionaldehyde. Lead tetra-acetate or sodium carbonate gave *trans*-β-acetylacrylic acid.[16a]

The MeO group in XVI is believed to be on the tertiary position rather than the secondary because this would accord with the expected direction of addition of methanol to XV, and because of the fact that the pseudoethylester of β-acetylacrylic acid (which would be formed from the Et analogue of XVI by elimination of water) was reported to be the product of photooxidation of XIV in ethanol.[4b]

As in the case of dimethylfuran, photooxidation of 2-methylfuran in benzene-petroleum ether at −30° produced a solution of the unstable ozonide XV, from which

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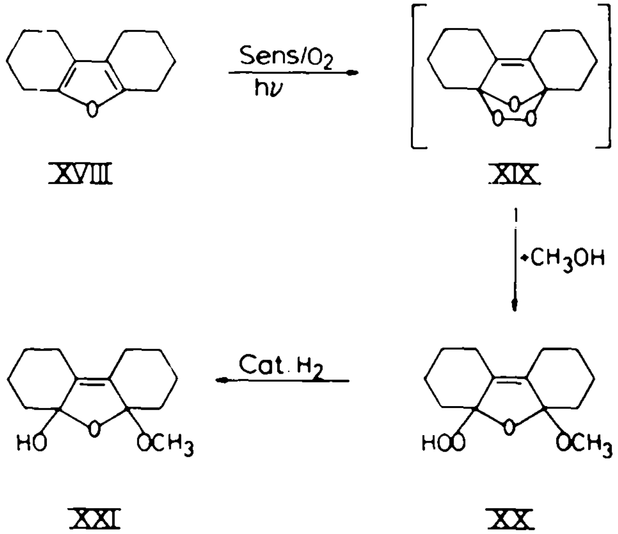
[18] Exchange of the protons on the OH and OOH groups appears to be sufficiently rapid that only a single resonance line, at the time-averaged position, appears.

the methoxyhydroperoxide XVI could be isolated in 34% yield on addition of two equivalents of methanol, and which on addition of triphenylphosphine[17] gave β-acetylacrolein.

Like dimethylfuran and methylfuran, dicyclohexanofuran (XVIII) gives a methoxyhydroperoxide (XX) on photooxidation in methanol. The formula $C_{13}H_{20}O_4$ was found, and a Zeisel determination indicated one methoxyl group. The infrared spectrum of XX showed a band at 2·85 μ, corresponding to an OOH-group,[11] but no C=O or OH absorption.

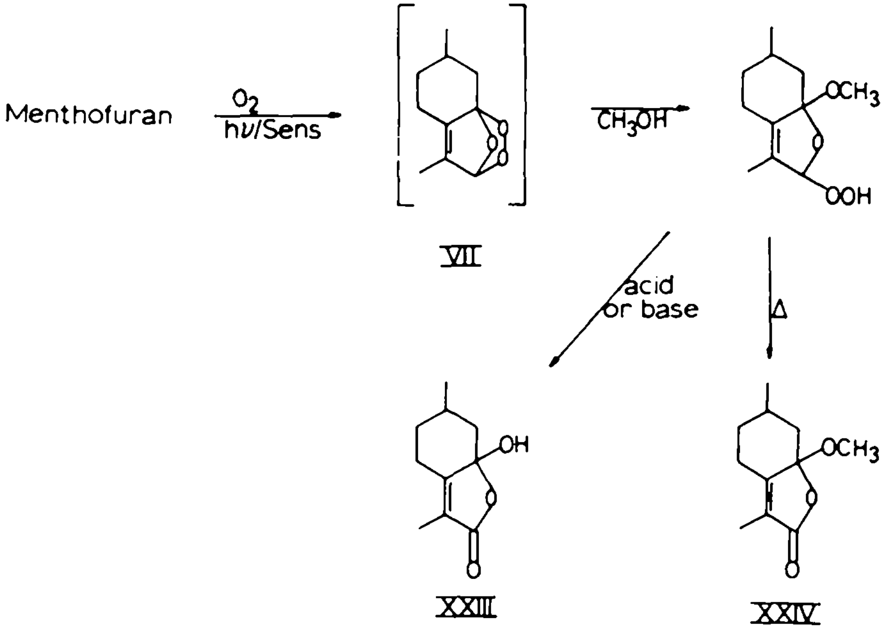
Catalytic hydrogenation of XX produced the hemiacetal XXI, m.p. 81°; at high dilution in CCl_4, XXI possesses OH absorption at 2·78 μ (an intermolecular H-bonded band at 2·86 μ disappears on dilution).[11] The structure of XXI follows from its molecular formula, $C_{13}H_{20}O_3$, the presence of a OMe group (indicated by a Zeisel determination), and the absence of C=O absorption in the IR.



As with the other furans, dicyclohexanofuran could be photooxidized in benzene-petroleum ether at −22° to give a solution which on treatment with methanol gave XX in 66% yield. If the solution was held at −40° for 12 hr before addition of methanol, the yield of XX dropped to 22%. Attempted isolation of the intermediate ozonide XIX by removal of solvent at −30° under argon from a freshly prepared solution gave a partly crystalline residue which decomposed violently on release of the vacuum, or on warming to about 0°.

In the light of the results discussed above, the photooxidation of menthofuran (VI)[7] was reinvestigated. Photosensitized oxygenation in methanol gave a crystalline peroxide whose properties require that it in fact have structure XXII (analogous to the methoxyhydroperoxides XI, XVI, and XX) rather than the originally proposed[7] structure VII. In the IR, XXII had absorption (CCl_4) at 2·845 (OOH),[11] and 8–10 μ (C—O), but none in the C=O region. The NMR spectrum ($CDCl_3$) had bands at −0·64 (1H, OOH),[15] 4·28 (1H, assigned to the acetal proton), 6·90 (3H, OCH_3), and 8·30 τ (3H, allylic Me). No UV absorption over 220 mμ was observed. The microanalysis was consistent with the formula $C_{11}H_{18}O_4$; a quantitative Zeisel determination indicated the presence of one OMe group. The results of quantitative peroxide and active hydrogen determinations were consistent with the presence of one O—O and one OH group. The compound decolorized bromine in carbon tetrachloride and alkaline permanganate solutions instantaneously.

Treatment of peroxide XXII wth aqueous KOH or methanolic HCl gave the Woodward-Eastman pseudoacid[19] (XXIII), which also formed when samples of the peroxide stood in air for several weeks at room temperature. Pseudoacid is also obtained on treatment of XXII with $Pb(OAc)_4$ in acetic acid.



