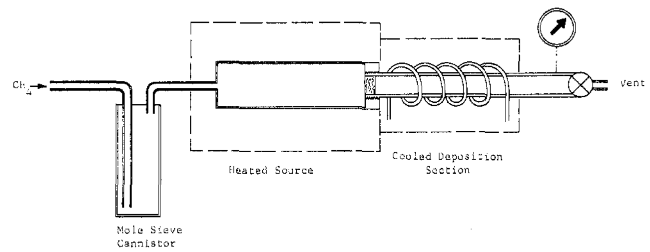

Figure 1. Schematic of clathrate formation apparatus.

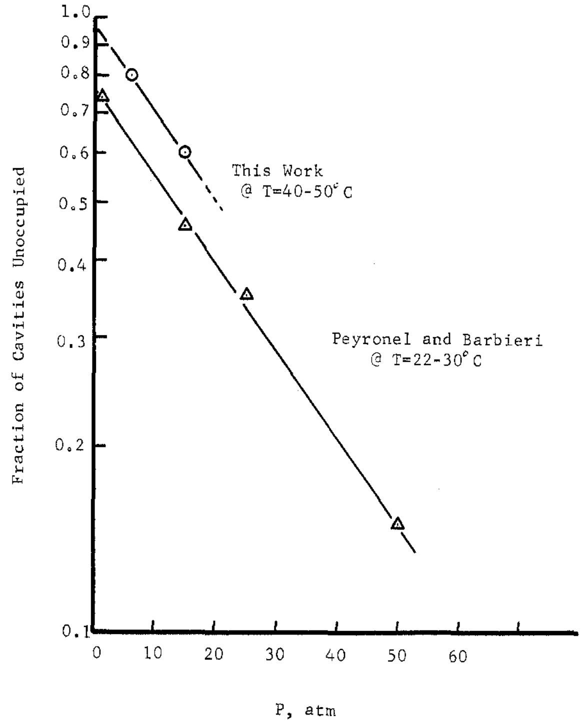

Figure 2. Pressure dependence of methane hydroquinone clathrate composition.

Hydroquinone sublimes readily at temperatures below its melting point, 170°, and the vapor pressure is adequate for transport and crystal growth at temperatures as low as 115–120°. The rate of crystal growth can be conveniently controlled by control of the sublimation or source temperature and control of the deposition temperature. We have found that, when a suitable gas such as methane is used as a carrier, enclathration of the gas tends to occur upon growth of the new hydroquinone crystals. Using this method, we have been able to produce gram quantities of the clathrate in a matter of a few hours in small-scale laboratory equipment, as opposed to the days to weeks required for the solution growth method. Inasmuch as water vapor tends to interfere with the formation of the clathrate structure, both the hydroquinone and the methane must be dried prior to use. This can be accomplished conveniently by passing both materials through a freshly outgassed mole sieve column.

A schematic of the apparatus used in this exploratory study is shown in Figure 1. Briefly, this apparatus consisted of three stainless steel chambers connected in series. The first of these was packed with mole sieve for drying the methane, and could be removed for regeneration of the sieve. The second chamber contained the source of predried hydroquinone, and was mounted in a furnace for control of the source temperature. The third chamber was water cooled for control of the deposition temperature. In operation, the system was flushed thoroughly with dry methane and then the vent valve was adjusted to discharge 10–20 cc/min at pressure. A glass wool plug between the source and deposition sections inhibited carryover of homogeneously nucleated hydroquinone crystals from the source section.

Several methane clathrate samples prepared at each of two pressures by this method were analyzed by flash injection of submilligram quantities (usually single crystals) of the clathrate into a gas chromatograph. Because of slight variations in composition, at least five analyses were made for each sample. For samples prepared at source temperatures of 120–130°, deposition temperatures of 40–50°, and a methane partial pressure of 6 atm, 20% of the cavities of the hydroquinone structure are filled with methane. At the same temperatures and a methane pressure of 15 atm, 40% cent of the cavities are occupied by methane. These data are compared with those of Peyronel and Barbieri in Figure 2. It can be seen that the pressure dependence is approximately the same as that shown by Peyronel and Barbieri, but the composition line is shifted to lower methane contents because of the higher formation temperature.

