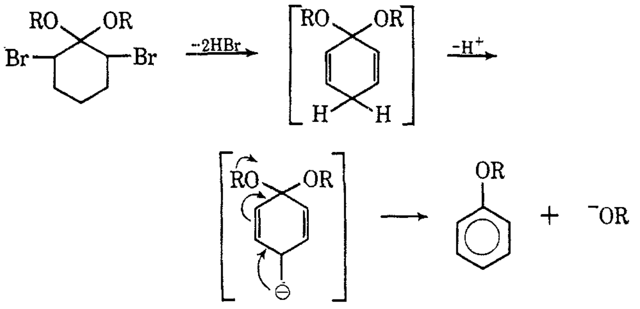
TABLE I

DEHYDROBROMINATION REACTIONS OF 2,6-DIBROMOCYCLOHEXANONE AND 4-BROMO-2-CYCLOHEXANONE KETALS

Reactant	Base	Mole ratio of base: reactant	Solvent	Reaction time, hr	Reaction temp, °C	Product	Yield, %
2,6-Dibromocyclohexanone dimethyl ketal	$NaOCH_3$	4:1	DMSO[a]	2	75	Anisole	49
2,6-Dibromocyclohexanone diethyl ketal	$NaOCH_3$	4:1	DMSO	2	75	Phenetole	10
2,6-Dibromocyclohexanone ethylene ketal	$KOC(CH_3)_3$	2:1	DMSO	2	75	2-Hydroxyethyl phenyl ether	36
2,6-Dibromocyclohexanone ethylene ketal	$KOC(CH_3)_3$	4:1	DMSO	2	75	2-Hydroxyethyl phenyl ether	39
2,6-Dibromocyclohexanone ethylene ketal	$NaOCH_3$	1:1	DMSO	2	75	2-Hydroxyethyl phenyl ether	0[b]
2,6-Dibromocyclohexanone ethylene ketal	$(C_2H_5)_3N$	2:1	Et_2O	48	36	2-Hydroxyethyl phenyl ether	0[c]
4-Bromo-2-cyclohexanone ethylene ketal	$NaOCH_3$	4:1	DMSO	2	75	2-Hydroxyethyl phenyl ether	20
4-Bromo-2-cyclohexanone ethylene ketal	$(C_2H_5)_3N$	6:1	Et_2O	20	36	2-Hydroxyethyl phenyl ether	17

[a] Dimethyl sulfoxide. [b] Recovery of the reactant was 87%. [c] Recovery of the reactant was 93%.

upon dehydrohalogenation under a variety of conditions. The respective aromatic ether and the reduction product 2-cyclohexenone ketal previously reported by Garbisch[2] were the only products identified in all attempts. Presumably the aromatic ethers are formed from an intermediate cyclohexadienone ketal by proton abstraction followed by the expulsion of an alkoxy group. Table I gives the conditions and the yields of the ethers isolated from the dehydrobromination of the 2,6-dibromocyclohexanone ketals of methanol, ethanol, and ethylene glycol. Since comparatively stringent conditions were necessary for dehydrobromination, the present work does not preclude the possibility of isolating cyclohexadienone ketals by some other method. However, the formation of 2-hydroxyethyl phenyl ether from 4-bromo-2-cyclohexenone ethylene ketal by dehydrobromination with triethylamine in ethyl ether would indicate that mild conditions are sufficient for the rearrangement to occur once a cyclohexadienone ketal has been generated.



Attempted isolation of the presumed intermediate cyclohexadienone ketals as Diels–Alder adducts by dehydrobromination in the presence of a large excess of cyclopentadiene or 1,3-cyclohexadiene was unsuccessful. Starting material was recovered when sodium cyclopentadienyl in tetrahydrofuran was used as the basic reagent.

There is a large body of information in the literature on dienone–phenol type rearrangements.[3,4] However, in almost all cases the reactants were disubstituted cyclohexadienones which under acidic catalysis or the influence of irradiation rearranged with the migration of one or more substituents. The present reaction is an apparently unique example of a dienone–phenol type rearrangement wherein a nonactivated ketal group is destroyed under basic conditions.

