1-Acetoxyspiro[cyclopentane-1,3'-indoline] (14). Two grams of the spiro indolenine compound 9 was treated with 2.0 g of $LiAlH_4$ in refluxing diethyl ether for 3 hr, then 0.5 ml of water, 0.5 ml of 15% NaOH, and 1.5 ml of water were added in succession. The ether phase was removed by filtration and to it 4.0 ml of pyridine and 2.0 ml of Ac_2O were added. After standing overnight at 10°, the solvent was evaporated to give 1.4 g (65%) of white crystals, which when recrystallized from hexane melted at 122-123.5: ir 1660, 1600, 1480, 1460, 1410, 755 cm^{-1}; nmr δ 6.92-7.32 (4 H, aromatic), 3.82 (singlet, 2 H, aliphatic), 2.22 (singlet 3 H, Ac), 1.83 (singlet, 8 H, aliphatic, spiro); mass spectrum *m/e* 215, 173, 130; uv 222 nm (ϵ 2000), 252 (8600), 280 (2300), 290 (1950). *Anal.* Calcd for $C_{14}H_{17}NO$: C, 78.14; H, 7.91; N, 6.51. Found: C, 78.85; H, 8.28; N, 6.22.

1-Methoxy-1,2,3,4-tetrahydrocarbazole (16). To 1,2,3,4-tetrahydrocarbazole (3.00 g) and pyridine (3.6 ml) in benzene (60 ml) was added at once *N*-bromosuccinimide (3.3 g) and dibenzoyl peroxide (1 mg), and the mixture was stirred overnight at room temperature. The clear benzene layer was decanted from the oily product which separated, and the oil was dissolved in methanol (20 ml) and run into excess sodium methoxide in methanol at room temperature. This mixture was stirred for 1 hr, then evaporated under vacuum, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ layer was washed with water twice, dried over Na_2SO_4 and evaporated to an oil which crystallized on standing (1.85 g, 52% yield). Recrystallization from hexane gave pale yellow rosettes melting at 74-76°: ir 3300, 1390, 1335, 1065, 910, 740; nmr[13] δ 8.13 (singlet, 1 H, NH), 6.92-7.50 (multiplet, 4 H, aromatic), 4.48 (1 H, α to OCH_3 at C-1), 3.38 (singlet, 3 H, OCH_3), 2.67 (multiplet, 2 H, aliphatic at C-4), 1.93 (multiplet, 4 H, aliphatic at C-2,3); mass spectrum *m/e* 201, 185, 170, 168; uv 230 nm (ϵ 17,800), 276 (7650), 283 (8150), 291 (6700). *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46; N, 6.97. Found: C, 77.73; H, 7.53; N, 6.89.

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Registry No. **8**, 942-01-8; **9**, 42540-51-2; **10**, 42540-52-3; **11**, 42540-53-4; **12**, 42540-54-5; **13**, 41058-67-7; **14**, 42540-56-7; **16**, 42540-57-8.

Supplementary Material Available. Full nmr data for compounds **10**, **12**, and **16** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-69.

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(12) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a CEC-110 spectrometer. Microanalyses were performed by Galbraith Laboratories. Ir spectra were run on a Perkin-Elmer 700 spectrometer. Uv spectra were obtained on a Beckman DB spectrometer.
(13) See paragraph at end of paper regarding supplementary material.

Condensations of Enol Ethers of β-Dicarbonyl Compounds with Dimethylsulfonium Methylide and Dimethyloxosulfonium Methylide

Constance M. Harris, Joseph J. Cleary, and Thomas M. Harris*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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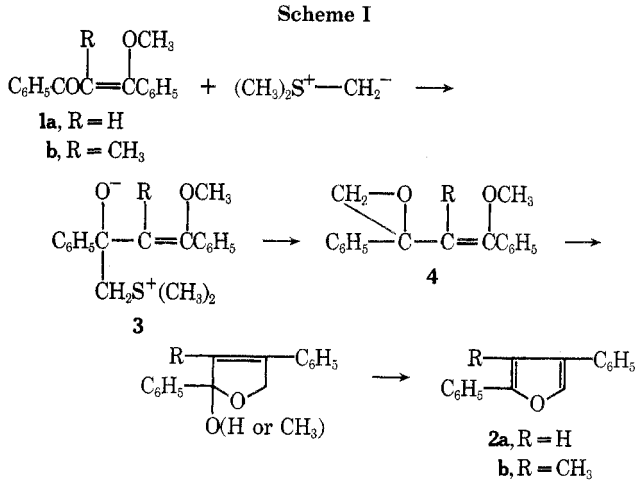
Condensations of dimethylsulfonium methylide with β-alkoxy-α,β-unsaturated ketones have been studied. The reactions of this ylide with the enol ethers of acyclic β diketones gave 2,4-disubstituted furans. Attack by the ylide occurred at the carbonyl carbon atoms. Easily rearranged epoxides are postulated as intermediates in furan formation. With the enol ether of a cyclic β diketone, 1,3-indandione, furanization of the epoxide intermediate was sterically prohibited and the condensation gave 3-(hydroxymethyl)indenone. The enol ethers of β-keto aldehydes reacted with dimethylsulfonium methylide to give two products. In addition to 3-substituted furans, the condensations gave 5-substituted 3,6-dihydro-(2*H*)-pyran-2-ols. Formation of the latter compounds has been rationalized to involve attack by one molecule of the ylide at the β positions of the unsaturated carbonyl compounds followed by a second molecule attacking the carbonyl groups. Rearrangement and hydrolysis of the resulting cyclopropyloxiranes would give the dihydropyran derivatives. β attack by dimethylsulfonium methylide on α,β-unsaturated ketones does not normally occur but is facilitated with the enol ethers of β-keto aldehydes by the reduced steric hindrance at the β positions. The condensations of dimethyloxosulfonium methylide with enol ethers of β diketones were also investigated. Twofold attacks occurred here, as well, but both attacks were by the same ylide molecule. Initial attack by the ylide at the β position, followed by formation of a new ylide by ionization of one of the remaining methyl groups, and finally intramolecular attack of the new ylides on the carbonyl groups, led to 3,5-disubstituted 1-methylthiabenzene 1-oxides.