Pyrolysis of the peroxide on the injection block of a gas chromatograph smoothly produced pseudoester XXIV, m.p. 41·5–42·5°. The structure of the pseudoester was readily established by its spectral and chemical properties, and by synthesis. In the IR, the compound absorbs at 5·62 μ, characteristic of the γ-oxygenated α,β-unsaturated γ-lactone functionality.[20,21] In the UV as well, absorption characteristic of this chromophore occurred at $\lambda_{max} = 216$ mμ ($\epsilon = 12{,}200$).[22] The NMR spectrum clearly showed the presence of a OMe group (3 protons at 6·95 τ), and an allylic Me (3 protons at 8·17 τ). The presence of the OMe group was confirmed by a quantitative Zeisel determination; microanalysis required the formula $C_{11}H_{16}O_3$. The pseudoester could be saponified to give the pseudoacid XXIII, from which it was also prepared by esterification with methanolic CHl.

The smooth formation of pseudoester XXIV from the peroxide XXII on pyrolysis provides evidence that the OMe group in the peroxide is in the tertiary position; this

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[19] R. B. Woodward and R. H. Eastman, *J. Am. Chem. Soc.* **72**, 399 (1950).

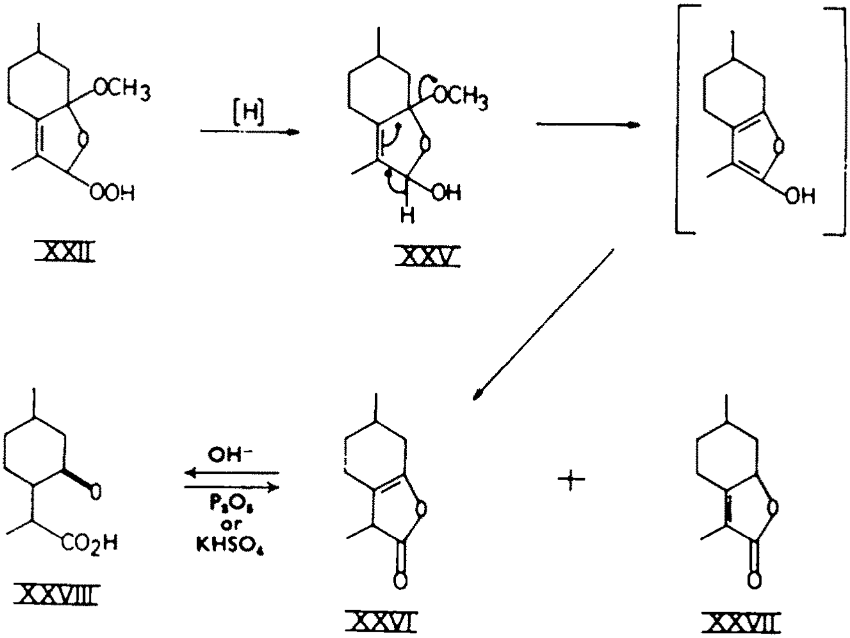
[20] L. V. Bellamy, *The Infrared Spectra of Complex Molecules* (2nd Edition) pp. 185–187. Wiley New York, (1958).

[21] The infrared spectrum of the pseudoacid XXIII is nearly identical in the carbonyl region.

[22] A. T. Nielsen, *J. Org. Chem.* **22**, 1539 (1957).

position would also be consistent with the expected direction of solvolytic opening of the peroxide bridge in the hypothetical intermediate ozonide VII; similar considerations led to the analogous conclusion in regard to peroxide XVI from methylfuran. Analogous pseudoesters have been reported to be the end products of photooxidation of other furans in alcoholic solution.[4b,5,6]

Reductions of XXII led to mixtures of products. Reductions with different amounts of $NaBH_4$ led to mixtures containing, along with small amounts of unidentified materials, varying amounts of menthofuran, pseudoester XXIV (from pyrolysis of unreacted starting material) and two lactones, XXVI and XXVII. The production of menthofuran would require two equivalents of borohydride,[23] the lactones, one equivalent. The lactones XXVI and XXVII (whose structures are discussed below) were principal products of reduction with all reagents, when reaction mixtures were examined gas chromatographically, and are formed by thermal elimination of methanol from the intermediate XXV.



Catalytic reduction of peroxide XXII with Raney Nickel produced the unstable hemiacetal XXV (m.p. 80–83°). The compound had a molecular formula $C_{11}H_{18}O_3$, as shown by microanalysis and molecular weight determination; a Zeisel determination demonstrated the presence of a methoxyl group. The IR had OH absorption at 2·78 μ[11] and 1·41 μ, but no absorption in the CO region.

Reduction of peroxide XXII with triphenylphosphine in ether[17] gave a residue with an IR spectrum similar to that of XXV. Vacuum distillation of this residue gave a mixture containing more than 85% XXVI and less than 15% XXVII; pure samples of XXVI could be obtained by gas chromatography on short columns. Lactone XXVI

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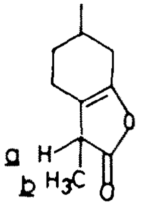
[23] H. Minato and T. Nagasaki, *Chem. Ind.* 899 (1965) report a similar reaction.

is extraordinarily labile, and tends to rearrange to the conjugated isomer XXVII very easily.[24] Solutions of XXVI in CCl_4 and many other solvents (but not in ether) developed IR bands characteristic of XXVII within a few hours at room temperature. Solutions of XXVI in ether were far more stable, as were neat samples, and both could be stored at −20° for several weeks without appreciable rearrangement.

The assignment of structure to lactone XXVI is based on the following evidence. The IR spectrum had strong absorption bands at 5·53 μ (characteristic of β,γ-unsaturated γ-lactones)[21] and 10·00 μ, among others. The NMR spectrum had significant peaks at 7·00 (1H, width at half-height 15 c/s.) and 8·76 τ (3H, doublet, $J = 7$ c/s), assigned to protons *a* and *b* respectively. Double irradiation experiments confirmed these assignments: irradiation of the band at 7·0 τ caused the 8·8 τ doublet to collapse to a sharp singlet, while irradiation of the 8·8 τ bands caused the peak at 7·0 τ to sharpen considerably, although residual long-range coupling still broadened the peak somewhat.



XXVI

The UV spectrum of the purest obtainable sample of XXVI showed only weak absorption attributable to the presence of small amounts of XXVII. The microanalysis was consistent with the formula $C_{10}H_{14}O_2$.

