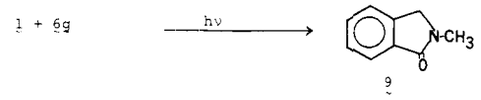
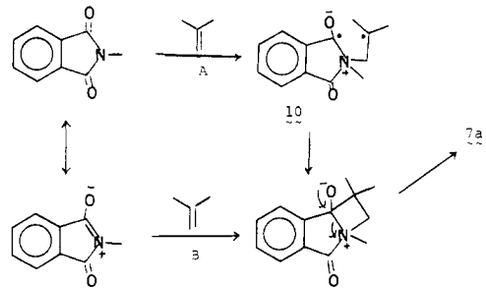
Suprisingly, irradiation of 1 with 2-methyl-2-butene or 2-methyl-2-pentene gave none of the expected substituted 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones and 2,3-dimethyl-2-butene gave a 5% yield of *N*-methylphthalimidine (**9**) as the only isolable product.[20]



9

There are several noteworthy points concerning these results. The observed reaction is totally regiospecific as was the corresponding reaction with dienes[16] and we suggest mechanistic routes A or B as the most reasonable ones. The reactivity



of the alkenes generally correlates with their ionization potentials (Table I), those alkenes with ionization potentials above 9 eV being reactive and those with ionization potentials below 9 eV unreactive. Clearly, electron-transfer processes cannot be important to these reactions unless the apparent correlation is due to counteracting steric effects. An alternative interpretation is that electron-transfer quenching of the reaction is taking place with those alkenes having low ionization potentials.[25] These points are being investigated.

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Sensitized Photoreduction of Dioxetanes to *cis*-1,2-Glycols: Solvent and Sensitizer Dependencies on the Singlet Oxygen Oxidation

Summary: Dioxetanes are convertible into *cis*-1,2-glycols by visible-light irradiations with relatively large amounts of xanthene dyes, such as Rose Bengal, in protic solutions under even aerated conditions to provide a new experimental probe for dioxetanes.

Sir: Previously we have reported[1] that the singlet oxygen oxidation of spirocyclic vinylcyclopropane **1** has given a new type of oxidation product **2** together with dialdehyde **3.** For the mechanism of formation of **2** there might be several possibilities, but at least a direct responsibility of singlet oxygen should be clear, since we have shown recently that quenchings of singlet oxygen by sodium azide have resulted in the complete suppression of formation of both **2** and **3.**[2] In this paper, we will further present evidences to support the concomitant formation of **2** and **3** by the reaction in various solvents and by an observation of unprecedented photosensitized reduction of dioxetanes to *cis*-1,2-glycols.

First of all, the relative yields of **2** and **3** in the reaction exhibited a marked solvent dependency as compiled in Table I.

It is clear that the polarity of solvents used plays no significant role, because in carbon disulfide and in pyridine the formation of **2** is predominant in each case. Interestingly, the formation of **2** in such inert solvents should be a conclusive evidence for its genesis with singlet oxygen. Except in a case with a benzene solution, where we had to use a polymer-supported sensitizer, the formation of **3** was favored in the reaction with protic solvents, and it is controlled by adjusting the solvent compositions as shown in the cases of a methanol–pyridine mixture.

In general, changes in sensitizers are known to be unimportant for singlet-oxygen oxidations. Comparative yields with Methylene Blue (MB) and Rose Bengal (RB) show this to be true for the process which leads to **2.** However, a dramatic change was observed for the yields of the dioxetane-related **3** when the reaction was carried out in methanol; with MB, **3** was the major product accompanied by trace amounts of **2,** but with RB, approximately equal amounts of **3** and the newly identified *cis*-glycol **4,** colorless needles, mp 56–57 °C, was formed. In the methanol–pyridine solvent mixtures and in methanol, the combined yields of **3** and **4,** with RB sensitization, were identical within experimental error to the yield of **3** with MB sensitization. Therefore, **4** has been derived from the precursor of **3**, i.e., the dioxetane (A) or its precursor (C) (Scheme I).