The reactions of sulfonium ylides with α,β-unsaturated ketones have been employed widely subsequent to the observations by Corey and Chaykovsky that dimethylsulfonium methylide preferentially attacks the carbonyl group to give epoxides, whereas dimethyloxosulfonium methylide attacks the β position to give cyclopropyl ketones.[1,2] The corresponding reactions of β-alkoxy-α,β-unsaturated ketones were of interest to us because both the epoxide and cyclopropane products should be capable of rearrangement to furans or to the related 1,4-dicarbonyl compounds. The reactions of both of the ylides with these enol ethers have now been investigated.[3]

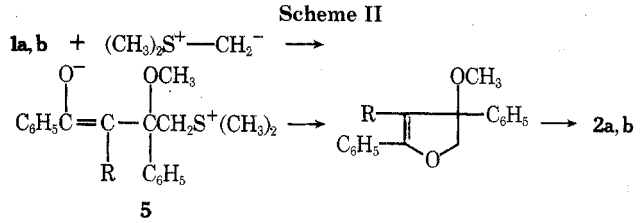
Dimethylsulfonium Methylide (DSM). The initial studies were undertaken with unsaturated methoxy ketone **1a**, which is readily available by methylation of dibenzoylmethane. Treatment of **1a** with 1 equiv of DSM gave 56% of a furanoid product, readily identified as the known[4] 2,4-diphenylfuran (**2a**, Scheme I). A similar condensation of DSM with ketone **1b** gave furan **2b** in 60% yield. No epoxide, cyclopropane, or 1,4 diketone was detected in either case; however, it is possible that small amounts of these were overlooked.

Scheme I

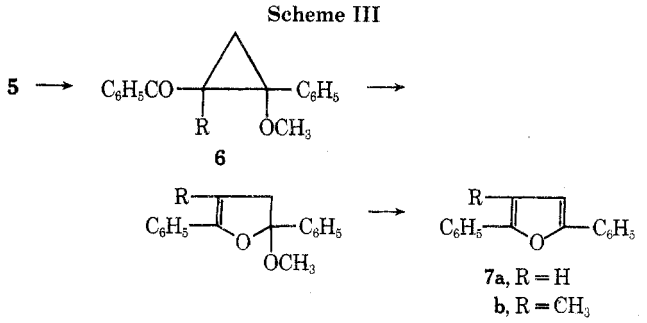


Several reaction pathways can be proposed to account for the formation of **2a** and **2b**. The products could have arisen by attack of the ylide at the carbonyl carbon atoms of **1a** and **1b** followed by cyclization of the resulting zwitterions **3** to epoxides **4**. Rearrangement and loss of methanol during work-up would yield **2a** and **2b** (Scheme I). An alternative is that the ylide attacked at the β positions of **1a** and **1b**; internal displacement of the resulting zwitterions **5** and loss of methanol would have led to **2a** and **2b** (Scheme II). It should be noted that zwitterions **5** might also have decomposed to give cyclopropyl ketones **6**, which could, in turn, rearrange to diphenylfurans **7a** and **7b** (Scheme III). These, however, are isomeric with the observed products.

Scheme II



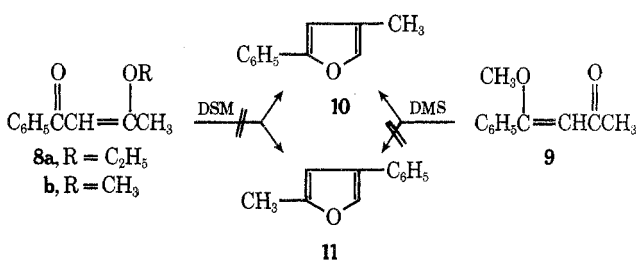
Scheme III



The pathway illustrated in Scheme I is supported by the precedent[2] of the reactions of simple α,β-unsaturated ketones with this ylide. However, it should be noted that starting with **1a** and **1b** Schemes I and II are indistinguishable because both give the same final products and none of the various intermediates have been detected. The two routes become distinguishable when enol ethers of *unsymmetrical* β diketones are employed, since the 1-phenyl groups of **1a** and **1b** become the β-phenyl substituents of **2a** and **2b** by Scheme I but the α substituents by Scheme II.

Appropriate unsymmetrical β-alkoxy-α,β-unsaturated ketones are of limited availability because the most common method for preparation of the enol ethers, O-alkylation of the corresponding β diketones, often gives mixtures with unsymmetrical diketones. One case in which a single enol ether of established structure has been obtained is the ethylation of 1-phenyl-1,3-butanedione with ethyl orthoformate to give enol ether **8a**.[5] Unfortunately, **8a** proved to be insufficiently reactive and was recovered unchanged after treatment with DSM. Treatment of 1-phenyl-1,3-butanedione with diazomethane gave a mixture of the isomeric enol ethers **8b** and **9**.[5b] These were not separable by chromatography but a portion of **8b** was isolated by crystallization, leaving a 1:3 mixture of **8b** and **9**. As with **8a**, **8b** failed to react with DSM. In contrast, the mixture of **8b** and **9** did react with the ylide to give furan **10**. The product can reasonably be assumed to have arisen entirely from **9** and, on this basis, the yield was 42% (Scheme IV). Formation of this product rather than furan **11** supports the exclusive operation of the pathway depicted in Scheme I in which initial attack by the ylide occurs at the carbonyl group.