These two sets of data at different temperatures may be used to estimate the energy of formation of the methane hydroquinone clathrate as approximately 6 kcal/mol. Considering the latitude in temperature measurements of both the current work and that of Peyronel and Barbieri, agreement between this value of the energy of formation and the value of 5.9 kcal/mol calculated by Van de Waals and Platteeuw[6] seems fortuitous. However, the results suggest that the same material is produced by this solventless approach as is obtained from the conventional solution growth method.

In way of demonstration of the general applicability of the method, oxygen and nitrogen hydroquinone clathrates have also been prepared using this approach and it is believed that the method can be extended to preparation of other clathrates, such as the gas hydrates, where the host material can easily be volatilized.

Registry No.—Methane hydroquinone clathrate, 16060-36-9.

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Synthesis of 3(2*H*)-Benzofuranones and 1,2-Dihydro-3*H*-indol-3-ones by Acid-Catalyzed Cyclizations of β-Keto Sulfoxides

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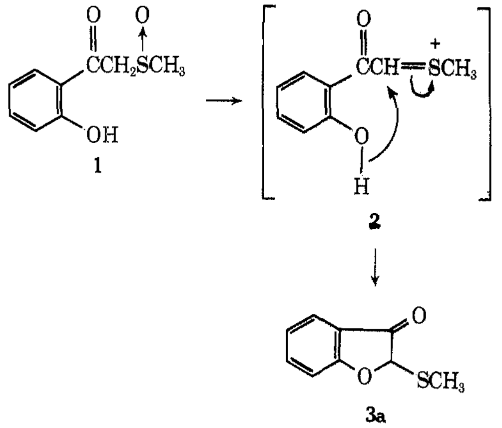
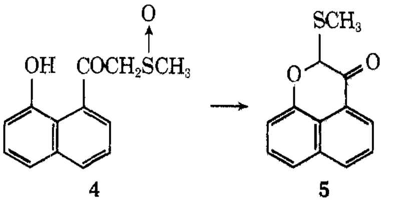
Our continuing interest in the use of β-keto sulfoxides for the synthesis of heterocyclic systems[1] led us to investigate the cyclization of 2-hydroxy-1-[(methylsulfinyl)acetyl]benzenes, 2-amino-1-[(methylsulfinyl)acetyl]benzenes, and 2-amido-1-[(methylsulfinyl)acetyl]benzenes with trifluoroacetic acid.

Recent publications on cyclizations involving Pummerer reaction intermediates to give carbocyclic rings,[2] 3,1-benzoxathian-4-ones,[3] and pteridines[4] prompt us to report our results in this area. The Pummerer reaction[5] continues to be of great synthetic[6] and mechanistic[7] interest. We envisioned that cyclization would take place *via* intramolecular nucleophilic attack by suitably situated oxygen and nitrogen functions on the cationic Pummerer intermediates (2 and 7) to give heterocyclic systems.

When 2-hydroxy-1-[(methylsulfinyl)acetyl]benzene (1) was heated under reflux in benzene containing trifluoroacetic acid for 40 min, 2-(methylthio)-3(2*H*)-benzofuranone (3a) was isolated in 45% yield. The spectral and analytical data were in agreement with the assigned structure. The ir spectrum showed a carbonyl band at 1720 cm^{-1}. The nmr spectrum showed the *S*-methyl at δ 2.13 (3 H, s), the methine proton (-OCHSMe) at δ 5.65 (1 H, s), and aromatic protons at δ 7.10–8.00 (4 H, m). The compounds (3a–d) prepared by this method are listed in Table I. The rearrangement is readily extended to the formation of six-membered rings, as illustrated by the conversion of 4 to 5.