The structure of **4** was established by IR (ν_{OH} at 3450 cm^{-1}) and NMR ($CLCl_3$) [δ 0.30–0.75 (7 H, m), 0.88 (1 H, m), 2.01 (1 H, m, $W_{h/2}$ = 8 Hz), 2.31 (1 H, m, $W_{h/2}$ = 8 Hz), 2.55 (2 H,

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Table I. The Singlet-Oxygen Oxidation of 1 under Various Conditions[a]

runs	dyes	solvents (molar compositions)	concn of dyes	total yields, %	product distributions 2	3	4	5	6
1	MB	pyridine/methanol (1:1)	55 mg/25 mL	85	2	97		1	
2	MB	methanol	40 mg/50 mL	74	3	96		1	
3	hematoporphyrin	carbon disulfide			100[b]				
4	RB	methanol	84 mg/30 mL	91	3	46	51	+	
5	RB	methanol	30 mg/50 mL	96	2	53	43	2	
6	RB	pyridine/methanol (1:1)	82 mg/25 mL	93	8	26	66	+	+
7	RB	pyridine/methanol (7:3)	86 mg/25 mL	94	12	24	64	+	
8	RB	pyridine/*tert*-butyl alcohol (7:3)	88 mg/35 mL	86	21	19	52		8
9	RB	pyridine/water (7:3)	85 mg/25 mL	85	4	29	67		
10	RB	pyridine	70 mg/20 mL	64	89	11			
11	RB[c]	benzene		50	50	50			
12	RB	acetone	82 mg/25 mL	74	62	12	8		18

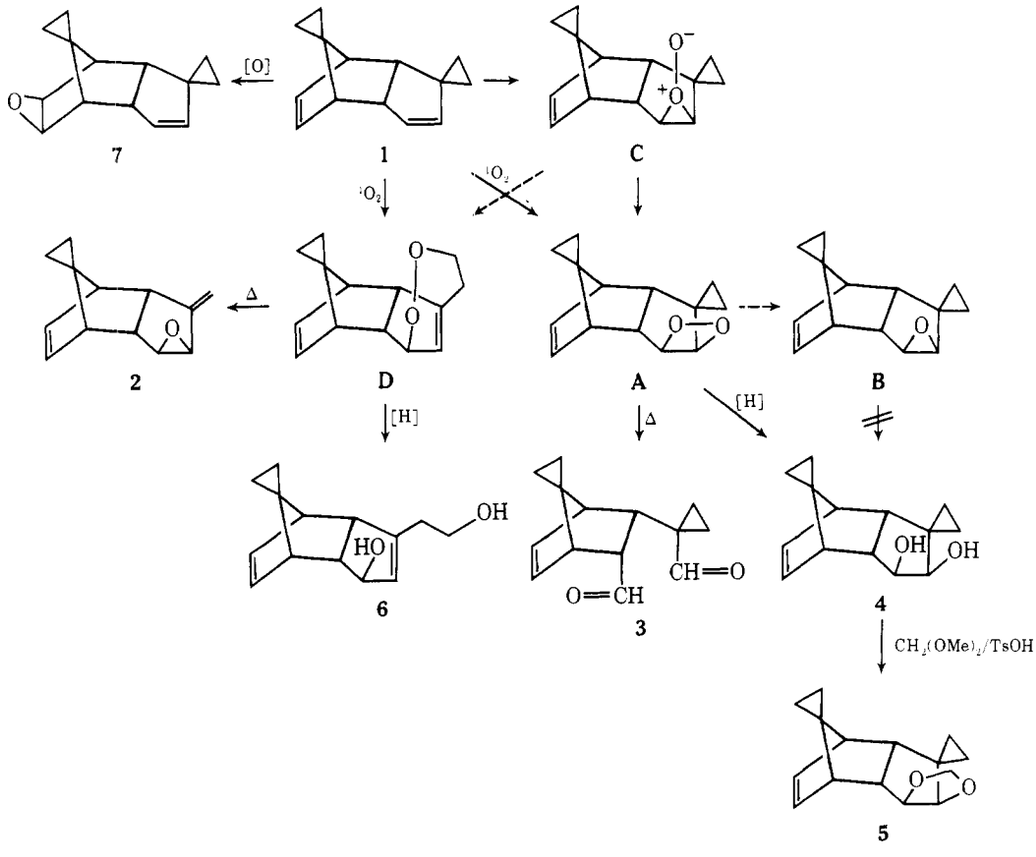
[a] Irrespective to volumes of solvents, amounts of 1 were adjusted as ~500 mg. [b] Analyzed by NMR spectrometry. [c] Supported on IR 401 resin.