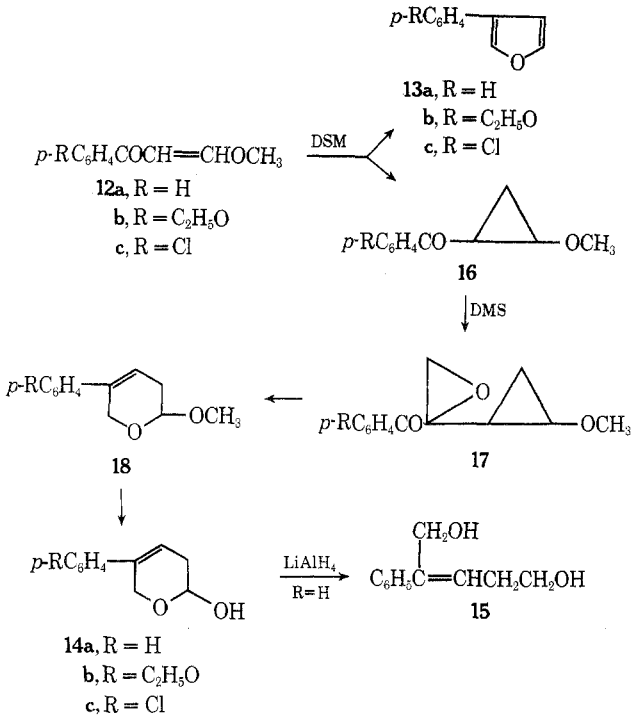
Scheme IV



β-Keto aldehydes invariably undergo enol alkylation at the aldehydic oxygen. The resulting enol ethers were employed as the next test of the reaction preference of DSM with β-alkoxy-α,β-unsaturated ketones. With β-methoxyacrylophenone (**12a**), the reaction of DSM gave 18% of furan **13a**, providing further confirmation of the first pathway. In addition, a second product, dihydropyran **14a**, was obtained in 39% yield. The structural assignment for **14a** was based on spectroscopic and chemical evidence. Elemental and mass spectral analyses established the empirical formula as $C_{11}H_{12}O_2$. The presence of the hemiacetal linkage was deduced from the fact that, although no carbonyl group was evident from the infrared spectrum, the compound readily yielded a semicarbazone. Reduction of **14a** to diol **15** confirmed this conclusion and indicated that the hemiacetal linkage was situated in a cyclic structure. The size of the heterocyclic ring and the location of the phenyl group and of the double bond were apparent from the spectra.

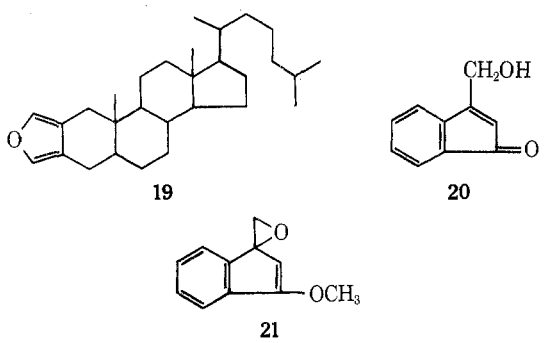
The formation of dihydropyran **14a** must involve a twofold attack on unsaturated ketone **12a** by DSM (Scheme V). Probably, initial attack by DSM is at the β position of **12a** leading to cyclopropyl ketone **16**, followed by a second attack at the carbonyl group giving cyclopropyl epoxide **17**. Rearrangement of **17** to acetal **18** and hydrolysis to hemiacetal **14a** can be expected to be extremely facile. The rearrangement process may be promoted by adventitious acidic catalysts or conceivably may involve an uncatalyzed isomerization.

Scheme V



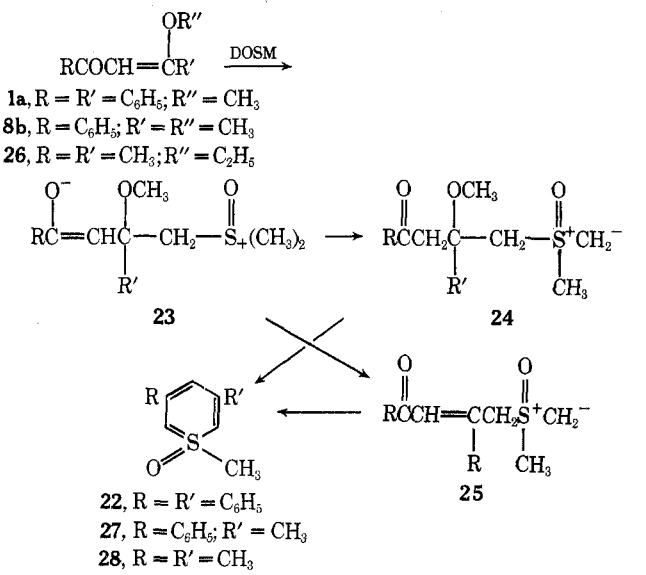
Similar results were obtained with two other β-methoxyacrylophenones. Ethoxy-substituted **12b** gave mainly (54%) dihydropyran **14b**, although a small amount of furan **13b** was isolated. Chloro-substituted **12c** gave low yields of both **13c** and **14c**.

Two other cases were investigated. 2-Methoxymethylenecholestan-3-one reacted with DSM to give 15% of furan **19**; the related dihydropyran was not observed. 3-Methoxyindenone, which cannot give either a furan or a dihydropyran, yielded 14% of keto alcohol **20**. Spiro epoxide **21** is probably an intermediate in its formation; furanization of **21** is sterically prohibited.



