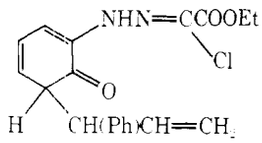
The above results can be accommodated within the frame of the following mechanistic picture. In accord with the known thermochemical behavior of aryl allyl ethers,[8] compounds **1a–c** are capable of undergoing a Claisen rearrangement reaction leading to 2,6-disubstituted phenols **4.** These primary products can then evolve according to one or both of the following pathways: (i) further migration of the allyl-type substituent to give 2,4-disubstituted phenols **6;** (ii) intramolecular nucleophilic displacement of the chlorine atom to afford 8-substituted 4*H*-1,3,4-benzoxadiazines **5.** The latter process, which is very fast in the presence of triethylamine, parallels the intermolecular reaction of 1-chlorohydrazones with phenol under basic catalysis.[9] Of course, a similar ring closure is possible for **6** to give **7.**

Examination of the results given in Table I reveals that the migration of the allyl substituent to the para position, which is lacking in the case of **1b,** proceeds rather easily in the case of **1c,** thus keeping the concentration of phenol **4c** under detectable values (by NMR). The actual formation of the latter compound is demonstrated by the isolation of the corresponding cyclization product **5c.** The observed preference for the para position in the Claisen rearrangement of **1c** could perhaps be the consequence of a steric hindrance by the phenyl group. This effect would be operating in the retroenolization of the primarily formed cyclohexadienone A, thus



A

favoring the alternative pathway, i.e., further migration of the substituent to the para position.

The tricyclic compounds **3** unquestionably arise from **2** via intramolecular 1,3-cycloaddition. In spite of the absence of a basic reagent, the formation of **2** is not surprising since 1-chlorohydrazones have been reported to undergo, although slowly, thermal elimination to give nitrile imines.[6]

Experimental Section

Melting points were taken on a Büchi apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 377 spectrophotometer. NMR spectra were usually obtained on a Varian A-60A instrument with Me_4Si as an internal standard; a Varian HA-100 instrument was used for compound **3b.**

Preparations of **1a, c** have been previously reported.[1]

Ethyl 2-Chloro-2-[2-(2-methylprop-2-enyloxy)phenylhydrazono]acetate (1b). This compound was prepared from 2-(2-methylprop-2-enyloxy)aniline[10] according to the precedure described for **1a,c**:[1] yield 56%; mp 51 °C (*n*-pentane); IR (Nujol) 3350 (NH) and 1740 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.37 (3 H, t, CH_2CH_3), 1.82 (3 H, s, CH_3), 4.30 (2 H, q, CH_2CH_3), 4.42 (2 H, s, CH_2), 4.8–5.2 (2 H, m, CH_2=), 6.7–7.6 (4 H, m, ar), 8.8 (1 H, broad s, NH). Anal. Calcd for $C_{14}H_{17}ClN_2O_3$: C, 56.66; H, 5.78; N, 9.44. Found: C, 56.80; H, 5.48; N, 9.31.

Reaction of 1-Chlorohydrazones 1 in Boiling Xylene. General Procedure. A solution of **1** (40 mmol) in dry xylene (2 L) was heated under reflux for 42 h. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel column (1 kg) to afford unchanged **1** followed by the products indicated in Table I. Eluents were light petroleum–diethyl ether (3:2) in the case of **1a,b** and benzene–ethyl acetate (4:1) in the case of **1c.**

Reaction of 1-Chlorohydrazones 4 and 6 with Triethylamine. General Procedure. A solution of 1-chlorohydrazone **4** or **6** (5 mmol) and triethylamine (25 mmol) in dry toluene (250 mL) was heated under reflux for 0.5 h. The mixture was then washed with aqueous HCl, dried over $MgSO_4$, and evaporated. The residue gave the cyclization product **5** or **7** in 90–95% yield. Compound **7a:** yellow crystals, mp 139 °C (from diisopropyl ether).

Registry No.—**7a,** 65465-87-4; 2-(2-methylprop-2-enyloxy)aniline, 55000-14-1.

Supplementary Material Available: Spectral (IR and NMR) and analytical data for compounds **3b, 4a,b, 5a,b, 6a,** and **7a** (2 pages). Ordering information is given on any current masthead page.

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Mild Procedure for the Cleavage of α-Hydroxy Ketoximes Using Dichlorocarbene†

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The fragmentation of *anti*-α-hydroxy ketoximes (**1**) to yield aldehydes or ketones (**2**) and nitriles (**3**) can be effected by a number of reagents such as phosphorus pentachloride,[1] benzenesulfonyl chloride–pyridine,[2] phosphoryl chloride–pyridine,[3] polyphosphoric acid,[4] thionyl chloride,[5] and phosphonitrile dichloride–pyridine.[6]

We now wish to describe a novel Beckmann fragmentation technique for *anti*-α-hydroxy ketoximes using dichlorocarbene as the reagent. The carbene was generated in situ in a two-phase system using a phase-transfer catalyst.[7] The method proceeds under mild conditions to give high yields of the corresponding carbonyl compound and the nitrile:

A wide variety of α-hydroxy ketoximes such as α-benzoin oximes, terpenoid-α-hydroxy ketoximes, and steroid-α-hydroxy ketoximes underwent fragmentation in high yields. The results are summarized in Table I.