disappeared on addition of D_2O), 2.65 (1 H, dd, J = 9.5, 4 Hz), 2.78 (1 H, ddd, J = 9.5, 4, 2.5 Hz), 3.66 (1 H, d, J = 5 Hz), 3.77 (1 H, dd, J = 2.5 Hz), 6.16 (1 H, ddd, J = 6, 3, 1 Hz), and 6.29 (1 H, ddd, J = 6, 3, 1 Hz)] spectral evidence together with the mild conversion of **4** into the *cis*-formal derivative **5**; a colorless liquid, which revealed pertinent IR (ν at 2950, 1095, and 970 cm^{-1}) and NMR ($CDCl_3$) [δ 0.08–0.75 (7 H, m), 0.90 (1 H, m), 2.05 (1 H, m, $W_{h/2}$ = 8 Hz), 2.36 (1 H, m, $W_{h/2}$ = 8 Hz), 2.74 (1 H, dd, J = 9, 5 Hz), 3.07 (1 H, dd, J = 9, 5 Hz), 4.08 (2 H, s), 4.88 (1 H, s), 4.90 (1 H, s), 6.22 (1 H, ddd, J = 6, 3, 1 Hz), and 6.32 (1 H, ddd, J = 6, 3, 1 Hz)] which exhibited J_{gem} of the methylene group in the formal function to be zero.[3]

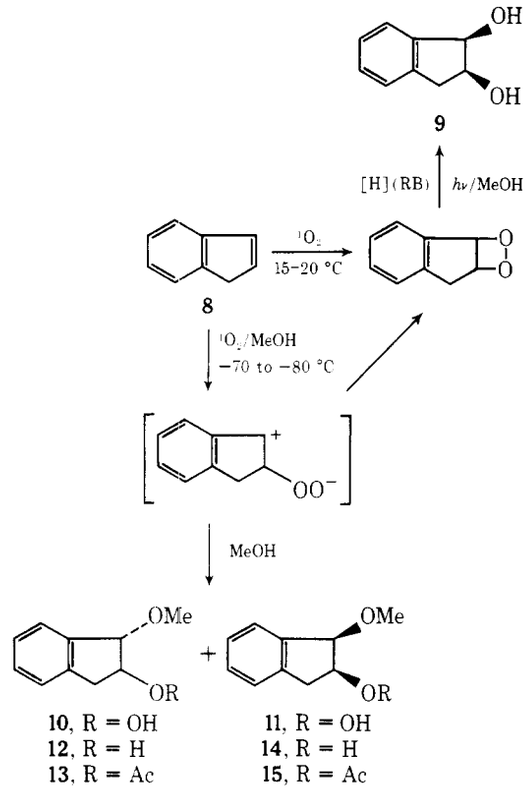
For the genesis of **4**, the hydrolysis of epoxide B or peroxirane C seems unlikely, since no methylated ether derived from the attack of solvent nucleophile is detectable. Only dioxetane A is capable of giving **4** under such mild conditions. Previously, the chemical reduction of dioxetanes by sulfides or other reagents[4,5] was known to give epoxides and other derivatives, but no photochemical 1,2-*cis*-glycol formation has been reported.[6] The present reaction is of preparative value, since moderately good yields of **4** are obtained. Protic solvents for the process is not limited to primary or secondary alcohols, since mixtures of pyridine with *tert*-butyl alcohol and with water also produced **4** in sufficiently good yields, but a partial decomposition of the dye was observed in these cases. In methanol, dye consumption was negligible.

Frequently, we have isolated two minor products, **6** and **7**, both colorless liquids. **7** was identical with the previously isolated epoxide.[2] The structure of **6** was deduced on the basis of NMR ($CDCl_3$) [δ ~0.4 (4 H, m), 1.70 (2 H, disappeared on addition of D_2O), 2.20 (1 H, m, $W_{h/2}$ = 10 Hz), 2.42 (1 H, m, $W_{h/2}$ = 10 Hz), 2.55 (2 H, br t, J = 7 Hz), 2.74 (1 H, m), 3.24 (1 H, t, J = 7 Hz), 3.26 (1 H, t, J = 7 Hz), 3.40 (1 H, m), 4.12 (1 H, br s, $W_{h/2}$ = 6 Hz), 5.38 (1 H, s), 5.93 (1 H, ddd, J = 6, 3,