Dimethyloxosulfonium Methylide (DOSM).—This ylide reacted with enol ether **1a** but failed to give any of the expected products. A sulfur-containing crystalline solid was obtained in 68% yield and was identified as thiabenzene oxide **22**.[6] Attack by DOSM occurs at the β position of **1a**. The resulting enolate anion (**23**) might have expelled dimethyl sulfoxide *via* internal displacement by the nucleophilic oxygen to give furan **2a** or by the carbanion to give cyclopropyl ketone **6**. Surprisingly, neither of these was a major course of reaction. Instead, either a direct proton transfer to give new ylide **24** or methoxide loss followed by reionization occurred to give ylide **25**. Both of these ylides are well structured for intramolecular attack on the carbonyl group to give, after elimination, the observed thiabenzene oxide (**22**) (Scheme VI). Similar reactions of **8b** and of enol ether **26** of acetylacetone with

Scheme VI



DOSM gave thiabenzene oxides **27** and **28** in yields of 46 and 29%, respectively.

Discussion

Although the epoxides (*e.g.*, **4**) that have been postulated as intermediates in the formation of furans by the condensation of DSM with enol ethers of β-dicarbonyl compounds were not isolated or detected, adequate precedents are available to support the contention that such intermediates would rearrange readily to furans. Burness observed that 3,4-epoxy acetals undergo facile rearrangements to 3-substituted furans.[7] Cornforth has also observed this reaction.[8] Equivalent transformations of epoxy ketones[9] and of acetylenic epoxides[10] have been reported. Cyclizations of *o*-hydroxystyrene oxides to benzofurans also appear to be facile processes.[11]

The introduction of substituents at the β position of furan is generally difficult, the α position being the preferred site of attack by most reagents.[12] The reaction of enol ethers of β diketones with DSM appears to have merit for the synthesis of 2,4-di- and 2,3,4-trisubstituted furans, particularly when the 2 and 4 substituents are identical. However, the usefulness of enol ethers for the synthesis of 3-monosubstituted, and probably 3,4-disubstituted, furans is doubtful on account of the competitive formation of dihydropyran derivatives. Fortunately, Garst and Spencer have recently described a related method which works well for both of the latter classes of furans.[13] Their procedure involves the condensation of DSM with *n*-butylthio ethers of β-keto aldehydes. With the thio ethers β attack is repressed and pyran derivatives are not observed.[14] It is noteworthy that these workers obtained spectral evidence of thio analogs of the intermediates proposed in Scheme I.

Twofold reactions of DSM with unsaturated carbonyl compounds are novel. Normally, initial attack at the carbonyl group blocks further attack at the double bond. With the β-methoxyacrylophenones, steric hindrance at the β position has been minimized, while the susceptibility of the carbonyl group to nucleophilic attack is simultaneously attenuated by electron donation by the β-methoxyl group. It is also likely that the aryl group plays an important part in directing the initial attack of DSM at the β position. Twofold condensations have occasionally been observed with DOSM where the order of reactivity with unsaturated ketones is normally C=C > C=O.[15]

The formation of thiabenzene oxides by the condensation of enol ethers of diketones with DOSM provides an attractive new approach to this interesting class of heterocyclics. The first example of the ring system (**22**) was prepared by Hortmann by the condensation of DOSM with 1,3-diphenylpropynone.[6] Hortmann and Harris have since demonstrated the generality of the reaction.[16] It is noteworthy that they have isolated allylide intermediates, the cyclizations of which probably involve isomerization to methylides **25**. Holt, *et al.*, have obtained thiabenzene oxides by the reaction of DOSM with certain β diketones.[17] 2-Acylcyclohexanones reacted satisfactorily, but the simple diketones, acetylacetone, benzoylacetone, and dibenzoylmethane (the enol ethers of which were used in the present study), gave only C-methylation products. Kishida, *et al.*, have prepared examples having functional substituents on the heterocyclic ring.[18]

Experimental Section

General Procedures. Dimethylsulfonium methylide (DSM) was prepared from trimethylsulfonium iodide and the anion of dimethyl sulfoxide (DMSO) at an approximate concentration of 0.25 *M* in a mixture of DMSO and tetrahydrofuran (THF) following the method of Corey and Chaykovsky.[2] Dimethyloxosulfonium methylide (DOSM) was prepared in DMSO at the same concentration by the reaction of trimethylsulfonium iodide and sodium hydride as described by the same workers.[2] Normal work-up of reaction mixtures involved addition of water and extraction into ether. The ethereal solutions were dried with $MgSO_4$ and concentrated *in vacuo*. Crude products were usually purified by chromatography on silicic acid. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Ultraviolet spectra were determined in 95% ethanol solution and nmr spectra in $CDCl_3$ [60 MHz referenced to internal $(CH_3)_4Si$]. Mass spectra were recorded at 70 eV; sample introduction was by means of the direct inlet.

Enol Ethers of β-Dicarbonyl Compounds. 1,3-Diphenyl-3-methoxy-2-propen-1-one (1a) was prepared by treatment of dibenzoylmethane with diazomethane.[19]

1,3-Diphenyl-2-methyl-3-methoxy-2-propen-1-one (1b). The enol form of 1,1-dibenzoylethane[20,21] was treated with excess ethereal diazomethane to give enol ether **1b** mixed with enol and keto tautomers of the diketone. Chromatography on alumina gave 25% of a mixture of *cis*- and *trans*-**1b** as a pale yellow oil: ν (neat) 2950, 1670, 1650, 1605, 1450, 1325, and 1125 cm^{-1}; nmr (stereoisomer A) δ 1.89 (s, CCH_3), 3.03 (s, OCH_3), 7.1–8.0 (m, C_6H_5), (stereoisomer B) 2.14 (s, CCH_3), 3.45 (s, OCH_3), 7.1–8.0 (m, C_6H_5); mass spectrum *m/e* (rel intensity) 252 (parent, 78), 251 (61), 105 (100), 77 (83).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.12; H, 6.33.

