965-67-3; **2** corresponding olefin, 963-75-7; **3**, 6084-76-0; **3** corresponding olefin, 1937-62-8; **4**, 2566-91-8; **4** corresponding olefin, 112-62-9; **5**, 6084-74-8; **5** corresponding olefin, 7439-44-3; **6**, 6084-75-9; **6** corresponding olefin, 1120-34-9; **7**, 38595-13-0; **7** corresponding olefin, 55915-70-3; **8** α-epoxide, 20230-22-2; **8** β-epoxide, 24375-46-0; **8** corresponding olefin, 570-74-1; **9** α-epoxide, 2515-12-0; **9** β-epoxide, 1975-34-4; **9** corresponding olefin, 601-57-0.

References and Notes

(1) (a) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, N.Y., 1971, pp 502–504; (b) *ibid.*, Vol. 2, 1974, pp 200 and 201.

(2) (a) P. Dowd and K. Kang, *J. Chem. Soc., Chem. Commun.*, 384 (1974); (b) J. M. Behan, R. A. W. Johnstone, and M. J. Wright, *J. Chem. Soc., Perkin Trans. 1*, 1216 (1975); (c) M. Rosenblum, M. R. Saidi, and M. Madhavararo, *Tetrahedron Lett.*, 4009 (1975); (d) J. E. McMurry and M. P. Flemming, *J. Org. Chem.*, **40**, 2555 (1975); (e) J. Rémion, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1385 (1976); (f) P. B. Dervan and M. A. Shippey, *J. Am. Chem. Soc.*, **98**, 1265 (1976).

(3) (a) S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953); (b) J. P. H. Verheyden and J. G. Moffatt, *J. Org. Chem.*, **35**, 2319 (1970). Trivial name for this compound is triphenylphosphite methiodide.

(4) In some cases, benzene was used as a cosolvent to increase the solubilities of materials in the reaction mixture.

(5) Novel methods of converting epoxides to olefins previously reported with retention of stereochemistry: (a) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112, 2539 (1959); (b) K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, **94**, 6540 (1972); (c) D. L. J. Clive and C. V. Denyer, *J. Chem. Soc., Chem. Commun.*, 253 (1973); (d) W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Am. Chem. Soc.*, **94**, 7170 (1972); (e) ref 2b.

(6) For generation and reactions of highly reactive anions using crown ethers, see: (a) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (b) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976).

(7) No deoxygenation of epoxides takes place by tetrabutylammonium iodide under the present conditions.

(8) N. S. Isaacs and D. Kirkpatrick, *Tetrahedron Lett.*, 3869 (1972).

(9) We are indebted to one of the referees for calling our attention to ref 8.

(10) No deoxygenation of epoxides could be made by methyltriphenylphosphonium bromide under the present conditions.

(11) IR spectra were recorded with a JASCO Model IRS spectrophotometer. NMR spectra were obtained using Varian HA-100D (100 MHz) and NV-21 (90 MHz) instruments. Mass spectra were determined on a Hitachi RMU-6C mass spectrometer. For TLC silica gel 60 F_{254} and 60 PF_{254} (E. Merck, A. G., Germany) were used. GLC analysis was performed on a Varian 1820-4 gas chromatograph. The organic solutions were dried over Na_2SO_4 and concentrated by vacuum rotary evaporator.

Allyl Ethers of Ethyl 2-Chloro-2-(2-hydroxyphenylhydrazono)acetate as Intermediates for the Synthesis of 4*H*-1,3,4-Benzoxadiazines

Luisa Garanti* and Gaetano Zecchi

Istituto di Chimica Industriale dell'Università, Centro del C.N.R. per la Sintesi e Stereochimica di Speciali Sistemi Organici, 20133 Milano, Italy

Received July 20, 1977

In a study of 1,3-dipoles bearing an alkenyl substituent, we found[1] that the reaction of 1-chlorohydrazone **1c** with triethylamine gave, in addition to the expected pyrazoline derivative **3c** arising from the intermediate nitrile imine **2c**, minor quantites of the isomeric 4*H*-1,3,4-benzoxadiazines **5c** and **7c**. Since few synthetic methods are available for this ring system,[2-5] further work was done on 1-chlorohydrazones of type **1** as possible precursors of 1,3,4-benzoxadiazines. In view of the fact that 1-chlorohydrozones are well known to follow a general pattern in a basic medium, giving rise to nitrile imines,[6] thermochemical reactions of **1a–c** seemed to be worthy of investigation.

Compounds **1a–c** slowly underwent change in boiling xylene to give a mixture of several products. In all cases, the reaction mixture was worked up before the complete disappearance of the starting substrate; in fact, longer times were not advantageous since formation of tar began to occur. Products, which were isolated by column chromatography, are indicated in Table I along with the corresponding isolation yields.