Scheme I



Scheme II

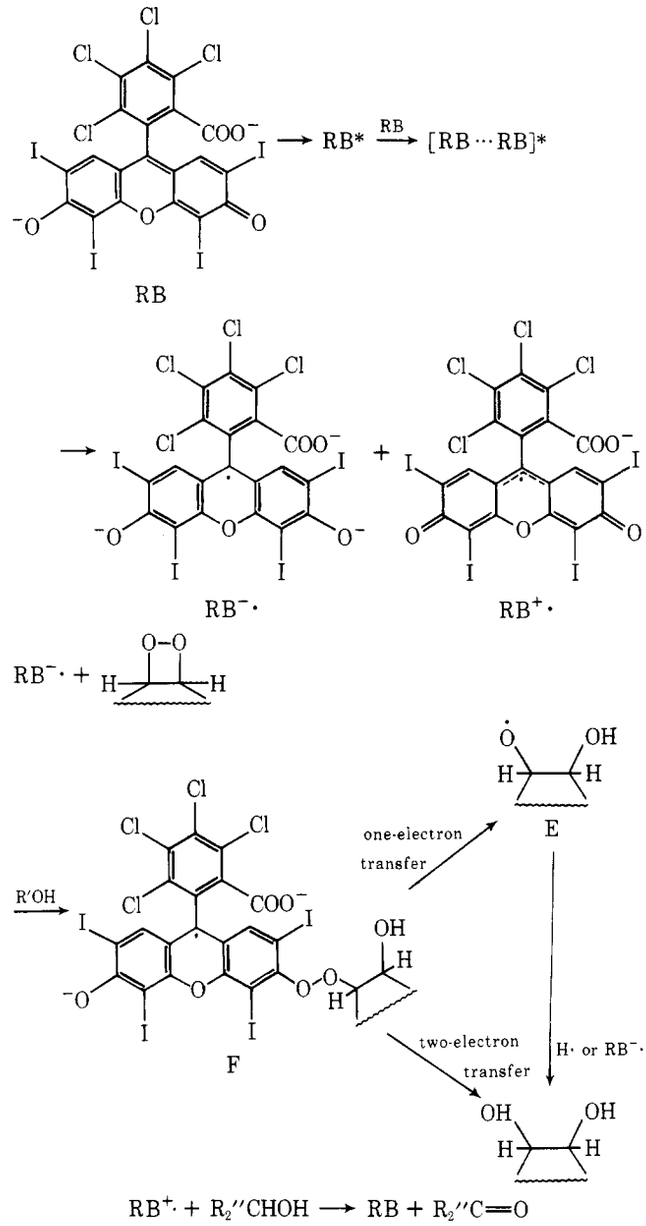


1 Hz), and 6.04 (1 H, ddd, J = 6, 3, 1 Hz)] and IR (ν_{OH} at 3460 cm^{-1}, but no ν_{CO}). The isolation of **6** would suggest the precursor of **2** to be a formal homo-Diels–Alder adduct, D, of **1** and molecular oxygen. Intermediacy of such a dioxacycloheptene with strained endo linkage or a dioxabicyclo[4.2.1]nonene would not be unreasonable in view of the anti-Bredt compounds.[7]