3-Ethoxy-1-phenyl-2-buten-1-one (8a) was prepared by treatment of benzoylacetone with ethyl orthoformate.[5] Treatment of benzoylacetone with excess ethereal diazomethane gave a mixture of **3-methoxy-1-phenyl-2-buten-1-one (8b)** and **4-methoxy-4-phenyl-3-buten-2-one (9)**,[5] from which a portion of the cis and trans isomers of **8b** crystallized.[5] The liquid fraction was distilled (88°, 0.25 mm) to give an oil which consisted (nmr) of 25% of **8b** and 75% of **9**. An authentic sample of **9**, needed for the analysis of the mixture of isomers, was prepared by treatment of 4-phenyl-3,4-dibromo-2-butanone with sodium methoxide;[5] the yield was not sufficiently high for the reaction to have preparative value.

3-Methoxy-1-phenyl-2-propen-1-one (β-methoxyacrylophenone, 12a) was prepared by acylation of acetophenone with methyl formate followed by methylation with methanolic HCl.[22]

3-Methoxy-1-(4-ethoxyphenyl)-2-propen-1-one (12b) was prepared by the same general procedure from *p*-ethoxyacetophenone. Distillation (145°, 0.25 mm) of the crude product gave 45% of the enol ether as an oil which solidified: mp 55.5–57.5° after recrystallization from CCl_4–hexane; ν (KBr) 2940, 1650, 1610 (sh), 1570, 1510, 1440, 1398, 1350, 1260, 1200, and 630 cm^{-1}; nmr δ 3.7 (3 H, s, OCH_3), 6.31 (1 H, d, J = 12 Hz, 2-CH), 6.85 (2 H, d, J = 9 Hz, aryl), 7.71 (1 H, d, J = 12 Hz, 3-CH), 7.83 (2 H, d, J = 9 Hz, aryl).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 70.00; H, 6.92.

3-Methoxy-1-(4-chlorophenyl)-2-propen-1-one (12c) was prepared similarly from *p*-chloroacetophenone.[22] Distillation (122–128°, 0.4 mm) gave 48% of **12c** as an oil which solidified: mp 64–65° after recrystallization from hexane; ν (KBr) 1655, 1580, 1265, 1200 cm^{-1}; nmr δ 3.73 (3 H, s, OCH_3), 6.24 (1 H, d, J = 12 Hz, 2-CH), 7.55 (4 H, A_2B_2, aryl), 7.71 (1 H, d, J = 12 Hz, 3-CH).

Anal. Calcd for $C_{10}H_9O_2Cl$: C, 61.07; H, 4.61; Cl, 18.03. Found: C, 61.33; H, 4.59; Cl, 17.77.

2-Methoxymethylenecholestan-3-one was prepared from cholestan-3-one as described by Storm and Spencer.[23]

3-Methoxy-2-inden-1-one. 1,3-Indandione was treated for 12 hr with excess ethereal diazomethane. The solution was washed with aqueous sodium hydroxide and with water, dried, and evaporated to leave 50% of the enol ether as a yellow solid. Recrystallization from hexane gave yellow needles: mp 65.5–67°; ν (KBr) 1710, 1620, 1565, 1430, 1385 cm^{-1}; nmr δ 3.95 (3 H, s, OCH_3), 5.04 (1 H, s, 2-CH), 7.2 (4 H, m, aryl).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.81; H, 5.12.

4-Ethoxy-3-penten-2-one (26) was prepared by treatment of acetylacetone with ethyl orthoformate.[24]

Reactions of DSM. Preparation of 2,4-Diphenylfuran (2a). Enol ether **1a** (1.19 g, 0.005 mol) in 10 ml of THF was added to a suspension of DSM [prepared from 2.04 g (0.01 mol) of trimethylsulfonium iodide] at −5°. The mixture was warmed to ambient temperature over a 90-min period and poured into water. The THF was partially evaporated under reduced pressure; ether extraction gave 0.946 g of crude product. Chromatography on silica gel (hexane elution) gave 0.622 g (56%) of furan **2a**, mp 107–108.5° and, after recrystallization from ethanol, 109.5–110.5° (lit.[4] mp 109°).

Preparation of 2,4-Diphenyl-3-methylfuran (2b). Enol ether **1b** (1.07 g, 0.0042 mol) in THF (10 ml) was added to DSM [prepared from 2.04 g (0.01 mol) of trimethylsulfonium iodide] at −5°. The mixture was allowed to warm to ambient temperature and, after a 3-hr reaction period, the usual work-up by extraction and chromatography (hexane elution) gave 0.594 g (60%) of **2b**: mp 125–130° and, after sublimation (80°, 0.025 mm), 128–130°;[25] ν (KBr) 1615, 1495, 1440, 1060, 890, 760, 750, 690 cm^{-1}; nmr δ 2.3 (3 H, s, CH_3), 7.13–7.83 (11 H, m, aryl + 5-CH); mass spectrum *m/e* (rel intensity) 234 (parent, 100), 205 (44), 191 (28), 77 (35).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found, 87.26; H, 6.13.

Preparation of 4-Methyl-2-phenylfuran (10). Treatment of enol ethers **8a** and **8b** with DSM failed to give furan **10** or **11**. In both cases the enol ethers were recovered from the reaction mixtures unaltered. Addition of 3.25 g (0.018 mol) of a 3:1 mixture of enol ethers **8b** and **9** to DSM [prepared from 4.08 g (0.02 mol) of trimethylsulfonium iodide] at −5° gave, after 3 hr at room temperature, 2.9 g of crude product, the nmr spectrum of which indicated that it consisted of mainly furan **10** and unaltered enol ether **8b**. Chromatography (elution with hexane–ether 90:10) gave 0.41 g (42%) of furan **10**, mp 38–40° (lit.[26] mp 40°). The chloromercuri derivative melted at 169.5–170.5° (lit.[26] mp 170.5–171°). The yield of furan **10** is calculated with the assumption that the compound had been formed exclusively from enol ether **9**.

