TABLE I

N-ACYL-α-AMINO KETONES (V)

X	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Me[a]	86–88.5	59	77.26	7.17	4.74	77.24	7.12	4.81
i-Pr[a]	79–81	62	77.98	7.79	4.33	77.94	7.63	4.64
i-Bu[a]	90–92	67	78.30	8.07	4.15	78.70	8.15	4.09
Ph[b]	109–112	73	80.64	6.49	3.92	80.24	6.69	3.91

[a] Solvent for crystallization, water–ethanol. [b] Solvent for crystallization, benzene–cyclohexane.

TABLE II

INFRARED AND NMR SPECTRAL DATA OF N-ACYL-α-AMINO KETONES (V)

	ν_{NH}^{Nujol}, cm^{-1}	$\nu_{C=O}^{Nujol}$,[a] cm^{-1}	$\nu_{C=O}^{Nujol}$,[b] cm^{-1}	τ (in 10% CCl_4); *J* values; area ratio
Me	3380	1670	1645	8.54 (s);[c] 3.86 (q);[d] 8.80 (d); J = 7.2 cps; 6:1:3
i-Pr	3420	1680	1660	8.48, 8.50 (s); 4.49 (d); 9.13, 9.54 (d); J = 7.2 cps; 3:3:1:3:3
i-Bu	3280	1685	1640	8.54 (s); 4.25 (t); 9.05, 9.26 (d); J = 5.4 cps; 6:1:3:3
Ph	3380	1675	1655	8.50, 8.59 (s); 3.46 (s); 3:3:1

[a] Ketone–carbonyl absorption. [b] Amide-I absorption. [c] Two methyl groups of α-phenylisobutyryl substituent. [d] α-Methynyl hydrogen.

TABLE III

OXAZOLES (VI)

X	Bp (mm) or mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Me	140–160 (0.5)	79	82.28	6.91	5.05	80.86[c]	6.99	5.13
Picrate[a]	130–131	..	59.28	4.38	11.06	59.46	4.37	10.86
i-Pr[b]	64.5–66	83	82.58	7.59	4.59	82.60	7.82	4.73
i-Bu[b]	47–49	83	82.72	7.89	4.38	82.79	7.95	4.29

[a] Solvent for crystallization, ethanol. [b] Solvent for crystallization, water–ethanol. [c] A satisfactory analysis was presumably not obtained by vaporization.

Anal. Calcd for $C_{27}H_{29}N_5O_5$: C, 64.40; H, 5.81; N, 13.91. Found: C, 64.36; H, 5.54; N, 13.88.

Ring Closure of Vb to 2-(α-Phenylisopropyl)-4-isopropyloxazole (VIb).—A solution of Vb (1.044 g) and phosphorus oxychloride (3 g) in toluene (10 ml) was refluxed for 4 hr and then water (10 ml) was added carefully to the solution. The reaction mixture was neutralized by 10% NaOH solution. The resulting mixture was extracted twice with each 100 ml of ether and the combined ether extract was washed with water and dried over anhydrous sodium sulfate. The oil that remained after the solvent was removed crystallized when cooled to room temperature. The product (VIb) was recrystallized from 20 ml of ethanol–water mixture to yield 0.82 g (83%): $\nu_{C=N}^{Nujol}$ 1550 cm^{-1};[7,8] nmr, τ 8.23 (s), 8.67 (d), 6.79 (septuplet); 6:6:1 in 10% CCl_4.[9] VIc showed $\nu_{C=N}^{Nujol}$ 1555 cm^{-1}; nmr, τ 8.25 (s), 9.03 (d); 6:6 in 10% CCl_4; λ_{max} 210 and 270 mμ in cyclohexane. VIa showed $\nu_{C=N}^{liq\ film}$ 1550 cm^{-1}; nmr, τ 8.28 (s), 7.69; 6:6 in 10% CCl_4. The picrate of VIa was obtained by heating with picric acid in ethanol.

Cyclization of Vb to 2-(α-Phenylisopropyl)-4-isopropylthiazole.—A mixture of Vb (927 mg) and phosphorus pentasulfide (291 mg) in dioxane (10 ml) was refluxed for 2 hr. Then 10 ml of water and 2 ml of concentrated HCl were added and the mixture was refluxed for 1 hr. The mixture was distilled under reduced pressure to remove distillable materials. Then residue was neutralized with 10% NaOH and the solution was extracted twice with 50-ml portions of ether. The combined ether extract was dried over anhydrous sodium sulfate. After removal of the ether by distillation, the resulting crystals were recrystallized from ethanol: mp 90–92°; yield, 65%; $\nu_{C=N}^{Nujol}$ 1530 and 1600 cm^{-1};[7,10] nmr, τ 8.20 (s), 8.74 (d), 6.93 (septuplet); 6:6:1 in 10% CCl_4.[9]

Anal. Calcd for $C_{21}H_{23}NS$: C, 78.46; H, 7.21; N, 4.36; S, 9.97. Found: C, 78.23; H, 7.07; N, 4.34; S, 9.82.,

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(9) P. Haake and W. B. Miller, *J. Am. Chem. Soc.*, **85**, 4044 (1963).
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Registry No.—Va, 13318-37-1; Vb, 13341-90-7; Vb 2,4-dinitrophenylhydrazone, 13341-91-8; Vc, 13342-75-1; Vd, 13342-76-2; VIa, 13342-77-3; VIa picrate, 13342-78-4; VIb, 13342-79-5; VIc, 13342-80-8; 2-(α-phenylisopropyl)-4-isopropylthiazole, 13342-81-9.

Rearrangement of 2,6-Dibromocyclohexanone Ketals

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Recently it was reported that cyclopentadienone ketals can be prepared and used for synthetic purposes in place of the extremely reactive parent compound.[1] Since we were interested in preparing Michael adducts of cyclohexadienone, it appeared that cyclohexadienone ketals might be stable enough to isolate as starting materials for this purpose. They could then hopefully be hydrolyzed *in situ* in the presence of acidic addends to form the desired 3,5-disubstituted cyclohexanones.

Our approach was to brominate the appropriate ketal of cyclohexanone by the method of Garbisch[2] to give the 2,6-dibromocyclohexanone ketals. However, we were not able to isolate any cyclohexadienone ketal

(1) P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).
(2) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

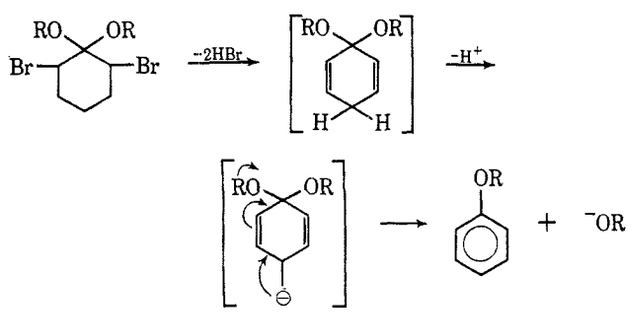
TABLE I

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.

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

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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); $n^{28}D$ 1.5318; nmr δ CCl_4, 2.43 (1 H, singlet, –OH), 3.88 (4 H, multiplet, $-OCH_2-CH_2O-$), 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.

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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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