Saponification of lactones XXVI and XXVII produced a mixture of the four diastereomeric keto acids XXVIII, the structures and reactions of which are described in the accompanying paper.[25] The three of these four acids which could be prepared in pure form were dehydrated with P_2O_5 and with $KHSO_4$ to give mixtures of XXVI and XXVII.[26]

Large amounts of the α,β-unsaturated γ-lactone XXVII were conveniently prepared by borohydride reduction of aqueous alkaline solutions containing the salt of the pseudoacid XXIII; XXVII precipitated directly from the alkaline solution in pure form and high yield. Reduction presumably proceeds via the open form XXIX of the pseudoacid, which was shown by Woodward and Eastman to exist in alkaline solution.[19] The fact that the lactone XXVII precipitates directly from alkaline solution without prior acidification is surprising, but analogous behavior has been observed in similar cases.[27]

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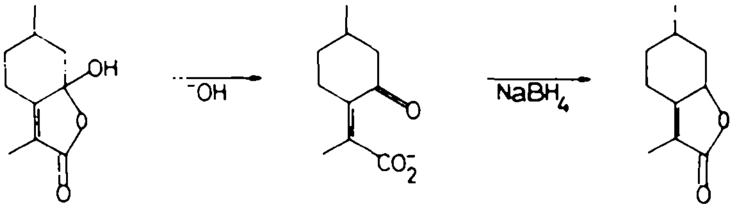
[24] Columns as short as eight inches had to be used for the collection of XXVI; on longer columns, rearrangement to XXVII is extensive because of the longer retention times or higher temperatures required.

[25] C. S. Foote, M. T. Wuesthoff and I. G. Burstain, *Tetrahedron* **23**, 2601 (1967).

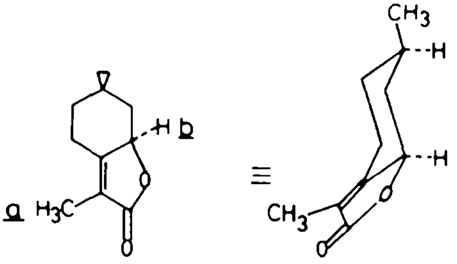
[26] It is likely that most of the XXVII found is produced by rearrangement of initially formed XXVI.

[27] H. Stobbe, *Liebigs Ann.* **308**, 89 (1899); see also R. B. Woodward and P. Yates, *J. Am. Chem. Soc.* **85**, 553 (1963), and Ref. 19.



XXIII XXIX XXVII

Compounds XXVII was found to have the empirical formula $C_{10}H_{14}O_2$, IR absorption at 5·67 (s) and 5·88 μ (w), and UV absorption at $\lambda_{max} = 217$ mμ (ε = 16,000). The IR and UV spectra are those of an α,β-unsaturated γ-lactone.[20–22] The NMR spectrum showed the presence of an allylic Me group, 8·28 τ (3H, triplet, J = 1 c/s), assigned to protons *a*; the *b* proton appears as the quartet of an ABX system. (1H, J = 6 and 11 c/s) centered at 5·4 τ. The values of the coupling constant for this proton suggest that it is axial. If the remote Me is equatorial, then the configuration of XVII is as shown below, which is the most stable configuration.[28,29]



SUMMARY

The products of photosensitized oxygenation in methanol of all four furans studied have very similar physical and chemical properties. That all of these compounds are methoxyhydroperoxides (XXX, rather than hydroxyendoperoxides as was originally suggested[7] for the menthofuran product) is clearly shown by the spectral data. Relevent IR data are summarized in Table 1. A strong indication that the hydroperoxyl and OMe groups are *trans* comes from the lack of observed intramolecular hydrogen bonding in the IR in any of the methoxyhydroperoxides.

Highly reactive peroxides, very probably of the ozonide structure XXXI, are intermediate in the formation of the methoxyhydroperoxides, as is clearly shown by the results of photooxidation in aprotic solvents at low temperatures. The ozonides, which are too reactive to isolate in these cases, can be reduced *in situ;* on addition of methanol they are converted to the methoxyhydroperoxides. It is thus the peroxide bridge, rather than the ether bridge which is cleaved. Various decomposition routes are open to both the ozonides and the methoxyhydroperoxides, depending on the conditions and the structure of the compound. The following scheme summarizes the reactions which have been shown to occur.

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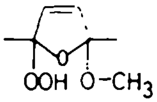
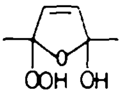
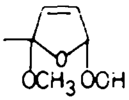
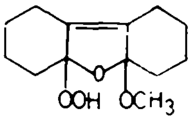
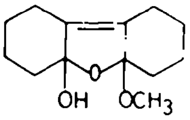
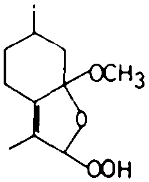
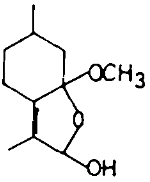
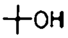
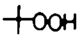
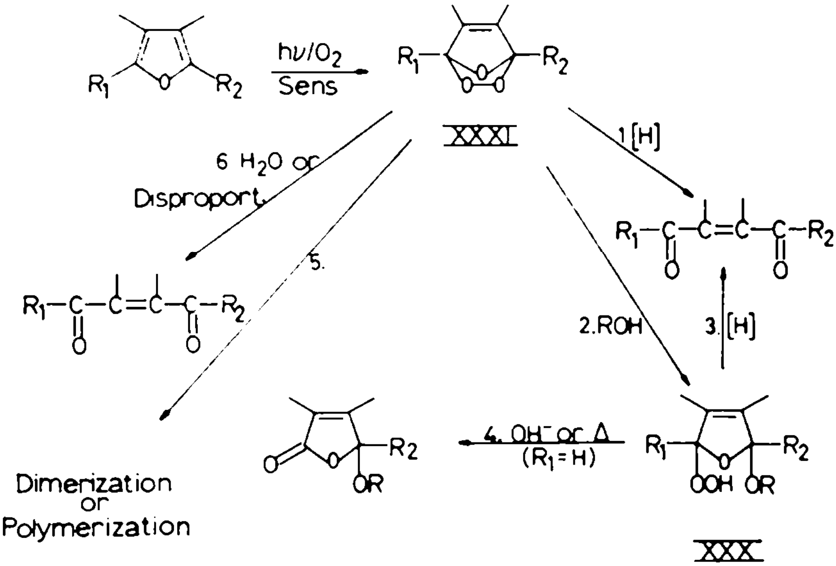
[28] N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry* Chap. 6, Holden-Day, San Francisco (1964).