Preparation of 3-Phenylfuran (13a) and 3,6-Dihydro-5-phenyl-(2*H*)-pyran-2-ol (14a). Enol ether **12a** (1.62 g, 0.01 mol) was added to DSM [prepared from 4.08 g (0.02 mol) of trimethylsulfonium iodide] at −5°. After 1 hr at ambient temperature, the usual work-up by extraction gave an oily, yellow solid, which was suspended in a small volume of CCl_4 and filtered to give 0.644 g of dihydropyran **14a**: mp 103–103.5° which was not increased by recrystallization from CCl_4 and sublimation (70°, 0.05 mm); ν ($CHCl_3$) 3580, 3400, 2930, 1495, 1450, 1110, 1065, 895 cm^{-1}; ν (KBr) 3360, 3260, 1460, 1140 cm^{-1}; λ_{max} 243 nm (ϵ 12,100); nmr δ 2.30 (2 H, m, 3-CH_2), 3.84 (1 H, d, J = 4.5 Hz, OH), 4.64 (2 H, m, 6-CH_2), 5.25 (1 H, m, 2-H), 6.05 (1 H, m, 4-CH), 7.30 (5 H, m, aryl); mass spectrum *m/e* (rel intensity) 176 (parent, 11), 131 (17), 130 (100), 129 (79), 128 (26), 115 (50), 91 (20).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.91; H, 6.90.

The semicarbazone of **14a** formed readily and quantitatively, mp 179–179.5° after recrystallization from ethanol.

Anal. Calcd for $C_{12}H_{15}N_2O_3$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.86; H, 6.45; N, 18.13.

The filtrate from above was chromatographed on silicic acid. Elution with hexane gave 0.262 g (18%) of furan **13a**: mp 53.5–55° and, after sublimation (30°, 0.05 mm), mp 58.5–59.5° (lit.[27] mp 58.5–59°); ν (KBr) 1570, 1170, 1050, 870, 750, 690 cm^{-1}; nmr δ 6.68 (1 H, m, 4-CH), 7.20–7.60 (6 H, m, aryl + 5-CH), 7.72 (1 H, m, 2-CH). Further elution with ether gave an additional 0.036 g of dihydropyran **14a** (total yield 39%).

Reduction of 14a. Dihydropyran **14a** (0.352 g, 0.002 mol) was treated for 3 hr with 0.200 g (0.0052 mol) of $LiAlH_4$ in 50 ml of anhydrous ether. Water was added and inorganic salts were removed by filtration. The ether layer was separated, dried, and evaporated. The residue was chromatographed on silicic acid (hexane elution followed by ether) to give 0.236 g (66%) of 2-phenyl-2-pentene-1,5-diol (**15**): mp 51–51.5° and, after recrystallization from CCl_4–hexane, 51–52°; ν ($CHCl_3$) 3250 (br), 2880, 1601, 990, 900 cm^{-1}; nmr δ 2.4 (2 H, dt, J_d = 2, J_t = 6 Hz, 4-CH_2), 3.6 (2 H, t, J = 6 Hz, 5-CH_2), 3.9 (2 H, broad, exchangeable with D_2O, 1- and 5-OH), 4.38 (2 H, s, 1-CH_2), 5.82 (1 H, t, J = 2 Hz, 3-CH), 7.24 (5 H, m, aryl).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.88; H, 7.89.

Preparation of 3-(4-Ethoxyphenyl)furan (13b) and 3,6-Dihydro-5-(4-ethoxyphenyl)-(2*H*)-pyran-2-ol (14b). Enol ether **12b** (2.06 g, 0.01 mol) was added to DSM [prepared from 4.08 g (0.02 mol) of trimethylsulfonium iodide] at −5°. After 2 hr at ambient temperature, work-up by extraction gave an ethereal solution, which when concentrated precipitated 1.20 g (54%) of dihydropyran **14b**: mp 115–116.5° and, after recrystallization from CCl_4, 120.5–121°; ν ($CHCl_3$) 3580, 3400, 2980, 2930, 1610, 1510, 1480, 1395, 1280, 1250, 1110, 1045, 900 cm^{-1}; ν (KBr) 3360, 1600, 1510, 1280, 1230, 1040, 900, 790 cm^{-1}; nmr δ 1.38 (3 H, t, J = 7 Hz, CH_2CH_3), 2.42 (2 H, m, 3-CH_2), 3.63 (1 H, d, J = 6 Hz, OH), 4.02 (2 H, q, J = 7 Hz, CH_2CH_3), 4.57 (2 H, m, 6-CH_2), 5.22 (1 H, m, 2-CH), 5.95 (1 H, m, 4-CH), 6.8 (2 H, d, J = 8 Hz, aryl), 7.23 (2 H, d, J = 8 Hz, aryl).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.88; H, 7.21.

The supernatant from above gave on chromatography (hexane elution) 0.155 g (8%) of furan **13b**: mp 80–82° and, after sublimation (50°, 0.05 mm), 81–83°; ν (KBr) 2960, 2910, 1580, 1510, 1490, 1460, 1390, 1230, 1030, 770 cm^{-1}; nmr δ 1.38 (3 H, t, J = 7 Hz, CH_2CH_3), 3.98 (2 H, q, J = 7 Hz, CH_2CH_3), 6.63 (1 H, m, 3-CH), 6.84 (2 H, d, J = 9 Hz, aryl), 7.35 (2 H, d, J = 9 Hz, aryl), 7.44 (1 H, m, 5-CH), 7.63 (1 H, m, 2-CH).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.97; H, 6.56.

