Product Analyses. Product analyses were carried out using a Perkin-Elmer vapor fractometer. The areas of the peaks were measured using a Honeywell Disc Integrator. For the product analyses of the *tert*-butyl- and *tert*-amylethylmethylsulfonium salts, accurately known quantities of the sulfonium salt, internal standard, and base were dissolved in the appropriate solvent and the solutions made up to the mark with solvent in a volumetric flask. Aliquots of the solution were transferred to ampoules and sealed. The sealed ampoules were placed in an appropriate constant-temperature bath for a time corresponding to 10–20 half-lives for the reaction. The ampoules were then removed from the bath and cooled to 10°. Upon opening the ampoules, a 50-μl aliquot of the solution was immediately injected into the gas chromatography apparatus. The amount of each material relative to the internal standard was then determined, and the absolute yield of each product was calculated.

A similar procedure was used for the analysis of the products of solvolysis of 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts with the following modification. After removal of the ampoules from the constant-temperature bath, a 5-ml aliquot of the solution was taken and dissolved in 25 ml of ether. The ether layer was washed, to remove the ethanol or acetic acid, and dried over potassium carbonate, and the ether solution was concentrated to a volume of 1 ml. A 50-μl aliquot of the solution was then delivered into the gc apparatus and analysis was carried out in the usual manner.

A summary of the chromatography columns, internal standards, and retention times for analysis of the various products is given in Table VIII.

Kinetic Measurements. The sulfonium salt was accurately weighed in a tared volumetric flask. Enough solvent to dissolve the salt, together with as many aliquots of standard stock solutions of base or salt as required, was added to the flask. The solution was then made up to the mark by addition of solvent. The sealed-ampoule technique was used. Each ampoule contained approximately 5.3 ml of solution. The ampoules were placed in a constant-temperature bath at 25.00 ± 0.02 or 50.00 ± 0.02°. At appropriate time intervals, the ampoules were removed from the bath. For reactions studied at 50° the ampoules were quenched in an ice–water bath and then equilibrated to 25.0°. A 5-ml aliquot of the solution and titrated with standard base or acid. For reactions at 25°, the ampoules were removed from the constant-temperature bath and immediately opened without quenching. A 5-ml aliquot of the solution was then titrated. The time recorded was that at the beginning of the titration. For reactions in solvent ethanol, the aliquots of the solution were transferred to a 50-ml volumetric flask containing 25 ml of boiled distilled water. Each sample was titrated with standard sodium methoxide in methanol using phenolphthalein as indicator. For reactions in acetic acid and 50% acetic acid–acetic anhydride, the solutions contained an excess of sodium acetate. Each aliquot was titrated for excess base with a standard solution of perchloric acid in acetic acid using *p*-naphtholbenzein as indicator. The "zero point" for each reaction was taken at least 4 min after the ampoules were placed in the constant-temperature bath. "Infinity" measurements were taken after 10 and 20 half-lives for the reactions.

The integrated first-order rate constants were calculated using the experimental infinity values, usually 100 ± 3% of the theoretical value. The rates were followed to *ca.* 85% completion.

Nuclear Magnetic Resonance Spectra and Characterization of Some Quinone Methides[1]

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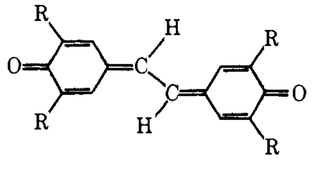
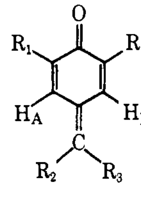
Abstract: A method is described for preparing nmr samples of even rather unstable quinone methides, by oxidation of the corresponding phenol in carbon tetrachloride solution with silver oxide. The nonequivalence of the ring protons in the nmr spectra of quinone methides with unsymmetrical substitution on the terminal methylene is attributed to van der Waals deshieldings. 4-Allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one was isolated as an unstable crystalline compound and fully characterized. The stabilizing influence of the vinyl substituent is reflected in the low rate of addition of neutral methanol. This quinone methide is reduced by $LiAlH_4$ to a 63:37 mixture of 4-allyl-2,6-dimethylphenol and 4-propenyl-2,6-dimethylphenol.