Attempts to rearrange 6-chloro-2-amino-1-[(methylsulfinyl)acetyl]benzene to the corresponding 1,2-dihydro-3*H*-indol-3-one were unsuccessful and gave a complex mixture. Protonation of the amino nitrogen, deactivating it as a nucleophile, is the probable reason for the failure of the reaction in this case. The problem was surmounted by the use of the amido function. The conversion of amide 6 to 1,2-dihydro-3*H*-indol-3-one (8) in 67% yield illustrates the reaction. The analytical and spectral data for 8 are in agreement with the assigned structure. The ir spectrum showed carbonyl bands at 1730 and 1650 cm^{-1}. The nmr spectrum showed the *S*-methyl at δ 1.92 (3 H, s), the methine proton (>NCHSMe) at δ 5.25 (1 H, s), and aromatic protons at δ 7.0–8.2 (9 H, m).

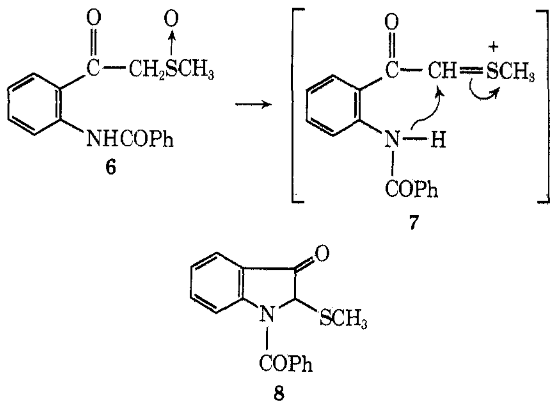
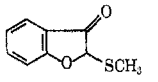
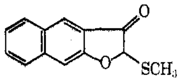
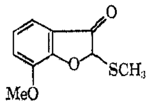
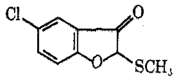
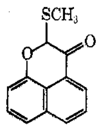
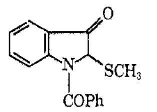


Table I[a]

Compd		Mp, °C (crystn solvent)	Yield, %
3a		81–82 (EtOH)	45
3b		118–120 (EtOH)	81
3c		103–105 (EtOH)	65
3d		76–78 (EtOH)	54
5		89–91 (EtOH)	64
8		126–128 (EtAc)	67

[a] Satisfactory analytical data (±0.3% for C, H, S, and N) were reported for all compounds listed in the table.

Experimental Section

Melting points were taken in open capillary tubes and were not corrected. Nmr spectra were recorded on a Varian Model A-60 spectrometer using TMS as an internal standard ($CDCl_3$ solvent). Thin layer chromatography was performed on commercial silica gel plates containing fluorescent indicator. A solvent system of ethyl acetate-cyclohexane (4:1) was used. Visualization was with 2537-Å light and iodine vapour.

General Reaction Procedure. A solution of the β-keto sulfoxide (0.01 mol) and trifluoroacetic acid (0.01 mol) in benzene (50 ml) was refluxed until tlc indicated the absence of the β-keto sulfoxide in the reaction mixture (40–90 min). The solvent was removed under pressure to give oils which crystallized on standing. Recrystallization (Table I) gave analytically pure material.

Acknowledgments. We would like to express our gratitude to Dr. R. C. Greenough for the spectral data and Mrs. U. Zeek for the elemental analysis.

Registry No.—**1**, 16697-77-1; **3a**, 51175-49-6; **3b**, 51175-50-9; **3c**, 51175-51-0; **3d**, 51175-52-1; **4**, 18500-87-3; **5**, 51175-53-2; **6**, 51175-54-3; **8**, 51175-55-4; 2-hydroxy-3-[(methylsulfinyl)acetyl]naphthaline, 51175-56-5; 2-hydroxy-3-methoxy-1-[(methylsulfinyl)acetyl]benzene, 51175-57-6; 4-chloro-1-hydroxy-2-[(methylsulfinyl)acetyl]benzene, 51175-58-7.

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