Preparation of 3-(4-Chlorophenyl)furan (13c) and 3,6-Dihydro-5-(4-chlorophenyl)-(2*H*)-pyran-2-ol (14c). Enol ether **12c** (1.96 g, 0.01 mol) was added to DSM [prepared from 4.08 g (0.02 mol) of trimethylsulfonium iodide] at −5°. After 90 min at ambient temperature, work-up by extraction and chromatography gave (hexane elution) 0.353 g (20%) of furan **13c**: mp 49–50° and, after sublimation (25°, 0.05 mm), 50–51° (lit.[28] mp 50–51°); ν (Nujol) 2930, 2860, 1515, 1460, 1380, 1170, 1090, 1060, 1020, 870, 830, 780, 720 cm^{-1}; λ_{max} 260 nm (ϵ 12,055) [lit.[28] λ_{max} 262 nm (ϵ 13,200)]; nmr δ 6.6 (1 H, m, 4-CH), 7.30 (4 H, m, aryl), 7.43 (1 H, m, 5-CH), 7.66 (1 H, m, 2-CH). Further elution with ether gave 0.174 g (8%) of dihydropyran **14c**: mp 65–77° and, after sublimation (65°, 0.075 mm), 80.5–82.5°; ν ($CHCl_3$) 3590, 3400, 2940, 1600, 1495, 1405, 1120, 1065, 1010, 900, 820 cm^{-1}; nmr δ 2.57–2.30 (2 H, m, 3-CH_2), 3.58 (1 H, m, OH), 4.57 (2 H, m, 6-CH_2), 5.25 (1 H, m, 2-CH), 6.03 (1 H, m, 4-CH), 7.25 (4 H, m, aryl).

Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26. Found: C, 63.02; H, 5.43.

Preparation of Cholestano[2,3-c]furan (19). 2-Methoxymethylene-3-cholestanone (0.80 g, 0.00182 mol) was added to DSM [prepared from 0.816 g (0.004 mol) of trimethylsulfonium iodide] at −5°. After 90 min at ambient temperature, the usual work-up, except that $CHCl_3$ was used for extraction, gave 0.855 g of a yellow gum, chromatography of which (hexane elution) gave 0.110 g (15%) of furan **19**: mp 99.5–102.5° and, after recrystallization from $CHCl_3$–CH_3OH, 105–105.5°; ν (KBr) 2910, 2840, 1455, 1440, 1370, 1030, 885, 765 cm^{-1}; nmr δ 0.7–2.8 (*ca.* 44 H, m, methyl, methylene, and methinyl), 7.0 (2, broad s, vinyls), mass spectrum *m/e* (rel intensity) 410 (parent, 100).

Anal. Calcd for $C_{29}H_{46}O$: C, 84.81; H, 11.29. Found: C, 85.16; H, 11.03.

Preparation of 3-(Hydroxymethyl)-2-inden-1-one (20). 3-Methoxy-2-inden-1-one (1.04 g, 0.0065 mol) was added to DSM [prepared from 1.42 g (0.007 mol) of trimethylsulfonium iodide] at −5°. After 1 hr at ambient temperature, the usual work-up by extraction and chromatography (ether–hexane elution) gave 0.146 g (14%) of indenone **20**: mp 111–113° and, after recrystallization from benzene and sublimation (87°, 0.05 mm), 114.5–115° (yellow needles); ν (KBr) 3300, 1705, 1610, 1580, 1455, 1430, 1260, 1050, 770 cm^{-1}; nmr (CD_3COCD_3) δ 2.78 (1 H, broad s, OH), 4.57 (2 H, d, J = 2 Hz, CH_2OH), 5.66 (1 H, t, J = 2 Hz, 2-CH), 7.09 (4 H, m, aryl); mass spectrum *m/e* (rel intensity) 160 (parent, 50), 132 (40), 131 (100), 103 (45), 77 (26).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.19; H, 5.10.

Reactions of DOSM. Preparation of 1-Methyl-3,5-diphenylthiabenzene 1-Oxide (22). Enol ether **1a** (2.0 g, 0.0084 mol) was added to 0.01 mol of DOSM (prepared from 2.2 g of trimethyloxosulfonium iodide). After 2 hr at ambient temperature and 1.5 hr at 50°, work-up by addition to water and extraction into ether gave 1.6 g (68%) of thiabenzene oxide **22**, mp 135–145° and, after recrystallization from methanol, 147.5–149° (lit.[6] mp 148–148.8°).

Preparation of 1,3-Dimethyl-5-phenylthiabenzene 1-Oxide (27). Enol ether **8b** (2.68 g, 0.0152 mol) was added to 0.02 mol of DOSM (prepared from 4.4 g of trimethyloxosulfonium iodide). After 2 hr at ambient temperature and 1 hr at 50°, work-up as with **22** gave 2.64 g of a red oil, which nmr indicated was mainly thiabenzene oxide **27**. Chromatography (ether–hexane elution) of 1.0 g of the oil gave 0.584 g (46%) of **27** as a yellow liquid, which was further purified by molecular distillation (110°, 0.07 mm).[16]

Anal. Calcd for $C_{13}H_{14}SO$: C, 71.52; H, 6.46; S, 14.68. Found: C, 71.38; H, 6.60; S, 14.74.

Preparation of 1,3,5-Trimethylthiabenzene 1-Oxide (28). Enol ether **26** (1.85 g, 0.00144 mol) was added to 0.00145 mol of DOSM (prepared from 3.18 g of trimethyloxosulfonium iodide). After 1 hr at ambient temperature and 2 hr at 50°, work-up by extraction and chromatography (ether elution) gave 0.656 g (29%) of thiabenzene oxide **28**, mp 66.5–68.5° and, after sublimation (60°, 0.03 mm), 69–70° (lit.[16] mp 70.4–71°).

Anal. Calcd for $C_8H_{12}SO$: C, 61.50; H, 7.73; S, 20.52. Found: C, 61.52; H, 7.56; S, 20.27.