Experimental Section

The dimethyl ketal of cyclohexanone was prepared by the method of Garbisch.[2] The diethyl ketal was prepared by the method of Grafen[5] and the ethylene ketal by the method of Wanzlick, *et al.*[6] 4-Bromo-2-cyclohexenone ethylene ketal was prepared by bromination of 2-cyclohexenone ethylene ketal according to the procedure of de Puy, *et al.*[7]

The identity of the aromatic ethers was confirmed by comparison of the physical and spectral properties and gas chromatographic retention times with authentic samples.

General Procedure.—A solution of 2,6-dibromocyclohexanone ethylene ketal (15.0 g, 0.05 mole) in 100 ml of dimethyl sulfoxide was treated with 11.2 g (0.1 mole) of potassium *t*-butoxide. The mixture was slowly warmed to 75° and then agitated at ambient temperature for 2 hr. The reaction mixture was poured into 400 ml of a saturated sodium chloride solution and the product was extracted with three 100-ml portions of pentane. The extracts were combined and dried and the pentane was evaporated under reduced pressure. The residual oil was fractionated to yield 2.5 g (36%) of a product: bp 232° (760 mm); $n^{23}D$ 1.5318; nmr δ CCl_4, 2.43 (1 H, singlet, –OH), 3.88 (4 H, multiplet, $-OCH_2CH_2O-$), 6.95 (5 H, multiplet, aromatic protons). The infrared spectrum and gas chromatographic retention time were identical with those of an authentic sample of 2-hydroxyethyl phenyl ether.

Registry No.—2-Hydroxyethyl phenyl ether, 122-99-6; 2,6-dibromocyclohexanone dimethyl ketal, 13270-35-4; 2,6-dibromocyclohexanone diethyl ketal, 13250-25-4; 2,6-dibromocyclohexanone ethylene ketal, 13250-26-5; 4-bromo-2-cyclohexanone ethylene ketal, 13250-27-6.

Acknowledgment.—This work was supported by the Foundational Research Program of the Director of Naval Laboratories.

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(3) "Molecular Rearrangements," P. de Mayo, Ed., Vol. I and II, Interscience Publishers, Inc., New York, N. Y., 1964.

(4) L. F. Fieser and M. Fieser, "Steroids," Reinhold Corp., New York, N. Y., 1959, p 327.

(5) P. Grafen, *Ann.*, **656**, 97 (1962).

(6) H.-W. Wanzlick, G. Gollmer, and H. Mily, *Chem. Ber.*, **88**, 69 (1959).

(7) C. H. de Puy, B. W. Ponder, and J. D. Fitzpatrick, *J. Org. Chem.*, **29**, 3508 (1964).

The Oxidation of α-Hydroxy Ketones with Dimethyl Sulfoxide

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The oxidation of epoxides to α-hydroxy ketones by dimethyl sulfoxide (DMSO) using boron trifluoride[1,2]

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(1) T. Cohen and T. Tsuji, *J. Org. Chem.*, **26**, 1681 (1961).

(2) E. Brousse and D. Lefort, *Compt. Rend.*, **261**, 1990 (1965).

or air[3] as catalysts has been reported. It is of interest to note that these investigators did not report the formation of any dicarbonyl compound, although it is known that alcohols are readily oxidized to the carbonyl group. Traynelis and Hergenrother,[4] for instance, have reported the oxidation of a large number of benzyl alcohols using DMSO with a stream of air passing through the reaction medium.

Believing that α-hydroxy ketones should readily oxidize to the diketone with DMSO, we proceeded to investigate this reaction. Several methods for the oxidation of alcohols with DMSO have been reported.[5,6] In our investigation, the method of Albright and Goldman[5] using DMSO in the presence of acetic anhydride was used. We now report the smooth oxidation of several acyloins to the diketone in good yield.

It is believed the oxidation proceeds through an intermediate **1** formed by the reaction of the sulfoxide with the acetic anhydride[5,7] (Scheme I). This species can then be attacked by the OH of the acyloin to give rise to the alkoxysulfonium salt **2**, which subsequently loses a proton to give the dicarbonyl compound **3**.