[29] The apparent isolation of only a single isomer of both XXVI and XXVII is worthy of note, since two diastereomeric forms are possible. In the case of XXVII, all routes of preparation involve either isomerization of XXVI or basic conditions, so that the observed product may merely be the more stable isomer (as models suggest). This point is discussed in more detail in the accompanying paper.[24]

Table 1. Infrared bands in OH region

COMPOUND		Wavelength (μ in dil. CCl_4) of band assigned to:	
		OH	OOH
	XI		2·848
	XII	2·750	
	XVI		2·86
	XX		2·85
	XXI	2·78	
	XXII		2·845
	XXV	2·78	
		2·768	
			2·823



Reactions 1–5 have been observed in this study; reaction 4 occurs only if $R_1 = H$.[8] Reaction 5 appears to be the usual result for alkylated furans if the oxidation is carried out in aprotic solvents at room temperature.[4b] Reaction 6 is added to account for a frequent course of the reaction in the case of arylated furans.[4b–f] In the case of menthofuran, instead of reaction 3, an intramolecular disproportionation leads instead to lactones XXVI and XXVII.

EXPERIMENTAL

All m.ps are uncorrected. Microanalyses were by Miss Heather King, UCLA, and by A. Bernhardt, Mülheim/Ruhr. IR spectra were taken on a Perkin–Elmer Model 137 infracord, calibrated with polystyrene films, or on a Beckman IR-4, except as noted. NMR spectra were taken on a Varian A-60 spectrometer (purchased with NSF Grant No. G-20207), and are relative to internal TMS, except as noted. The decoupling experiment was carried out by Miss Ilse Gebhard on a Varian HR-60 spectrometer equipped with a field-locking device constructed by Mr. R. Gillespie. UV spectra were taken on a Cary Model 14 spectrophotometer. Gas chromatography was carried out with a Perkin–Elmer Model 154 (thermal conductivity detector) or Model 800 (flame ionization detector) chromatograph.

Photosensitized oxygenation of dimethylfuran (IX)

Dimethylfuran, 3·00 g (0·031 mole), and Rose Bengal (0·034 g) in 250 ml MeOH were irradiated with a 625 watt incandescent lamp (Sylvania Sungun) in a water-cooled immersion apparatus through which O_2 was recirculated. Within 5 min. 686 ml O_2 (STP, 0·031 mole) were taken up, at which time the reaction ceased abruptly. After removal of solvent with a rotary evaporator, the crude residue was washed with cold ethyl ether, then with pet. ether. The solid residue was sublimed (63°, 0·15 mm) to give 3·60 g (0·0225 mole, 72%) of *2-methoxy-5-hydroperoxy-2,5-dimethyldihydrofuran* (XI), m.p. 75–76° (after recrystallization from ether). The compound freed I_2 strongly from KI-AcOH. (Found: C, 52·4; H, 7·5; OMe, 18·8; Mol. Wt., 177 [osmometer]. $C_7H_{12}O_4$ requires: C, 52·5; H, 7·5; OMe, 19·4%; Mol. Wt., 160.)

The product had an IR band (CCl_4, 0·005M) at 2·848 μ (OOH);[10,11] other bands of significance appeared at 3·32, 6·93, 7·30, 7·43, 7·83, 8·55, 8·9, 9·18, 9·54, 9·58, 10·47 and 11·32 μ (in $CHCl_3$). The NMR spectrum ($CDCl_3$) had peaks at 0·78,[12] 3·98, 6·64, 8·42 and 8·47 τ (all sharp singlets) with relative areas 1:2:3:3:3.

The p-*nitrobenzoate* (m.p. 91–92°) was made by the procedure of Brewster and Ciotti,[13] and had a significant IR band ($CHCl_3$) at 5·64 μ, corresponding to a perester.[13]

The 2,4-dinitrophenylhydrazone was prepared and had m.p. 286°d; the mixture m.p. with a sample (m.p. 284°d) prepared under the same conditions from 2,5-dimethoxy-2,5-dimethyldihydrofuran (prepared by the method of Levisalles[16]) was 284°d.

Hydrolysis of 2-methoxy-5-hydroperoxy-2,5-dimethyldihydrofuran (XI)

When stirred with 10 ml dist. water, 1·499 g (9·4 mmoles) of the peroxide XI dissolved in 15 min. After 30 min, the soln was saturated with NaCl, filtered, and extracted with 4 10 ml portions of ether. The ether extracts were dried and evaporated to yield 0·683 g (4·7 mmoles, 50%) of crystalline *2-hydroxy-5-hydroperoxy-2,5-dimethyldihydrofuran* (XII) which, after sublimation (110°, 0·35 mm) and recrystallization from ether, had m.p. 134–136°. The product freed I_2 strongly from KI-AcOH. (Found: C, 49·5; H, 6·9. $C_6H_{10}O_4$ requires: C, 49·3; H, 6·9%.)

The IR spectrum (CCl_4, 0·005M) had bands at 2·835 (OOH) and 2·750 μ (OH);[10,11] other significant bands appeared at 7·06, 7·2, 8·07, 8·40, 8·80, 9·00, 9·23, 10·42, 10·67, 11·25, 11·82 and 12·96 μ (in Nujol). The NMR spectrum (D_2O) had bands at 4·03, 5·40 (HOD), and 8·63 τ (relative to external TMS in $CDCl_3$); all were sharp singlets of relative area 2:2:6 respectively.[18] In dioxane, the peaks were at 4·05, 4·72 (OH and OOH) and 8·60 τ (relative to dioxane at 6·30), all sharp singlets of relative area 2:2:6.

The 2,4-dinitrophenylhydrazone had m.p. 284°, not depressed by admixture of the 2,4 dinitrophenylhydrazone from 2,5-dimethoxy-2,5-dimethyldihydrofuran.[16] (Found: C, 45·8; H, 3·4; N, 23·8: Calc. for $C_{18}H_{16}N_8O_8$: C, 45·8; H, 3·4; N, 23·7%.)

In the IR spectrum, (CCl_4, 0·005M), t-butyl alcohol and t-butyl hydroperoxide absorb at 2·768 and 2·823 μ, respectively.[10] In the NMR spectrum ($CDCl_3$), t-butyl hydroperoxide absorbs at 1·08 τ.

Reduction of 2-methoxy-5-hydroperoxy-2,5-dimethyldihydrofuran (XI)

(a) *With triphenylphosphine.* To a soln of 2·4 g (0·015 mole) XI in 50 ml ether were added slowly, with cooling, 3·9 g (0·016 mole) triphenylphosphine in 100 ml ether. After standing 1 hr, the soln was concentrated and the residue sublimed (80°, 12 mm) to give 1·58 g (89%) of XIII, m.p. 78°.

(b) *With* H_2/*Raney nickel.* A soln of 16 g (0·1 mole) XI in 300 ml MeOH was shaken 4·5 hr with Raney Ni under 1 atm H_2, at which time 4410 ml (0·198 mole) had been taken up. Distillation gave 10 g (90%) acetonylacetone, b.p.$_{12}$ 91° (reported[20] b.p.$_{25}$ 88–89°); the *bis-p*-nitrophenylhydrazone had m.p. 210° (reported[21] 210–212°), undepressed on admixture with authentic material.