Ingold and Brownstein[3] report that the stilbene quinones Ia and Ib have nmr spectra in which both the ring protons and the alkyl protons are nonequivalent. Similar nonequivalence has been reported for indophenols[4] and for quinone methides of type II (R_1 = *tert*-butyl; R_2 = H; R_3 = CH_3, OCH_3, CN, etc.),[5] and has been attributed to molecular asymmetry.[3] However, no detailed explanation of the spectral nonequivalence has been offered, doubtless because some of the compounds whose spectra should be studied are quinone methides too unstable to isolate.



Ia, R = *tert*-butyl
Ib, R = *tert*-amyl



IIa, $R_1 = CH_3$; $R_2 = R_3 = H$
IIb, $R_1 = CH_3$; $R_2 = H$; $R_3 = CH_3$
IIc, $R_1 = CH_3$; $R_2 = H$; $R_3 = CH{=\!=}CH_2$
IId, $R_1 = C(CH_3)_3$; $R_2 = R_3 = H$
IIe, $R_1 = C(CH_3)_3$; $R_2 = H$; $R_3 = CH_3$
IIf, $R_1 = C(CH_3)_3$; $R_2 = R_3 = CH_3$

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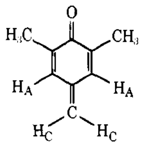
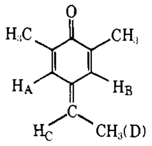
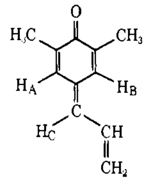
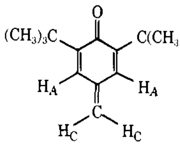
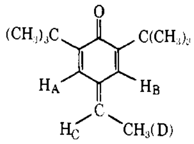
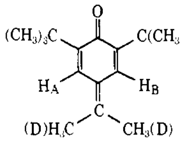
[2] Address correspondence to: Department of Chemistry, The University of Newcastle, New South Wales, Shortland 2308, N.S.W., Australia.

[3] S. Brownstein and K. U. Ingold, *J. Amer. Chem.Soc.*, **84**, 2258 (1962).

[4] G. M. Coppinger and J. L. Jungnickel, *J. Chem. Phys.*, **38**, 2589 (1963).

[5] A. Rieker and H. Kessler, *Tetrahedron*, **24**, 5133 (1968).

Table I. Nmr Spectra of Quinone Methides in CCl_4 Solution

Quinone methide	Ring alkyl, δ	H_A, δ	H_B, δ	H_C, δ	Other protons, δ
 IIa	1.90 (1)	6.76 (1)[a]		5.49 (1)[a]	
 IIb	1.87 (1) 1.92 (1)	6.64 (2) $J_{AB} = 1.5$	7.09 (2) $J_{AB} = 1.5$	6.11 (4) $J_{CD} = 7.8$	D, 2.02 (2) $J_{CD} \sim 10$[b]
 IIc	1.95[c]	6.82 (2) $J_{AB} = 1.2$	7.24 (2) $J_{AB} = 1.2$	6.29 6.52	1H, 6.70–7.07 (m) 1H, 5.51 (2), $J = 2.1$ and 5.70 (2), $J = 2.1$ 1H, 5.39 (1)
 IId	1.23 (1)	6.77 (1)		5.58 (1)	
 IIe	1.23 (1) 1.26 (1)	6.60 (2) $J_{AB} = 2.4$	7.07 (2) $J_{AB} = 2.4$	6.16 (4) $J_{CD} = 7.2$	D, 2.05 (2) $J_{CD} = 7.2$
 IIf	1.23 (1)		7.13 (1)		D, 2.13 (1)

[a] The signals are slightly broadened, which might indicate a very small J_{AC} value; J values are in hertz. [b] J_{CD} is uncertain since half the doublet is overlapped. [c] The signal is very broad (6 Hz at half-height) and is presumed to be double.

We have now been able to prepare solutions of the necessary quinone methides by oxidizing the corresponding phenol in carbon tetrachloride with silver oxide. Quinone methides even as unstable as IIa persisted long enough for the nmr spectra to be measured, and IIc proved stable enough to be isolated for chemical studies. The series of nmr spectra we have obtained do furnish an explanation for the spectral nonequivalences which have been reported.