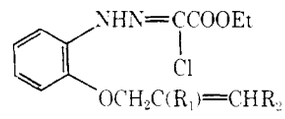
Table I. Reaction of 1-Chlorohydrazones 1 in Boiling Xylene[a]

Compd	Registry no.	Unreacted substrate, %[b]	Products	Registry no.	Mp, °C[c]	Yield, %
1a	61364-10-1	25	**4a**	65465-81-8	103	33
			6a	65465-82-9	129	11
			3a	61364-13-4	*d*	8
			5a	65465-83-0	101[e]	13
1b	65465-79-4	31	**4b**	65465-84-1	91	34
			3b	65495-44-5	132	9
			5b	65465-85-2	97[e]	17
1c	65465-80-7	29	**3c**	65465-86-3	*d*	16
			6c	61364-17-8	*d*	10
			5c	61364-19-0	*d*	20
			7c	61364-18-9	*d*	13

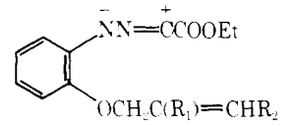
[a] After 42 h. [b] Recovered by column chromatography. [c] From diisopropyl ether. [d] See ref 1. [e] Yellow crystals.

Control experiments showed that compounds **4a,b** and **6a,c** are not stable in boiling xylene but slowly react to afford the corresponding 4*H*-1,3,4-benzoxadiazines **5a,b** and **7a,c**.[7] Some **6a** was detected in the product arising from **4a**.

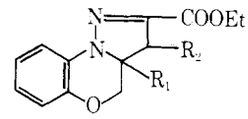
The ring closure of **4a,b** and **6a,c** to **5a,b** and **7a,c** was greatly accelerated in the presence of basic agents. In fact, it was complete within 30 min by treating **4a,b** and **6a,c** with triethylamine (5 mol) in boiling toluene. Under these conditions, the cyclization products **5a,b** and **7a,c** were obtained in quantitative yields.



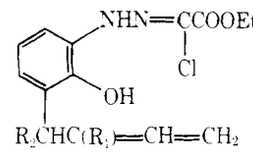
1



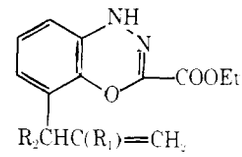
2



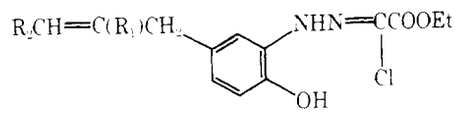
3



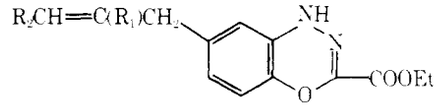
4



5



6



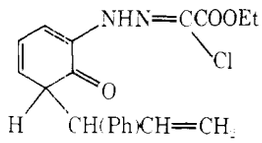
7

a, $R_1 = R_2 = H$
b, $R_1 = Me$; $R_2 = H$
c, $R_1 = H$; $R_2 = Ph$

0022-3263/78/1943-2077$01.00/0

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.

References and Notes

(1) L. Garanti, A. Sala, and G. Zecchi, *J. Org. Chem.*, **42,** 1389 (1977).
(2) R. Huisgen and R. Fleischmann, *Justus Liebigs Ann. Chem.*, **623,** 47 (1959); R. Huisgen, G. Binsch, and H. Koenig, *Chem. Ber.*, **97,** 2884 (1964).
(3) W. Ried and E. Kahr, *Chem. Ber.*, **103,** 331 (1970).
(4) A. J. Elliot and M. S. Gibson, *J. Chem. Soc., Perkin Trans. 1,* 2915 (1972); A. J. Elliot, M. S. Gibson, M. M. Kayser, and G. A. Pawelchak, *Can. J. Chem.*, **51,** 4115 (1973).
(5) P. W. Chow and N. Ishikawa, *Bull. Chem. Soc. Jpn.*, **47,** 2079 (1974).
(6) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2,** 565 (1963).
(7) The product mixture arising from **1a** could have contained a small amount of **7a,** which however was not isolated.
(8) S. J. Rhoads and N. R. Raulins, *Org. React.*, **22,** 1 (1975).
(9) A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J. Chem. Soc., Perkin Trans. 2,* 44 (1972).
(10) R. Fusco, L. Garanti, and G. Zecchi, *J. Org. Chem.*, **40,** 1906 (1975).

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

Jayant N. Shah,* Yagnesh P. Mehta, and Girish M. Shah

Research and Development Centre, Indian Petrochemicals Corporation Limited, Baroda 391 346, India

Received September 30, 1977

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.

0022-3263/78/1943-2078$01.00/0