Photosensitized oxygenation of 2,5-dimethylfuran in benzene-petroleum ether

A soln of 4·8 g (0·05 mole) IX was irradiated at −24° in 80 ml benzene and 40 ml pet. ether containing 75 mg dinapthylenethiophene (water excluded). After 1148 ml O_2 (103%) had been taken up (55 min) portions of the resulting soln, which had a penetrating acrid odor, were subjected to the following reactions:

(a) *With methanol.* A 40 ml portion was added to 150 ml MeOH and held 2 hr at room temp. After removal of the MeOH (12 mm) the residue was crystallized from pet. ether at −30°, giving 1·2 g (40%) of XI, m.p. 76°.

(b) *With triphenylphosphine.* A 40 ml aliquot was added to 4·7 g (0·017 mole) triphenylphosphine in 50 ml pet. ether. After the soln had stood for 2 hr (room temp), the solvent was removed and the residue sublimed at 78–80° (12 mm) to give 1·05 g XIII (56%), m.p. 78° (reported[19] m.p. 78°).

(c) *Dimerization.* The remaining 40 ml of soln were allowed to stand at room temp. After 5 hr, the acrid odor had disappeared, and no reaction could be detected on addition of triphenylphosphine. After concentration and treatment of the residue with ether–pet. ether, 0·6 g of *dimer*, needles (m.p. 154°) was obtained. (Found: C, 56·7; H, 6·3; Mol. Wt., 240 [cryoscopic, benzene]. $C_{12}H_{16}O_6$ requires: C, 56·2; H, 6·3%; Mol. Wt., 256.) The compound sublimed at 120°, and exploded violently if heated in a capillary. It gave peroxide tests, and the IR spectrum had C═C absorption at 6·15 μ, but no bands for OH or C═O.

Photosensitized oxygenation of 2-methylfuran (XIV) *in methanol*

A soln of 8·2 g (0·1 mole) of 2-methylfuran was dissolved in 150 ml MeOH containing 100 mg Rose Bengal. The soln was irradiated, and took up 2310 ml O_2 (103%) in 58 min. After removal of the solvent in vacuum, the residue was dissolved in 150 ml ether and rapidly filtered through 5 g alumina

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[20] D. M. Young and C. F. H. Allen, *Org. Syn.* **16**, 26 (1936).

[21] K. Auwers and M. Hessenland, *Ber. Dtsch. Chem. Ges.* **41**, 1826 (1908).

to remove the dye. The filtrate was concentrated to 20 ml, and 100 ml of petr. ether added. After standing at −40°, the soln deposited 11·6 g (80%) of *2-methoxy-5-hydroperoxy-2-methyldihydrofuran* (XVI), colorless crystals, m.p. 80°. (Found: C, 49·2; H, 6·7; MeO, 20·4; Mol. Wt., 135 [cryoscopic, benzene]. $C_6H_{10}O_4$ requires: C, 49·3; H, 6·9; MeO, 21·2%; Mol. Wt., 146.) The compound decomposed over 100°, or after several days at room temp. The IR spectrum had bands at 2·82 and 1·44 μ (OOH); no bands were present in the CO or OH region.

Photosensitized oxygenation of 2-methylfuran (XIV) *in benzene–petroleum ether*

2-Methylfuran (8·2 g, 0·1 mole) was dissolved with 50 mg dinapthylenethiophene in 50 ml benzene and 100 ml petr. ether. Upon irradiation at −30°, with water carefully excluded, the soln absorbed 2380 ml O_2 (106%) in 162 min. The resulting acrid-smelling soln was added immediately to a soln of 27 g (0·105 mole) triphenylphosphine in 300 ml petr. ether, cooled to −20°. The soln grew warm, and triphenylphosphine oxide was precipitated. After filtration, the soln was distilled, to yield 3·4 g (35%) XVII, b.p.$_{18}$ 71–73° (reported[32] b.p.$_{18}$ 68°). (Found: C, 60·9; H, 6·1. Calc. for $C_5H_6O_2$: C, 61·2; H, 6·2%.) The IR spectrum had strong bands (C═C and C═O) at 5·65, 5·89, 6·10 and 6·21 μ; the aldehyde C—H band appeared at 3·63 μ. A soln of ozonide similarly prepared from 4·1 g (0·05 mole) 2-methylfuran in 60 ml benzene and 60 ml pet. ether at −30° was added to 300 ml MeOH, and the resulting soln allowed to stand for 3 hr at room temp. The MeOH was evaporated, and the viscous residue treated with ether–pet. ether (1:2) and cooled to −40°, to yield 2·5 g (35%) of XVI, m.p. and mixture m.p. with material prepared by oxidation in MeOH, 79–80°.

Reactions of hydroperoxide (XVI) *from 2-methylfuran*

(a) *With triphenylphosphine.* To a soln of 11·68 g (0·08 mole) XVI in 100 ml ether at 0° was added a soln of 21 g (0·081 mole) triphenylphosphine in 150 ml pet. ether. After 2 hr, the precipitated phosphine oxide was filtered, and the colorless residue distilled twice to give 4·2 g (54%) of XVII, b.p.$_{18}$ 72°, with IR spectrum identical to that reported above.

(b) *With* H_2*/Raney nickel.* A soln of 7·2 g (0·05 mole) XVI in 100 ml MeOH was shaken with Raney Ni at 1 atm under H_2, with good cooling. After 80 min, the soln had taken up 1910 ml (0·085 mole) H_2; the soln was filtered and distilled to give 2·5 g (51%) levulinaldehyde, b.p.$_{18}$ 72° (reported[33] b.p.$_{18}$ 70–72°), characterized as 1-methylpyridazine, m.p. 193–194° (reported[33] m.p. 196°).

(c) *With* $Pb(OAc)_4$. To a soln of 2·92 g (0·02 mole) XVI in 50 ml HOAc were added in portions 8 g (0·021 mole) $Pb(OAc)_4$ with cooling. When the violent reaction had subsided, Pb^{4+} was precipitated ($PbSO_4$), the soln filtered, concentrated, (*in vacuo*) diluted with H_2O, and extracted several times with ether to yield, after evaporation of the ether, 1·6 g (70%) *trans-β*-acetylacrylic acid, m.p. 124°, needles from pet. ether; (reported[33] m.p. 124°).

