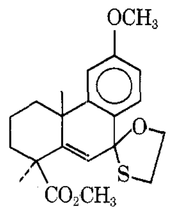
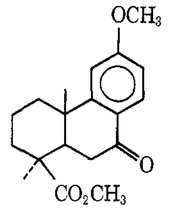
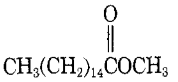


5

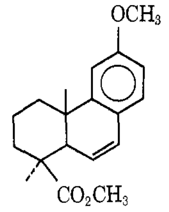


6



$CH_3(CH_2)_{14}COCH_3$

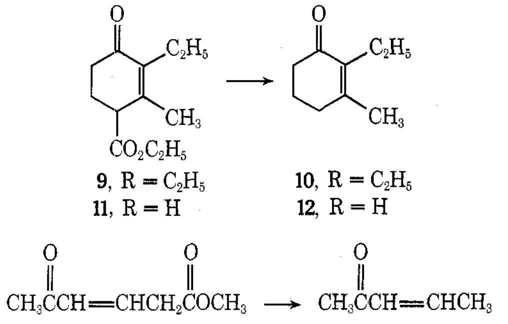
7



8

of this reagent to the esters shown in Scheme I. A mixture of 6 equiv of Dabco and 1 equiv of the appropriate ester was dissolved in 16 equiv of *o*-xylene and refluxed (165°) for 6 hr. The resulting olefins were obtained in approximately 98% yield by glc analysis and were identical by ir, nmr, and gc–mass spectral comparison with authentic samples.

Scheme I



9, R = C_2H_5
11, R = H
10, R = C_2H_5
12, R = H
13
14

The facile cleavage of ethyl and methyl δ-keto β,γ-unsaturated esters with a reagent (Dabco) that does not cleave saturated esters by either the *O*-alkyl cleavage or hydrolytic routes suggests that a mechanism similar to that reported by Krapcho and Lovey[7] for the cleavage of β-keto esters with sodium chloride and DMSO is probably operative.

Experimental Section

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained using a Jeolco Minimar spectrometer. Tetramethylsilane was used as an internal standard. Infrared spectra were obtained using a Perkin-Elmer Model 137 G spectrophotometer. Gas-liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 0.25 in. o.d.) bent in a U shape and packed with 3% SE-30 on 100/120 mesh GCQ at a column temperature of 270° with a helium flow rate of 90 ml/min was used for all glc analyses.

Dehydrobromination–Decarbmethylation of Bromo Ketone 1. Bromo ketone 1 (500 mg, 1.27 mmol) was added to a solution of 1,4-diazabicyclo[2.2.2]octane (Dabco, 856 mg, 7.62 mmol) and 2.42 ml of *o*-xylene. The reaction was allowed to reflux at 165° for 6 hr. The ether extract of the acidified (5% HCl) reaction mixture was washed with 5% aqueous sodium carbonate solution, dried over anhydrous sulfate, and evaporated *in vacuo*. Fractional crystallization of the residue from 20:1 methylene chloride–methanol yielded 318.5 mg (80%) of a white, crystalline compound 4 and 24.7 mg (10%) of white, crystalline compound 2. Compounds 2 and 4 were identical by ir, nmr, glc retention time, and mixture melting points with authentic samples.

General Procedure for the Decarbalkylation of δ-Keto β,γ-Unsaturated Esters. δ-Keto β,γ-Unsaturated Keto Esters 5–9, 11, and 13. A solution of Dabco (1.712 g, 15.24 mmol) and 2.54 mmol of the appropriate ester was dissolved in 4.85 ml of *o*-xylene and the resulting mixture was allowed to reflux at 165° for 6 hr. The usual work-up of the acidified reaction mixture yielded the corresponding ketone, which was identical by ir, nmr, glc retention time, and mixture melting points with an authentic sample.

Acknowledgments. We wish to thank the graduate school and the Biological and Physical Sciences Institute for partial financial support. We express our sincere appreciation to Dr. Ian K. Walker, Department of Scientific and Industrial Research, Wellington, New Zealand, for generous supplies of podocarpic acid.

Registry No.—**1**, 37931-64-9; **9**, 51051-65-1; **11**, 487-51-4; **13**, 51051-66-2; Dabco, 280-57-9.

References and Notes

(1) National Defense Education Act Graduate Fellow, 1971–1973.

(2) E. Wenkert, *et al.*, *J. Org. Chem.*, **30**, 713 (1965).
(3) E. Wenkert, *et al.*, *Can. J. Chem.*, **41**, 1924 (1963).
(4) D. H. Miles and E. J. Parish, *Tetrahedron Lett.*, 2987 (1972).
(5) E. J. Parish and D. H. Miles, *J. Org. Chem.*, **38**, 1223 (1973).
(6) E. J. Parish and D. H. Miles, *J. Org. Chem.*, **38**, 3800 (1973).
(7) A. P. Krapcho and A. J. Lovey, *Tetrahedron Lett.*, 957 (1973).