Scheme I

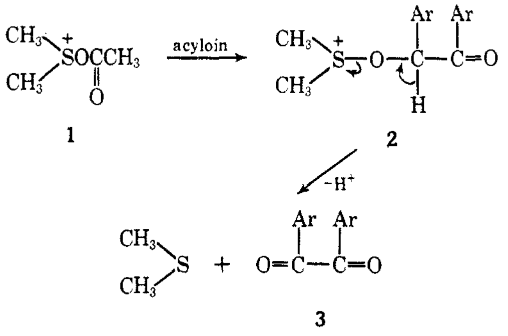

Table I gives the melting points and percentage yields of the products obtained in the oxidation. The yields of the dicarbonyl compounds obtained in the oxidation of benzoin and anisoin were good, indicating that little or no cleavage of the α-hydroxy ketone took place. The comparative low yield in the furoin to furil oxidation may be due to cleavage or to formation of degradation products. The nature of these is currently under investigation. Infrared studies of the diketone obtained in each case showed the absence of the OH and confirmed the structure of the product. The results of an elemental analysis[8] of each diketone agreed with the theoretical calculations. The diketone was further confirmed by the preparation of a 2,4-dinitrophenylhydrazone (2,4-DNPH) derivative as indicated in Table I.

Table I
Results of Oxidation with DMSO

Compd oxidized	Product	Yield, %	Mp (lit.), °C	Mp (lit.) of 2,4-DNPH derivative, °C
Benzoin	Benzil	77	93.5–94.5 (95)	187–189 (189, 185)
Anisoin	Anisil	88	131–133 (133)	188[a] (unknown)
Furoin	Furil	31	162–164 (165)	212.5–213 (215)

[a] The substance obtained upon reaction of anisil with the 2,4-DNPH reagent was submitted to infrared analysis and to a molecular weight determination with a mass spectrometer (CEC-21-103C, direct probe). Both analyses confirmed the suspicion that the derivative obtained was actually the mono-2,4-dinitrophenylhydrazone of anisil.

Preliminary investigations with two aliphatic acyloins, namely, 3-hydroxy-2-butanone and 2-hydroxycyclohexanone, indicate that DMSO–acetic anhydride solution does oxidize aliphatic acyloins to the diketone. However, using the same procedure as that used for the aromatic acyloins only low yields were obtained. Present investigations are concerned with modifying this procedure.

Experimental Section

Oxidation of α-Hydroxy Ketone.—The α-hydroxy ketone (0.01 mole) was placed in a flask containing 20 ml of acetic anhydride and 30 ml of DMSO. After stirring at room temperature for approximately 16 hr, the contents of the reaction flask were poured into 250–300 ml of ice water. The aqueous solution was extracted with three 50-ml portions of ether, benzene, or $CHCl_3$. The extract was washed with three 50-ml portions of 5% $NaHCO_3$ solution and four 50-ml portions of water, then dried with anhydrous Na_2SO_4 and decolorized with Norit. Following filtration, the organic solvent was removed using a rotatory evaporator, leaving the crystalline diketone. One recrystallization usually gave a relatively pure product. For melting points, yields, and melting points of the 2,4-dinitrophenylphyrazones prepared, see Table I.

Registry No.—Dimethyl sulfoxide, 67-68-5; benzil, 134-81-6; anisil, 1226-42-2; anisil 2,4-DNPH derivative, 13449-03-1; furil, 492-94-4.

Acknowledgments.—M. V. D. gratefully acknowledges a 1966 Research Initiation Summer Faculty Fellowship from the University of Colorado Council on Research and Creative Work.

[3] T. Tsuji, *Tetrahedron Letters*, 2413 (1966).

[4] V. J. Traynelis and W. L. Hergenrother, *J. Am. Chem. Soc.*, **86**, 298 (1964).

[5] J. D. Albright and L. Goldman, *ibid.*, **87**, 4214 (1965).

[6] K. E. Pfitzner and J. G. Moffatt, *ibid.*, **85**, 3027 (1963).

[7] J. D. Albright and L. Goldman, *ibid.*, **89**, 2416 (1967).

[8] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Aromatic Cyclodehydration of 2-Benzylphenyl and 2-(1-Naphthylmethyl)phenyl Benzo[*b*]thienyl Ketones[1]

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The currently accepted mechanism for Bradsher's aromatic cyclodehydration reaction[3] was postulated in 1949 (see Chart I).[4] The reaction involves reversible protonation of the carbonyl oxygen atom to form a

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[3] C. K. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

[4] C. K. Bradsher and F. A. Vingiello, *ibid.*, **71**, 1434 (1949).