(d) *With alkali.* A soln of 1·46 g (0·02 mole) XVI in 50 ml dioxan and 10 ml water, containing 3 g Na_2CO_3 was heated on the steam bath for 1 hr until it gave a negative peroxide test. The soln was acidified, the solvent was removed, and the residue taken up in ether to yield 0·9 g (80%) *trans-β*-acetylacrylic acid, m.p. and mixture m.p. with material prepared above, 124°.

Preparation of dicyclohexanofuran (XVIII)

1,1-Dicyclohexenyl (m.p. 25–26°), prepared according to the procedure of Gruber and Adams,[34] 16·2 g (0·10 mole) was photooxidized in 100 ml MeOH and 50 ml isopropyl alcohol with 100 mg Rose Bengal. The soln took up 2990 ml O_2 (0·13 mole) in 244 min. Concentration gave a viscous residue (22·1 g). This residue was dissolved in 10 ml C_6H_6 and slurried with 40 g Al_2O_3 (activity 3, neutral) and added to the top of a column of 500 g Al_2O_3 (activity 2, neutral), prepared with pet. ether. Elution with pet. ether gave a fraction which on removal of the solvent gave 9·8 g (51%) of 3,4,5,6-*dicyclohexano*-1,2-*dioxene*-4, colorless crystals (m.p. 54° from EtOH, b.p.$_{0.01}$ 72–73°, n_D^{20} 1·5218 for a supercooled melt). (Found: C, 73·8; H, 9·1; Mol. Wt., 189 [cryoscopic, benzene]. $C_{12}H_{18}O_2$ requires: C, 74·2; H, 9·3%; Mol. Wt., 184.) The compound reacted with triphenylphosphine only above 120°, and could be heated nearly to boiling in a capillary before decomposition occurred.

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[32] N. Clauson-Kaas and F. Limborg, *Acta Chim. Scand.* **1**, 619 (1947).

[33] L. Wolff, *Leibigs Ann.* **264**, 245 (1891).

[34] E. E. Gruber and R. Adams, *J. Am. Chem. Soc.* **57**, 2555 (1935).

The compound was recovered unchanged after being heated with dil. HCl. In the IR., no absorption was present in either the CO or OH region.

A soln of 5·8 g of the peroxide in 50 ml MeOH containing 5 ml 10% NaOH was allowed to stand at 25° (ice cooling required) for 1 hr, at which time no further peroxide test was observed. The soln was partitioned between 50 ml pet. ether and 100 ml H_2O, the pet. ether layer was washed 3 times with water, and the solvent evaporated to give 4·7 g (81%) of crystalline *2-hydroxy-2,5-dihydro-2,3,4,5-dicyclohexanofuran* (m.p. 72–78°), with an IR. band (thin film) at 3·1 μ, but no C=O absorption. After 1 hr, the IR sample developed bands at 6·02 and 6·25 μ (furan).

The unstable ketal (3·9 g, 0·02 mole) was dissolved in 50 ml pet. ether, and the soln passed through a column of 30 g Al_2O_3 (activity 2, neutral), followed by 200 ml pet. ether. The pet. ether was removed to give 3·3 g (94%) of 2,3,4,5-*dicyclohexanofuran* (XVIII), b.p.$_{12}$ 139–140°, m.p. 16° (from EtOH), n_D^{20} 1·5220. (Found: C, 81·3; H, 9·10. $C_{12}H_{16}O$ requires: C, 81·6; H, 9·1%.) The compound gives a deep blue color with chloranil, and fluoresces brightly in UV light (λ_{max} 435 mμ). In the IR, the compound has, among others, bands at 6·02 and 6·25 μ. With maleic anhydride in benzene, it forms an *adduct*, m.p. 168°. (Found: C, 70·1; H, 6·8. $C_{16}H_{18}O_4$ requires: C, 70·0; H, 6·6%.)

Photosensitized oxygenation of dicyclohexanofuran (XVIII) *in methanol*

A soln of 1·76 g (0·01 mole) XVIII in 50 ml MeOH with 50 mg Rose Bengal took up 228 ml (0·01 mole) O_2 within 5 min. The MeOH was removed *in vacuo*, the residue dissolved in 30 ml warm pet. ether, filtered, and cooled to −30°, whereupon colorless crystals of *2-methoxy-5-hydroperoxy-2,5-dihydro-2,3,4,5-dicyclohexanofuran* (XX) (2·2 g, 92%) precipitated, m.p. 101°. (Found: C, 64·7; H, 8·4; MeO, 12·8; Mol. Wt., 244 [cryoscopic, benzene]. $C_{13}H_{20}O_4$ requires: C, 65·0; H, 8·4; MeO, 12·9%; Mol. Wt., 240.) The peroxide is quite soluble in most common organic solvents, with the exception of pet. ether, and gives a blue coloration with dichromate-H_2SO_4–ether, consistent with its formulation as a α-hydroperoxy ether. In the IR, the absorptions at 2·86 and 1·45 μ (CCl_4) are characteristic for the OOH group;[11] no bands were present in the OH or C=O region.

Reduction of peroxide XX

A soln of 1·2 g (5 mmoles) XX in 50 ml MeOH was shaken with Raney Ni under 1 atm. H_2. After 18 min, 121 ml (5·5 mmoles) H_2 were taken up. Filtration followed by evaporation of the solvent gave 1·08 g (96%) of *2-hydroxy-5-methoxy-2,5-dihydro-2,3,4,5-dicyclohexanofuran* (XXI) as colorless crystals, m.p. 81° from pet. ether. (Found: C, 69·3; H, 8·7; MeO, 13·9; Mol. Wt., 228 [cryoscopic, benzene]. $C_{13}H_{20}O_3$ requires: C, 69·6; H, 9·0; MeO, 13·8%; Mol. Wt., 224.) The compound decolorizes bromine in $CHCl_3$ and permanganate in acetone, and is decomposed by acids to a brownish resin. The IR spectrum has bands at 2·78 and 2·86 μ; the latter band disappears on dilution.

Photosensitized oxygenation of dicyclohexanofuran(XVIII) *in benzene-petroleum ether*

A soln of 3·52 g (0·02 mole) XVIII in 30 ml benzene and 90 ml pet. ether with 50 mg dinaphthylene thiophene took up 458 ml O_2 (0·02 mole) at −22°, with water carefully excluded, to give soln A. The solvent was removed at −30° and 12 mm (under argon) from 60 ml of this soln. The partly crystalline residue decomposed violently upon release of the vacuum or on warming to about 0°.

On treatment of 30 ml of the cold soln A (containing 5 mmoles of peroxide) with 50 ml of MeOH (cooled to −20°), the temp rose to about −5°. After about 2 hr at room temp, the solvent was removed to give 0·8 g (66%) of methoxyhydroperoxide, m.p. and mixture m.p. with XX, 101°. Repetition of the experiment with a soln which had been kept at −40° for 12 hr gave only 22% of peroxide XX along with peroxidic resins.