Solventless Preparation of Hydroquinone Clathrates

Robert W. Coutant

Battelle, Columbus, Ohio 43201

Received November 23, 1973

The hydroquinone clathrates have long been recognized for their unusual physicochemical properties.[1] Structurally, these materials consist of two interpenetrating three-dimensional hydrogen-bonded networks of hydroquinone that enclose a set of cavities capable of accommodating a variety of small molecules such as O_2, N_2, CH_4, HCl, SO_2, Ar, Kr, etc. The composition of these clathrates is generally dependent upon the pressure and temperature conditions under which the material is formed, with the upper limit being one molecule of "guest" for every three molecules of the "host," hydroquinone. However, once the clathrate is formed, the materials remain stable under conditions far removed from thermodynamic equilibrium. For example, Peyronel and Barbieri[2] report the pressure required to produce the composition $CH_4 \cdot 3C_6H_4(OH)_2$ as approximately 100 atm at 22–30°. The structure is stable, however, at ambient conditions.

Many technological applications have been suggested for these clathrates,[3,4] but realization of their potential has, in part, been hampered by the inconvenience usually associated with the methods of their preparation. Generally, the hydroquinone clathrates have been prepared by precipitation from alcohol solutions. Resistance to mass transport by the intervening liquid phase generally requires that the clathrates be precipitated slowly, with time periods of days to weeks not being uncommon.[5] Furthermore, the tendency for hydroquinone to undergo oxidation in solution presents the risk of introduction of impurities into the crystalline product when the solution growth method is used.

Past experience with crystal growth by chemical vapor deposition methods leads us to believe that the hydroquinone clathrates might be prepared by direct reaction between the guest and host materials. The advantages to such an approach are obvious; the intervening liquid phase with its attendant mass transfer resistance is removed from the system, and continuous production, as opposed to batch production, is more readily attainable.

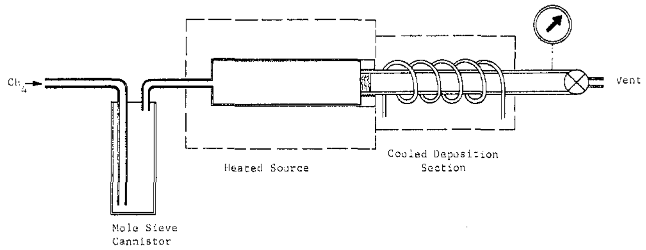


Figure 1. Schematic of clathrate formation apparatus.

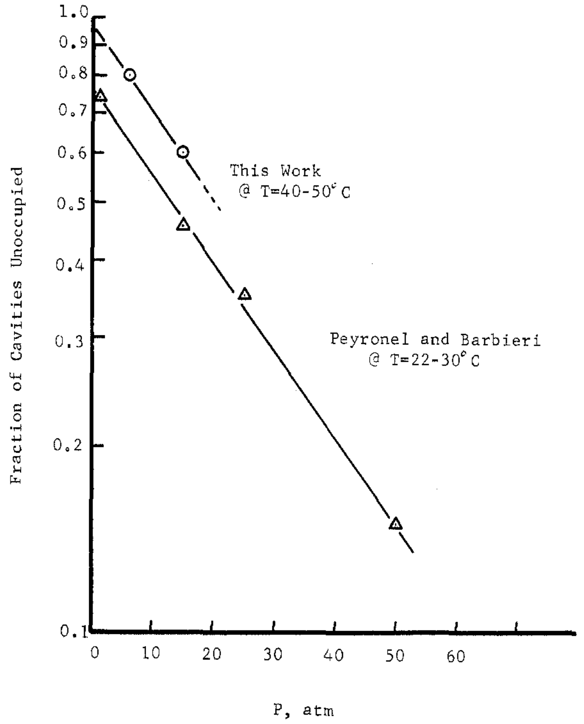


Figure 2. Pressure dependence of methane hydroquinone clathrate composition.

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.

References and Notes

(1) H. M. Powell in "Non-Stoichiometric Compounds," L. Mandelcorn, Ed., Academic Press, New York, N. Y., 1964, pp 438–490.
(2) G. Peyronel and G. Barbieri, *J. Inorg. Nucl. Chem.*, **8**, 582 (1958).
(3) M. Hagan, "Clathrate Inclusion Compounds," Reinhold, New York, N. Y., 1962, pp 143–164.
(4) W. D. Schaeffer and W. S. Dorsey, *Advan. Petrol. Chem. Refining*, **6**, 119 (1962).
(5) Reference 3, pp 117–142.
(6) J. H. van der Waals and J. C. Platteeuw, *Advan. Chem. Phys.*, **2**, 1 (1959).

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

David T. Connor* and M. von Strandtmann

Department of Organic Chemistry, Warner-Lambert Research Institute, Morris Plains, New Jersey 07950

Received December 18, 1973

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-ben-