Results and Discussion

Nmr Spectra. The results listed in Table I confirm and extend those obtained by other workers.[3,5] In the spectra of symmetrical quinone methides (IIa, IId, IIf) there is only one nmr signal for the two ring protons, and likewise only one for the two ring alkyl groups. However, both these groups of protons give rise to two signals when the terminal methylene substituents, R_2 and R_3, are different (as in IIb, IIc, and IIe). The ring protons, being no longer equivalent, now couple (J = 1.2–2.4 Hz). The nonequivalences in the unsymmetrical quinone methides, and the actual magnitudes of the ring proton chemical shifts, can be interpreted by considering the series of quinone methides IId, IIe, and IIf.

A possible explanation for the nonequivalence of the ring protons in IIe invokes the magnetic anisotropy of the terminal *C*-methyl bond. The methylene is not free to rotate,[5] and ring proton H_B will then be shielded while H_A is deshielded. The chemical-shift difference is, however, much larger than is observed from such effects,[6a] and the deshielding of *both* the ring protons in IIf by the two methyl groups is incomprehensible. A variation on this explanation proposes rotation of the terminal methylene group when methyl substituents are present to cause steric interaction with the nearby ring hydrogens. The partial removal of the methylene from conjugation would increase the electron deficiency at

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(6) (a) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon, London, 1959, p 117; (b) p 61.

positions β to carbonyl, and thus decrease the shielding of the protons attached there. On this basis, H_A in IIe is at the lower field, while H_B is at the higher field because of shielding from the *C*-methyl bond. However, the low shielding of the ring protons in IIf would require quite substantial rotation of the methylene group from the ring plane if the shielding effect of the *C*-methyl bonds is to be overcome. It is quite clear from the uv spectral data in Table II that there is not reduced conjugation of the terminal methylene in the quinone methides IIe and IIf.

Table II. Effects of Methylene Substitution on the Uv Spectra[a] of Quinone Methides

Quinone methide	Isooctane λ_{max}, nm	Log ϵ
IId	285	4.45
IIe	299	4.42
IIf	314	4.40

[a] Data from L. J. Filar and S. Winstein, *Tetrahedron Lett.*, 9 (1960).

Yet another explanation would propose buckling of the quinone methide ring to relieve steric interactions between the terminal methyl group, the ring hydrogen H_B, and the adjacent *tert*-butyl group; such buckling would be asymmetric in IIe but not in IIf. However, the chemical-shift difference between H_A and H_B in IIe is unaffected when the *tert*-butyl groups are replaced by the much less bulky methyl groups in IIb.

We therefore propose an explanation based on the sizable van der Waals deshieldings which can occur when hydrogen atoms are constrained to lie closer than the sum of their van der Waals radii.[7] Examination of Cenco Petersen molecular models reveals that H_B in IIe is, at most, 2.08 Å from two skewed hydrogens on the terminal methyl D; at closest, it is 1.41 Å from an eclipsed hydrogen. The average separation is, then, substantially less than the sum of two van der Waals radii for hydrogen (2.4 Å). The resultant deshielding of H_B must be large enough to more than offset both the anisotropic shielding by the *C*-methyl bond and the shielding attributable to inductive release from methyl. On the other side of the methylene group, H_C and H_B are too far apart (2.46 Å) for van der Waals repulsion to become important. H_A actually shows an upfield shift from the δ value observed for IId, which we attribute to inductive release from the terminal methyl into the π-bond system of IIe.[8]

The nonequivalence of the *tert*-butyl groups might arise from minor van der Waals interactions with the ring hydrogens, or by long-range anisotropy effects from the terminal *C*-methyl bond, or by some degree of buckling of the ring by steric interactions which could make the two positions α to carbonyl nonequivalent to a minor extent. The two *tert*-butyl signals are not attributable to restricted rotation since they are in the intensity ratio 1:1 and not 1:2, and such restricted rotation would be expected even in the symmetrical quinone methides IId and IIf.

The chemical shift of the ring protons H_B in IIf surprisingly fails to show the shielding effect of the extra methyl when compared with IIe. Possibly the *C*-methyl in IIe is "bent back" from H_B to reduce the van der Waals interaction, whereas the extra methyl substitution in IIf precludes the relief of strain in this way and the van der Waals deshielding is maximized.