Photosensitized oxygenation of menthofuran (VI)

Menthofuran, 19·6 g, (0·097 mole) was dissolved in 250 ml MeOH containing ca. 100 mg Rose Bengal. The soln was irradiated with a 625 watt incandescent lamp (Sylvania Sungun) in a water-cooled immersion irradiation apparatus through which O_2 was recirculated. After 10 min, 2140 ml O_2 (STP, 0·096 mole) had been taken up, and the reaction ceased abruptly. The MeOH was evaporated in a rotary evaporator, and the residue taken up in ether. The ether was washed with water, treated with activated charcoal, dried, and evaporated. Ligroin was added to the residue, and the soln allowed to stand overnight at −20°, during which time slow crystallization occurred. The product was washed with a little cold pentane and dried to yield 11·1 g (0·052 mole, 53%) of colorless crystals of 3-*methoxy-9-hydroperoxy-3,9-dihydromenthofuran* (XXII), m.p. 73–76°. A purified sample ($[\alpha]_D^{20}$ = 17·8°, *c* = 33·9) melted at 77–78°. Br_2 (in CCl_4) and basic permanganate solns were instantly decolorized. The IR spectrum (CCl_4, 0·01M) had OH absorption at 2·845 μ;[10,11] in $CHCl_3$ the spectrum had principal bands at 2·9, 6·90, 7·50, 8·55, 8·82, 9·40, 9·80, 10·38, 10·52 and 11·78 μ. In the UV, the compound had only end absorption at 220 mμ. The NMR spectrum ($CDCl_3$) had bands at −0·64 (1H),[16] 4·28 (1H), 6·90 (3H), and 8·30 τ (3H), all singlets; in addition, unresolved multiplets in the region 7·5–8·5 τ, and two doublets (2H and 3H) at 8·85/8·98 and 9·08/9·18 τ were present. (Found: C, 61·9; H, 8·5; OMe, 14·0; Mol. Wt., 217 [cryoscopic, benzene]. $C_{11}H_{18}O_4$ requires: C, 61·7; H, 8·5; OMe, 14·5%; Mol. Wt., 214.)

The active O_2 titration of the peroxide was carried out according to the procedure of Siggia.[24] To a soln of 216·6 mg of the peroxide (1·001 mmoles) in 50 ml EtOH were added 1 ml of glacial AcOH and 1 ml sat. KIaq; the soln was held at 75° for 5 min, then titrated to a starch end-point; 18·67 ml of 0·100N thiosulfate soln were required, corresponding to 0·93 active O_2/mole.

The active H was determined by a modified Zerevitinoff procedure, using LAH;[25] 53·8 mg of the peroxide evolved 11·13 ml H, which corresponds to 1·98 active H_2/mole; one active H is produced by the O—O bond (which is reduced to OH).

Rearrangement of menthofuran peroxide (XXII) *to pseudoacid* (XXIII)

(a) *Under basic conditions.* Peroxide XXII, 0·50 g (2·3 mmoles) was suspended in 500 ml H_2O to which 5 drops of 10% NaOHaq were added. After 2 hr at room temp, all but about 50 mg of material had dissolved. The soln was filtered, and the colorless filtrate acidified with 10% HCl. The partially crystalline greenish ppt was dissolved in hot benzene, filtered with active charcoal, and allowed to crystallize. After 2 further recrystallizations, 0·13 g (0·72 mmoles, 31%) of colorless crystals were obtained, m.p. 188–188·5°; the mixture m.p. with XXIII (reported[19] m.p. 188–189°) was 187·5–188·0°.

(b) *Under acidic conditions.* A small amount of XXII was dissolved in MeOH to which 5% HCl soln was added until the soln became cloudy. The mixture was refluxed for 2 hr, cooled, diluted with water, and extracted with ether. The ether soln was dried, the ether evaporated, and the residue recrystallized twice from benzene to give colorless plates, m.p. 187–188°, mixture m.p. with XXIII, 188–189·5°.

(c) *On long standing.* A small amount of XXII was allowed to stand at room temp; after 3 days, the crystals had become a colorless, viscous oil, which solidified after 4 weeks. The mixture, which now gave only a weak peroxide test with KI/AcOH was recrystallized from benzene to give colorless plates, m.p. and mixture m.p. with XXIII, 188–189°.

Pyrolysis of menthofuran photoperoxide (XXII)

A sample of the peroxide was dissolved in benzene and injected into the gas chromatograph (column, 200°, injection block 250°). A single product, of the same retention time as XXIV, was formed. This product was collected from the gas chromatograph, and had an IR spectrum (CCl_4) identical to that of pure *pseudoester* (XXIV), whose characterization is described below.

Formation of pseudoester (XXIV) *from pseudoacid* (XXIII)

Pseudoacid XXIII, 100 mg (0·55 mmole) was refluxed 4 hr in 10 ml MeOH containing 0·5 ml conc HCl. Most of the MeOH was evaporated, the residue was taken up in ether, and the soln was washed 3 times with water and dried. The ether was evaporated, and the residue recrystallized from pentane at −20° to yield 35 mg of colorless needles of XXIV (0·18 mmoles, 33%), m.p. 41·5–42·5°. (Found: C, 67·4; H, 8·3; OMe, 16·3. $C_{11}H_{16}O_3$ requires: C, 67·3; H, 8·2; OMe, 15·8%). The IR spectrum (CCl_4) had characteristic bands at 5·62, 5·85 w and 10·4 μ. The NMR spectrum (CCl_4) had distinguishable peaks at 6·95 (3H), 8·17 (3H) and 9·0/9·1 τ (3H). The UV spectrum (MeOH) had λ_{max} = 216 mμ (ε = 12,200).

Saponification of pseudoester (XXIV)

A soln of 5·0 g (0·026 mole) pseudoester in 5 ml MeOH and 10 ml water was refluxed with 1·0 g (0·025 mole) NaOH for 1 hr. The soln was cooled and acidified with 6N HCl. The ppt was recrys-

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[24] S. Siggia, *Quantitative Organic Analysis via Functional Groups* (3rd Edition) Wiley, New York (1963).

tallized from MeOH/water to give 4·5 g (0·025 mole, 97%) of XXIII, plates, m.p. 188°. The IR spectrum was identical with that of a sample of pseudoacid prepared from menthofuran,[18] and had characteristic IR bands at 2·70, 2·90, 5·68, 5·85 w, 9·95 and 10·37 μ. The NMR spectrum ($CDCl_3$) had, among others, bands at 8·12 (3H) and 8·90/9·00 τ (3H). The UV spectrum (MeOH) had λ_{max} = 215 mμ (ε = 11,400).