To know the generality of the reaction, we have extended the experiments to indene (**8**), whose reaction with singlet oxygen has been extensively studied.[8,9] When a mixed solution of methanol and pyridine (3:7) containing **8** and RB (90 mg in 25 mL) was irradiated by a tungsten lamp at room temperature under an oxygen atmosphere, formation of *cis*-1,2-dihydroxyindan [**9**: 21%; mp 102–103 °C (lit.[10] 107–110 °C); NMR ($CDCl_3$) δ 2.86 (1 H, dd, J = 16.5, 3.5 Hz), 3.00 (1 H, dd, J = 16.5, 6 Hz), 3.33 (2 H, disappeared on addition of D_2O), 4.32 (1 H, apparent q), 4.84 (1 H, d, J = 5 Hz), 7.20 (4 H, m);[10] IR ν_{OH} at 3530 cm^{-1}] occurred, together with <1% of homophthalic dialdehyde. In contrast, when the reaction was performed at −70 to −80 °C, the formation of **9** was suppressed to 9.4%, and *trans*-2-hydroperoxy-1-methoxyindan (**10**) and *cis*-2-hydroperoxy-1-methoxyindan (**11**), both colorless liquids with combined yields of 73%, were obtained. The structure of **10**, the major component (**10**/**11** = 4:1 according to the NMR determination), was established, after isolation by silica gel column chromatography, on the basis of the NMR ($CDCl_3$) [δ 2.88 (1 H, dd, J = 17, 4 Hz), 3.32 (1 H, dd, J = 17, 7 Hz), 3.51 (3 H, s), 4.80 (2 H, overlapped m with mutual J_{vic} = 3 Hz), 7.20 (4 H, m), and 8.88 (1 H, **OOH**)] spectrum along with chemical derivation into the methoxy alcohol **12**[9] and its acetate **13** [colorless liquid; NMR ($CDCl_3$) δ 2.06 (3 H, s), 2.81 (1 H, dd, J = 17, 4 Hz), 3.50 (1 H, dd, J = 17, 7 Hz), 3.52 (3 H, s), 4.77 (1 H, d, J = 3 Hz), 5.39 (1 H, ddd, J = 7, 4, 3 Hz), and 7.25 (4 H, m)]. Similarly, **11** was converted into the methoxy alcohol **14**, colorless oil,[11] and its acetate **15** [NMR ($CDCl_3$) δ 2.10 (3 H, s), 3.12 (2 H, d, J = 6 Hz), 3.44 (3 H, s), 4.72 (1 H, d, J = 5 Hz), 5.44 (1 H, td, J = 6, 5 Hz), and 7.24 (4 H, m)] (Scheme II).

In the reaction of **8**, especially at room temperature, substantial decomposition of RB occurred. This is probably due to the formation of the hydroperoxy derivatives.

Scheme III



In conclusion, *cis*-glycol formation during sensitized irradiations has provided a new experimental probe for dioxetane intermediates, and an apparent correlation of the yields of the glycol to concentrations of the sensitizer seems to make it plausible to consider the "D–D*" mechanism, intensively studied by Koizumi and co-workers,[12] as shown in Scheme III.[13]

For the latter step of the reduction, a two-electron transfer process seems to be favorable over a one-electron process, since we have failed to detect a keto alcohol, which should be formed from E, a radical, or a peroxy intermediate, F.

Recently, Frimer et al.[14] expressed doubt for the proposed involvement of dioxetanes during the reaction of singlet oxygen oxidation with vinylcyclopropanes.[15,16] Present results constitute a reconfirmation of such intermediates. The discrepancy can be explained by the difference in substrate structural types; Frimer et al. used acyclic olefins, while ours were cyclic olefins.

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(11) In ref 8 and 9, the formation of two methoxy alcohols have been described. These authors assigned them as **12** and *trans*-1-hydroxy-2-methoxyindan. Although we have detected a trace of a third hydroperoxy derivative, only **12** and **14** were characterized after the reduction.
(12) M. Koizumi and Y. Usui, *Mol. Photochem.*, **4**, 57 (1972).
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Rapid Elimination Reactions of Vinyl Ethers and Sulfides with Potassium 3-Aminopropylamide. Vinyl Sulfides as Acetylene Equivalents[1]

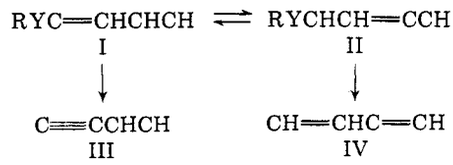
Summary: Potassium 3-aminopropylamide reacts rapidly with vinyl sulfides and vinyl ethers at room temperature to produce elimination products; vinyl sulfides yield alkynes with a high degree of selectivity, while vinyl ethers yield dienes or mixtures of dienes and alkynes. The reaction allows a mild, efficient transformation of vinyl sulfides into terminal acetylenes.

Sir: Potassium 3-aminopropylamide (KAPA) has been shown to be exceptionally active in base-catalyzed prototropic reactions[2] and in the elimination of vinyl and aryl halides.[3a] Reaction of vinyl compounds with hyperbases capable of catalyzing rapid prototropic isomerization raises the possibility of competing vinyl–alkyl interconversion, giving rise to dienes, rather than alkynes, from elimination (Scheme I);[3b] in general, simple alkynes and noncumulated dienes are not interconverted by hyperbases.