The nmr spectra (Table I) of the 2,6-dimethyl compounds IIa, IIb, and IIc show that our analysis of the chemical shifts on the basis of van der Waals interactions is of general validity.

Preparation and Isolation of Quinone Methides. Our simple procedure for preparing fairly concentrated solutions of quinone methides, by oxidation of the corresponding phenol with silver oxide, considerably extends the range of these important reaction intermediates which have been characterized by nmr. The quinone methides can, however, only be obtained from phenols with alkyl groups at positions 2 and 6; we were unsuccessful with *p*-cresol, 2-*tert*-butyl-4-methylphenol,[9] 4-isopropylphenol,[9] and 4-allylphenol.

We confirm previous observations[10] that the 2,6-dimethylquinone methides such as IIa and IIb are quite unstable and cannot be isolated even at low temperatures. However, the quinone methide IIc, which had previously been prepared by Filar and Winstein[10] only in very dilute solutions, was seen during the nmr studies to be rather more stable than IIb. We succeeded in crystallizing IIc from pentane at low temperatures, and fully characterized it by ir, nmr, uv, and elemental analysis. This quinone methide, **4-allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one,** is the first of this type to be characterized and isolated. The crystalline material has a half-life of less than 1 hr at 20°.

The higher stability of IIc than of IIb, conferred by the extra double bond in conjugation, is also reflected in the rates of addition of neutral methanol ($k_1 = 6.72 \times 10^{-5}$ sec^{-1} at 25° for the former, and $k_1 = 3.1 \times 10^{-2}$ sec^{-1} at 23° for the latter[10]). Two isomeric methoxyphenols were expected from the addition of methanol to the allylidene–quinone system of IIc, but the two products obtained were too unstable for positive identification. The products of $LiAlH_4$ reduction of IIc were more tractable, and both 4-allyl-2,6-dimethylphenol and 4-propenyl-2,6-dimethylphenol were isolated, in 63:37 ratio.

Experimental Section

Nmr spectra were measured with a Varian A-60 spectrometer, using tetramethylsilane as internal standard. Ir spectra were recorded with a Perkin-Elmer 421 spectrometer, and uv and ir spectra with a Cary 14 instrument.

Isooctane (Matheson Coleman and Bell spectroquality reagent) was dried over Linde molecular sieves. Methanol (Baker analyzed reagent) was fractionated first from CaH_2, and then from dry sulfanilic acid.[11] The water content (by Karl Fischer reagent) was <100 ppm.

Preparation of Phenols. 4-Allyl-2,6-dimethylphenol was prepared by rearrangement of 2,6-dimethylphenyl allyl ether.[12] The crude phenol, bp 80–84° (0.5 mm) and n^{26}D 1.5385, was converted into its **3,5-dinitrobenzoyl ester,** mp 148.0–148.5°, which crystallized from ethanol as very pale yellow filaments.

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(7) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 87, 5247 (1965), and references cited therein.

(8) Despite this inductive release, the signal from H_C in IIe is found further downfield than in IId. This downfield shift is, however, commonly observed for such methyl-substituted double bonds.[6b]

(9) Observations reported to us by Dr. L. J. Filar.

(10) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, 9 (1960).

(11) J. A. Riddick and E. E. Toops, *Tech. Org. Chem.*, 7, 335 (1955).

(12) D. S. Tarbell and J. F. Kincaid, *J. Amer. Chem. Soc.*, 62, 728 (1940).

Anal. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.68; H, 4.52. Found: C, 60.60; H, 4.70. Alkaline hydrolysis of this ester afforded the pure phenol, n^{25}D 1.5369 (lit. 1.5370,[12] 1.5368,[13] 1.5365[14]); phenylurethane, mp 145–146° (lit.[15] mp 144.5–145.5°); nmr (CCl_4) δ 2.12 (s, 6 H, aromatic CH_3), 3.14 and 3.25 (2 H, CH_2), 4.53 (s, 1 H, OH), 4.86–4.96 (m, 1 H, allylic), 5.06–5.21 (m, 1 H, allylic), 5.60–6.14 (m, 1 H, allylic), and 6.69 (s, 2 H, aromatic H); uv (isooctane) had λ_{max} 200 (log ϵ 4.621), 219 sh (3.935), 230 sh (3.672), 270 inflection (3.138), 275 (3.246), 278 (3.246), and 283 (nm (3.265).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.46; H, 8.69. Found: C, 81.34; H, 8.87. The other phenols were kindly supplied by Dr. Leo Filar of the Hercules Powder Co., Inc., Wilmington, Del.