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Registry No. *cis*-**1b**, 42392-85-8; *trans*-**1b**, 42392-86-9; **2b**, 42392-87-0; **8b**, 42392-88-1; **12a**, 3617-15-0; **12b**, 42392-90-5; **12c**, 41850-77-5; **13b**, 42392-92-7; **13c**, 20842-12-0; **14a**, 42392-94-9; **14a** semicarbazone, 42392-95-0; **14b**, 42392-96-1; **14c**, 42392-97-2; **15**, 42392-98-3; **19**, 34984-39-9; **20**, 42393-00-0; **26**, 1540-24-5; **27**, 42393-02-2; **28**, 32398-62-2; *p*-ethoxyacetophenone, 1676-63-7; *p*-chloroacetophenone, 99-91-2; 3-methoxy-2-inden-1-one, 42393-04-4; 1,3-indandione, 606-23-5; 2-methoxymethylene-3-cholestanone, 42393-05-5.

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Baeyer–Villiger Oxidation of $\Delta^{1(9)}$-Octalone-2 and $\Delta^{1(8)}$-Indanone-2[1]

Andrew DeBoer* and Richard E. Ellwanger

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82070

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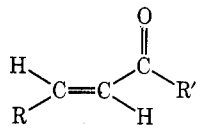
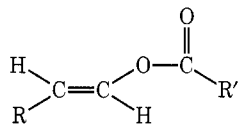
The reactions of $\Delta^{1(9)}$-octalone-2 and $\Delta^{1(8)}$-indanone-2 with trifluoroperacetic acid and *m*-chloroperbenzoic acid have been investigated under a variety of reaction conditions. The reaction conditions which were varied included temperature, reaction time, acidity, and equivalents of oxidizing agent used. Product distributions are reported. Oxidations using trifluoroperacetic acid gave complex product mixtures which resulted from reactions of the initially formed products with more trifluoroperacetic acid or with the trifluoroacetic acid which was produced during the reaction. Varying the above-mentioned variables did not greatly simplify the problem. Oxidation reactions using *m*-chloroperbenzoic acid gave the simplest product mixtures; *e.g.*, $\Delta^{1(9)}$-octalone-2 gave exclusively an epimeric mixture of epoxy lactones when 2 equiv of the peracid was used.

The outcome of the Baeyer–Villiger oxidation of α,β-unsaturated ketones, given by the general formula **1**, seems to be highly dependent upon the nature of the ketone and the reaction conditions used.[2] The primary oxidation products, enol esters (**2**) and epoxy ketones (**4**), are rarely isolated. In general the major product is the epoxy ester (**3**), which is no doubt derived from the enol ester (**2**).[3]



1



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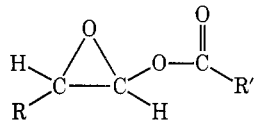

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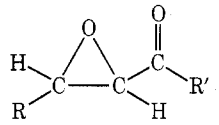
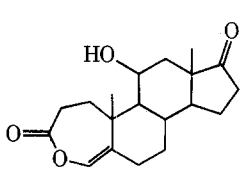


4

Several Δ^4-3-keto steroids have been subjected to Baeyer–Villiger oxidation reactions. The reaction of perbenzoic acid with 11β-hydroxyandrost-4-ene-3,17-dione in the presence of anhydrous perchloric acid in chloroform gave a 60% yield of the enol lactone **5**.[4] In contrast to this, oxidation of cholest-4-en-3-one with trifluoroperacetic acid (TFPAA) gave what was reported as a good yield of **6**.[5] It has been shown that the aldehyde lactone **6** resulted from the acid-catalyzed rearrangement of an intermediate epoxy lactone.[6] This has been confirmed by the oxidation of testosterone acetate with perbenzoic acid, in which all of the intermediates were isolated and characterized.[7]



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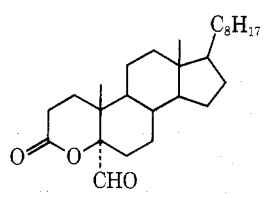
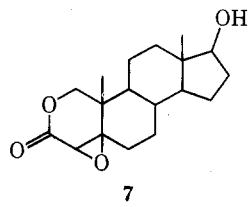


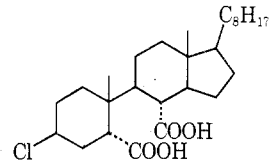
6



7

Although hydrogen peroxide oxidation of α,β-unsaturated ketones usually leads to the formation of epoxy ketones, it has been found that in the presence of a catalytic amount of selenium dioxide Δ^4-3-keto steroids are converted into enol lactones.[8]

The alkaline hydrogen peroxide oxidation of *A*-nortestosterone leads to the formation of **7**, presumably *via* the epoxy ketone which is subsequently converted to **7**.[9] The oxidation of 3β-chlorocholest-5-en-7-one with TFPAA gave **8**.[10]



8

In contrast to the data available concerning the above, very few data are available which deal with the Baeyer–Villiger oxidation of simple α,β-unsaturated ketones. Oxidation of 2-cyclohexenone with TFPAA yielded a small amount of 2-hydroxyadipic acid.[11] Reaction of 3-phenyl-2-cyclopentenone with perbenzoic acid gave 4-oxo-4-phenylbutanoic acid.[12]

In view of the lack of information available on the Baeyer–Villiger oxidation of simple α,β-unsaturated cyclic ketones, and, in view of the fact that in most instances a rather complex mixture of products was obtained, this work was carried out to develop processes which would give good yields of intermediates such as **13**, **20**, **21**, and **24** (see Scheme I). In our case these intermediates were always isolated as stereoisomeric pairs. An attempt was made to correlate product distributions with the reaction conditions employed. Also, the use of "buffered" oxidation reaction conditions (TFPAA and disodium hydrogen phosphate) in the oxidation of α,β-unsaturated ketones seems not to have been thoroughly studied. Since it appears that