Hydrogenation of menthofuran peroxide (XXII) *with Raney nickel*

Peroxide XXII (4·28 g, 0·02 mole) was shaken under 1 atm H_2 in 100 ml MeOH in the presence of Raney Ni. The soln grew warm, and H_2 uptake was initially rapid, but ceased after the uptake of 280 ml H_2 (0·013 mole). Other attempts at hydrogenation led to uptake of between 40 and 70% of the theoretical amount. After filtration and removal of the solvent *in vacuo*, the residue was taken up in 30 ml pet. ether, and cooled to −40°, to give 1·9 g (48%) of trans-3-*methoxy-9-hydroxy*-3,9-*dihydromenthofuran* (XXV), m.p. 80–83°. (Found: C, 66·4; H, 9·0; MeO, 14·6; Mol. Wt., 178 [cryoscopic, benzene]. $C_{11}H_{18}O_3$ requires: C, 68·6; H, 9·2; MeO, 15·6%; Mol. Wt., 198·2.) The compound decomposed after one day at room temp to give a viscous mass from which XXIII crystallized after a further 14 days. In the IR, the compound had OH absorption at 2·78 and 1·41 μ.

Reduction of menthofuran peroxide with sodium borohydride

Three reductions of XXII were carried out with different amounts of $NaBH_4$ in MeOH. The solns were stirred for ½ hr, then diluted with water and extracted with ether; the ether solns were washed twice with water, dried, and evaporated; the residue was analyzed by gas chromatography. The products were collected and identified by comparison of their IR spectra and retention times with those of authentic samples. The results are summarized in Table 2.

TABLE 2. PRODUCTS OF REDUCTION OF MENTHOFURAN PHOTOPEROXIDE (XXII)

Reagents		Amounts		
XXII	g	1·00	1·00	0·50
	mmoles	4·67	4·67	2·33
$NaBH_4$	g	0·075	0·125	1·00
	meq.	7·93	13·3	106
Products		**Percent in reaction Mixture**		
VI		8	30	60
XXVI		20	35	30
XXVII		10	10	5
XXIV		40	10	0
Unidentified		20	15	5

Reduction of menthofuran peroxide with triphenylphosphine

A soln of 2·0 g (9·4 mmoles) of XXII in 20 ml ether was added dropwise to a refluxing soln of triphenylphosphine[17] in 30 ml ether during 1·5 hr. The soln was refluxed 1 hr, chilled to −5°, and filtered to remove the triphenylphosphine oxide. The ether was removed with a rotary evaporator, and the residue (which had strong IR bands (CCl_4) at 2·85, 6·85, 8·55, 8·9, 9·3, 10·3, 11·7, 13·4, 13·8 and 14·4 μ, but only traces of absorption in the 5·5–6·0 μ region) distilled in a modified Hickman still at 0·2 mm (oil bath 105–120°); the IR spectrum showed the distillate to consist of about 85% of the *β-γ-unsaturated γ-lactone* (XXVI) and 15% of the *α,β-unsaturated γ-lactone* (XXVII). Lactone XXVI was separated from the mixture, after many trials, in nearly pure form by gas chromatography on an 8′ × ¼′ column of 10% Silicone oil DC-220 on Diatoport S at 99° using high gas flow rate. (Found: C, 72·1; H, 8·5. $C_{10}H_{14}O_2$ requires: C, 72·3; H, 8·5%.) The IR spectrum of lactone XXVI had significant bands at 5·53(s), 5·82(w), 7·85, 8·28, 9·22, 10·0(s), 11·05(w), and 11·45 (w) μ. The NMR spectrum had bands at 7·0(1H), 8·0(4H) and 8·3 τ(2H), all broad and unresolved, and sharp doublets (3H each) at 8·70/8·82 and 8·88/9·00 τ. The UV spectrum had only weak absorption below 230 mμ, probably caused by the presence of small amounts of α,β-unsaturated lactone XXVII.

Rearrangements of β,γ-unsaturated lactone (XXVI *to α-β-unsaturated lactone* (XXVII)

The unconjugated lactone XXVI rearranged to the conjugated lactone XXVII under the following conditions.

(a) *Distillation on a spinning-band column.* Crude lactone XXVI, 24 g (0·145 mole, prepared by high-vacuum distillation of the reduction mixture of menthofuran peroxide with triphenylphosphine) was distilled on a spinning band column to give 9·9 g (0·0595 mole, 41%) of nearly pure XXVII, b.p.$_{18}$ 157°, n_D^{20} = 1·4982, $[\alpha]_D^{20}$ = −37·6°, d_{20}^{4} = 1·058, m.p. = −1°.

(b) *In the gas chromatograph.* A sample of XXVI which had been collected from the gas chromatograph (as described above), and which was shown by its IR spectrum to contain almost no XXVII was reinjected (injection block 173°, column 120°) onto a 3′ column of 20% DC-220 Silicone oil (retention time 23 min). A substantial peak corresponding to the retention time of XXVII was found; in addition, the peak which corresponded to XXVI was very broad, and when recollected had an IR spectrum which corresponded to a mixture of XXVI and XXVII, with XXVII predominating. As it was necessary to keep both retention time and column temp low in order to collect pure XXVI, very short columns were used for this purpose. It was also found that XXVI in CCl_4 or many other solvents rearranged to XXVII.

Preparation of α,β-unsaturated γ-lactone (XXVII) *from pseudoacid*

To a soln of 6·5 g (0·036 mole) XXIII and 1·7 g (0·42 mole) NaOH in 70 ml H_2O was added 0·75 g (0·079) of $NaBH_4$. The reaction mixture was left for 1 hr, then extracted with ether. To the aqueous soln was added 0·34 g (0·036) additional borohydride; the reaction mixture was left in the refrigerator overnight, then extracted with ether. The combined ether extracts were dried and evaporated to yield 5·0 g (0·030 mole, 84%) of XXVII which solidified at about 5°, and was essentially pure as shown by VPC. The IR spectrum had bands (CCl_4) at 5·67(s), 5·92(w), 9·10, 9·31 and 9·65 μ. The UV spectrum (MeOH) had λ_{max} = 217 mμ (ε = 16,600). The NMR spectrum (CCl_4) had an AXY quartet (1H, J = 6 and 11 c/s) centered at 5·4 τ; a triplet (3H, J = 1 c/s) at 8·28 τ and a doublet (3H, J = 6 c/s) at 9·05 τ. (Found: C, 72·5; H, 8·3. $C_{10}H_{14}O_2$ requires: C, 72·3; H, 8·5%.)