A tentative reaction pathway on the lines previously suggested[2b,5,8] for the observed Beckmann fragmentation of *anti*-α-hydroxy ketoximes is shown in Scheme I.

Experimental Section

All melting points are uncorrected. IR spectra were determined on a Perkin-Elmer infracord spectrometer in Nujol and as KBr pellets. All α-hydroxy ketoximes were prepared by previously reported procedures and were fully characterized prior to use. All known products were confirmed by comparison of their IR spectra with authentic samples.

† Dedicated to Professor Bal Dattatrays Tilak on the occasion of his 60th birthday.

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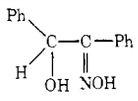
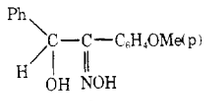
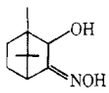
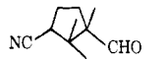
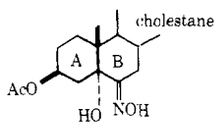
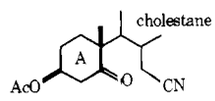
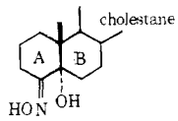
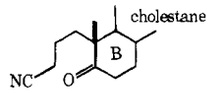
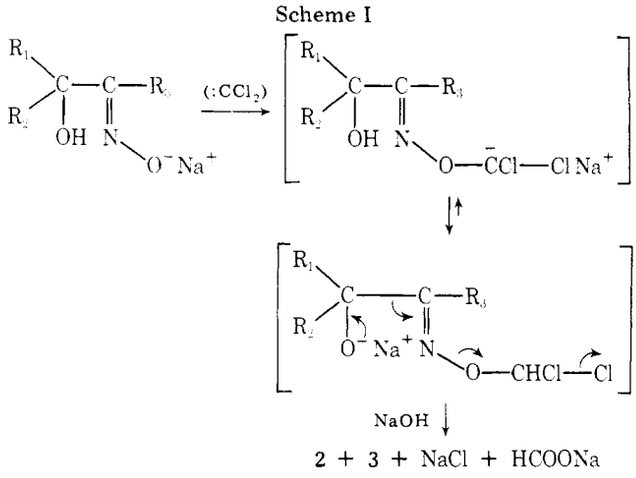
Table I. Yields of Products from the Fragmentation of α-Hydroxy Ketoximes

α-Hydroxy ketoximes	Registry no.	Mp, °C	Product	Registry no.	Yield,[a] %	Mp or bp (Torr) °C	Lit. mp or bp (Torr), °C
 1a	574-13-0	150[c]	PhCHO PhCN	100-52-7 100-47-0	80[b] 76	236 191 (760)	236[c] 191[c] (760)
 1b	65414-48-4	136[d]	PhCHO p-OMeC$_6$H$_4$CN	874-90-8	74[b] 65	236 62	236 62[c]
 1c	3221-98-4	157–58[e]		65414-49-5	85[b]	195–96	
 1d	65451-08-3	179[f]		27270-59-3	85	96	96–7[g]
 1e	65452-44-0	190 and 212[h]		65414-50-8	86	66	66–68[h]

[a] Isolated yields of products purified by chromatography or distillation. [b] Isolated as 2,4-dinitrophenylhydrazone. [c] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", Wiley, New York, N.Y., 1965. [d] M. Tiffeneau and J. Levy, *Bull. Soc. Chim. Fr.*, **49**, 725 (1931). [e] R. A. Chittenden and G. H. Cooper, *J. Chem. Soc. C*, **49**, (1970). [f] L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3938 (1949). [g] L. Knof, *Justus Liebigs Ann. Chem.*, **642**, 194 (1961). [h] Reference 5.

Scheme I



General Procedure for the Reaction of the Dichlorocarbene with the α-Hydroxy Ketoximes. Cleavage of 2-*exo*-Hydroxy-3-hydroxyiminobornane (1c). To a solution of **1c** (9.15 g, 50 mmol) in chloroform–ethyl acetate (200 mL, 1:1 v/v) was added 40% sodium hydroxide (50 mL, 0.7 mol) followed by benzyltriethylammonium chloride (2.2 mmol) with stirring. Upon addition of 40% sodium hydroxide, the formation of a white precipitate was observed. The reactants were refluxed for 30 min, during which time the precipitate slowly went into complete solution. The progress of the reaction was followed by TLC (silica gel; benzene–ethyl acetate (5:1) as eluent). The organic layer was then separated, washed with 2 N HCl (5 mL) and water, and dried. IR (CCl_4) of product showed 2240 (CN) and 1723 cm^{-1} (CO). The crude product was converted into its 2,4-dinitrophenylhydrazone and recrystallized from ethanol as yellow needles (14.6 g, 85%): mp 195–96 °C; IR (KBr) ν_{max} 3280 and 2220 cm^{-1}. Anal. Calcd for $C_{16}H_{19}N_5O_4$: C, 55.65; H, 5.50; N, 20.29. Found: C, 55.80; H, 5.62; N, 20.13.

Registry No.—**1c** DNP, 65414-47-3; dichlorocarbene, 1605-72-7.

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Synthesis of Methylaryloxypropanolamines[1]

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Several years ago we initiated a project directed toward developing a general synthesis of α-methylaryloxypropanolamines. These compounds were of interest because of their reported selective β-adrenergic blocking action.[2-5] The route proposed for the synthesis of these compounds consisted of

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