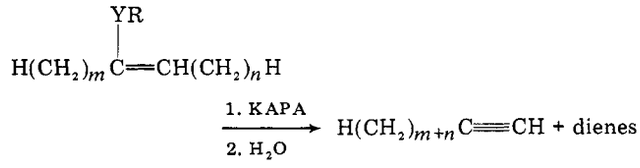
Base-catalyzed equilibrations of olefins, ethers, and sulfides containing a nonconjugated double bond have been studied;[4] examination of the data and conditions indicate the ease of I ⇌ II to be Y = CH_2 ≪ Y = O < Y = S. In general, elimination has not been reported to accompany these equilibrations; however, few cases have been examined in which eliminations to noncumulated dienes and to alkynes (or allenes) are simultaneously possible, reactions largely being limited to allylic or propenyl systems. In fact, O'Connor and Lyness[4a] have reported slow formation of conjugated dienes during equilibration of 1-alken-1-yl sulfides with KO-*t*-Bu/Me_2SO.[5] A priori, elimination (1,2 or 1,4) of allylic structures to the more stable[6] conjugated dienes should be more facile than elimination of vinyl structures to alkynes, if base and leaving group are the same.

We find that KAPA reacts readily with both vinyl ethers and vinyl sulfides at room temperature to produce elimination products in good yield. In contrast to results obtained with KO-*t*-Bu/Me_2SO,[4a,5] eliminations with KAPA produce considerable proportions of alkynes, with vinyl sulfides yielding alkynes with high selectivity. Under the conditions of elimination, allenes and internal acetylenes are isomerized by KAPA in seconds to the anions of 1-alkynes;[2a] thus only 1-alkynes and noncumulated dienes were found as products after hydrolysis. These results are summarized in Scheme II.

Scheme I



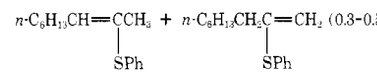
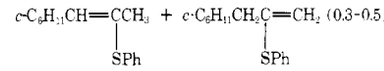
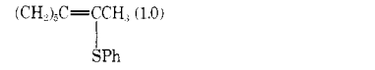
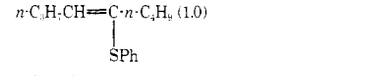
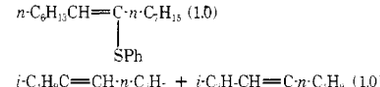
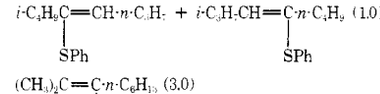
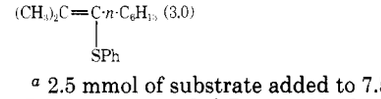
Scheme II



			1-alkyne/diene
$n \geq 1, m = 0$	Y = O	R = CH_3	1:50
$n \geq 1, m = 0$	Y = S	R = C_6H_5	100:1
$n = 0, m > 1$ $n \geq 1, m = 1$	Y = O	R = CH_3	3:2
$n = 0, m > 1$ $n \geq 1, m = 1$	Y = S	R = C_6H_5	50:1
$n, m > 1$	Y = O	R = CH_3	1:2
$n, m > 1$	Y = S	R = C_6H_5, CH_3	15:1

GLC analysis of samples withdrawn and quenched revealed a constant "pattern" of the diene product mixtures which was

Table I. Reaction of Phenyl Vinyl Sulfides with KAPA[a]

substrate (time, h)[b]	product[c]	yield,[d] %
	1-nonyne	86
	3-cyclohexyl-1-propyne	83
	cyclohexyl acetylene	59[e]
	1-nonyne	83[f]
	1-pentadecyne	82
	8-methyl-1-nonyne	80[f]
	8-methyl-1-nonyne	62

[a] 2.5 mmol of substrate added to 7.5 mL of ~1.3 M KAPA in APA solution, 25 °C. [b] Prepared by heating an equimolar mixture of ketone and thiophenol with a trace of sulfuric or toluenesulfonic acids in benzene with azeotropic removal of water to Linde 4A molecular sieves in a Soxhlet extractor. [c] Product identification by comparison with authentic samples. [d] Reaction mixtures were subjected to normal extractive workup with pentane as the organic phase, dried over $MgSO_4$, treated with nonane or decane as internal standard, and analyzed by GLC (Carbowax 20M or polymethylphenylsilicone). [e] Plus ~15% ethylbenzene. This aromatization is under further study. [f] Average of three runs. Variations were ~±5%.

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