Preparation of Carbon Tetrachloride Solutions of Quinone Methides for Nmr Measurements. The stable quinone methides IIe and IIf were each prepared by oxidation of the corresponding phenol with alkaline ferricyanide and were isolated in crystalline form.[16,17] The other quinone methides are very much less stable, and were therefore not isolated prior to nmr measurement. A suitable technique involved shaking the phenol (30 mg) in carbon tetrachloride (1 ml) with silver oxide (100 mg, Baker and Adamson reagent) in a glass-stoppered test tube during 10 min. The oxidant was allowed to settle, and the supernatant liquor was drawn off for immediate nmr measurements. Generally, no significant amount of the phenol remained, and very little dimerization of the quinone methide had yet occurred, so that clean nmr spectra with accurate integrals were obtained. 2,6-Di-*tert*-butyl-4-methylphenol was found to need a much longer oxidation period (40 min). 2,4,6-Trimethylphenol yielded by far the least stable quinone methide,[10] and a red precipitate of the stilbene quinone appeared before all the phenol was oxidized. The spectrum of the quinone methide could be positively identified by examining the nmr spectra at various stages in the oxidation, but it was not possible to get an integral of this spectrum.

Uv Spectrum of 4-Allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one. Optimum ϵ values in the uv spectrum of this quinone methide, IIc, were obtained when a 2×10^{-3} *M* solution of the phenol in isooctane was stirred with powdered silver oxide (6 mol/mol of phenol) in a stoppered flask during 30 min. The inorganic material was removed by rapid filtration through a sintered glass disk and was washed with two 2-ml portions of isooctane. The combined filtrates were made up to standard volume in isooctane for immediate spectral measurements. The uv spectra in solvents other than isooctane were obtained by diluting the filtered isooctane reaction mixture 100-fold in the desired solvent. The uv spectra are recorded in Table III.

Table III. Uv Spectrum of the Quinone Methide IIc

$\lambda_{max}^{isooctane}$, nm	Log ϵ	$\lambda_{max}^{Et_2O}$, nm	Log ϵ	$\lambda_{max}^{CCl_4}$, nm	Log ϵ
213.5	4.025	212	4.043		
218	4.005	218 sh	3.606		
234	3.398	234	2.866		
242	3.382	243	3.124		
251	3.248	251	3.004		
~302[a]	3.801	298[a]	3.555	305[a]	3.770
310[a]	3.918	311[a]	3.621	315[a]	3.819
329	4.655	331	4.652	336	5.623

[a] These bands have been graphically resolved from the much stronger band near 330 nm.

Oxidation for longer periods, or with a greater excess of oxidant reduced the ϵ values.

Isooctane solutions 1.9×10^{-3} *M* in the quinone methide IIc were reasonably stable near 20°, the ϵ value at 329 nm dropping to 50% of the initial value after 35 days and to zero after 5 months. The 1.9×10^{-3} *M* solutions were not unduly sensitive to air, the ϵ value at 329 nm decreasing by only 3% after a 30-min exposure.

Isolation of 4-Allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one. 4-Allyl-2,6-dimethylphenol (104 mg) was stirred 100 min in dry pentane (250 ml) with silver oxide (3.0 g) at 20°. The solution was then filtered, chilled to −50°, and sucked down to 10 ml with an oil pump. The residual solution was warmed to 0° and filtered in a moisture-free apparatus to remove traces of polymer. The filtrate was then cooled in Dry Ice–acetone and reduced to 5 ml by suction. **4-Allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one** (IIc) crystallized as yellow microneedles, which were collected and sucked dry at −78° (1 mm); mp 37–38°.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.47; H, 7.56. Found: C, 82.51; H, 7.55. This quinone methide was characterized by the ir fundamental bands (CCl_4) at 1641 (ϵ 95), 1620 (305), and 1596 cm^{-1} (115) which match those observed in other quinone methides,[10] by the nmr spectrum (Table I), and by a comparison of the uv spectrum (Table III) with those of other quinone methides (Table II). Solutions of the freshly prepared solid IIc gave the same uv, ir, and nmr spectra as those obtained when this quinone methide was prepared in solution without prior isolation.

The solid quinone methide polymerized within 1 hr at 20°. Monitoring of the polymerization by uv revealed that the solid monomer stored successfully for 20 hr at −78° but was only 80% pure after 5 days.

Reduction of the Quinone Methide IIc. 4-Allyl-2,6-dimethylphenol (202 mg, 1.25 mmol) was oxidized during 120 min with silver oxide (1.00 g) in dry pentane (400 ml). The filtered solution was added dropwise during 60 min to $LiAlH_4$ (200 mg, 5.3 mmol) in dry ether (80 ml). After the usual hydrolysis and work-up, pyrogallol (50 mg) was added to inhibit polymerization, and the ether solution was dried (Drierite) before removing the solvent by aspiration at 20°. The residue was extracted with three 5-ml portions of isooctane. The combined extracts were filtered to remove pyrogallol and then immediately analyzed by uv. The analysis showed the combined yield of 4-allyl- and 4-propenyl-2,6-dimethylphenol in several runs to be 83–89%, and the proportions of these two phenols were, respectively, 63.4 ± 0.4 and 36.6 ± 0.4%. A saturated solution of pyrogallol in isooctane had zero absorbance at the wavelengths (259.5 and 283 nm) used in the analysis.

4-Allyl-2,6-dimethylphenol was identified in the reaction mixture by its retention time in vpc (2 m, 25% SE-30, 60–80 mesh Chromosorb W, 60 ml of He/min, 170°), and the eluted sample had the same ir and uv spectra as the authentic compound. **2,6-Dimethyl-4-propenylphenol** was difficult to isolate because it polymerized rapidly, but a low recovery was made from a 0.5-m vpc column at 100°. The material so obtained was crystallized from cold pentane as white platelets, mp 76.5–77.5°, and was stored at −78° since it slowly polymerized even at 0°.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.46; H, 8.69; mol wt, 162. Found: C, 81.26; H, 8.95; mol wt (Rast, 10% solution), 183. Spectral characteristics include: uv (isooctane) λ_{max} 212 (log ϵ 4.416), 216 (4.404), 223 (4.163), 260 (4.188), 269 (4.061), 293 (3.301), and 305 sh nm (3.093); ir (CCl_4) γ_{OH} near 3620 cm^{-1}.

Rate of Addition of Methanol to the Quinone Methide IIc. A 1.25×10^{-4} *M* solution was prepared in isooctane by the usual silver oxide oxidation of the phenol. A 2-ml aliquot was diluted to 50 ml with methanol, and this solution was examined spectrophotometrically in a 10-cm cell jacketted at 25.0 ± 0.1° in a Cary-11 uv instrument. The absorbance, *A*, of the quinone methide at the 338-nm λ_{max} was measured some 20 times during the first 3 half-lives. A_∞ was measured after 7–10 half-lives and was essentially zero. First-order rate constants, k_1, were calculated from the usual expression, $k_1 = (2.303/t)\log(A_0 - A_\infty)/(A_t - A_\infty)$, and were constant to ±2% within a run. The average of three runs was $k_1 = (6.72 \pm 0.08) \times 10^{-5}$ sec^{-1}.

Vpc analysis (0.5 m, 25% SE-30, 60 ml of He/min, 135°) of the reaction mixture revealed two products, shown by ir to be hydroxylic, which polymerized too rapidly to permit characterization.

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(13) F. Kalberer, K. Schmid, and H. Schmid, *Helv. Chim. Acta*, **39**, 555 (1956).

(14) D. Y. Curtin and R. J. Crawford, *J. Amer. Chem. Soc.*, **79**, 3156 (1957).

(15) F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 779 (1957).

(16) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **81**, 1176 (1959).

(17) C. D. Cook and B. E. Norcross, *ibid.*, **78**, 3797 (1956).