Table III

10^3[DMA], M	10^3[2,4,6-Cl_3Ph_2], M	ϕ_r
4.56	5.24	0.16[a]
4.56	3.50	0.12[a]
4.56	1.75	0.10[a]
4.56	0.87	0.057[a]
5.5	2.01	0.22

[a] Slope and intercept obtained from plot of ϕ_r^{-1} vs. $[ArCl]^{-1}$. The slope[a] for these four numbers is 0.011 M, and the intercept is 4.7.

Table IV

10^3[4-$ClPh_2$], M	ϕ_r[a]	10^3[4-$ClPh_2$], M	ϕ_r[a]
5.90	0.28	2.36	0.15
4.02	0.21	1.18	0.092

[a] Slope from plot of ϕ_r^{-1} vs. $[ArCl]^{-1}$. Slope = 1.5×10^{-3} M; intercept = 2.2.

Photochemistry of Aryl Chloride/*N,N*-Dimethylaniline Systems. For the fluorescence quenching experiments, the concentration of the chloride was kept very low so that the DMA would absorb the light; consequently, the amount of quenching was always small, and the data were somewhat irreproducible from run to run. The following quenching constants (M^{-1}) were obtained: 4-chlorobiphenyl/DMA/cyclohexane, 36, 32; 4-chlorobiphenyl/DMA/methanol, 40, 61; 2,4,6-trichlorobiphenyl/DMA/cyclohexane, 31; 2,4,6-trichlorobiphenyl/DMA/methanol, 60, 97; 2,2′,5,5′-tetrachlorobiphenyl/DMA/cyclohexane, 31; 2,2′,5,5′-tetrachlorobiphenyl/DMA/methanol, 35, 62. No quenching was observed for any of these halides with *N*-ethylcarbazole or with acridine.

2,2′,5,5′-Tetrachlorobiphenyl/DMA/Methanol. The results shown in Table II were obtained.

2,4,6-Trichlorobiphenyl/DMA/Methanol. The experiments indicated in Table III were all done in duplicate, except for the last one which was a time study (eight solutions altogether). All ϕ_r values were evaluated by the "log" method.

4-Chlorobiphenyl/DMA/Methanol. The DMA concentration was 5.5×10^{-3} M throughout. All ϕ_r values were obtained by extrapolating back to $t = 0$ from a series of eight ampules each (Table IV).

Table V

10^3[DMA], M	10^3[4-$ClPh_2$], M	ϕ_r[a]
5.95	1.23	0.0040[b]
5.95	3.69	0.0086[b]
5.95	6.14	0.0124[b]
4.95	2.08	0.0091[c]
4.95	5.20	0.0131[c]
5.4	3.77	0.0130[c]
5.4	5.20	0.0165[c]
5.4	1.05	0.0041[c]

[a] Slope and intercept obtained from plot of ϕ_r^{-1} vs. $[ArCl]^{-1}$. [b] Slope[a] = 0.28 M^{-1}; intercept = 36. [c] Slope[a] = 0.21 M^{-1}; intercept = 30.

4-Chlorobiphenyl/DMA/Cyclohexane. The first series of experiments were duplicate analyses and were not extrapolated to time zero. The second series were all extrapolated to $t = 0$ from a series of eight ampules (Table V).

The experiments with 4-chlorobiphenyl were also analyzed by a different method, but with similar results. From Scheme III and on application of the steady-state approximation to ^1D and to $^1(D \cdot ArCl)$, eq 5 is obtained. Integration affords

$$\frac{-d[ArCl]}{dt} = \left(\frac{k_8}{k_7 + k_8}\right)\left(\frac{k_6[ArCl]}{k_5 + k_6[ArCl]}\right)I_{abs} \quad (5)$$

$$\Delta[ArCl] + \ln([ArCl]_0/[ArCl])/K_{SV} = (k_8/(k_7 + k_8))I_{abs}t \quad (6)$$

Calling the left-hand side of this equation f(A), a plot of f(A) vs. I_0t gives the slope as $k_8/(k_7 + k_8)$. The value of $(\phi_r)_0$ corresponding to $[ArCl]_0$ can be obtained by substituting back into an equation analogous to eq 4. In practice this method proved more cumbersome and no more effective than the extrapolation of ϕ_r itself.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. DMA, 121-69-7; DMH, 764-13-6; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; 4-chlorobiphenyl, 2051-62-9; 2,4,6-trichlorobiphenyl, 35693-92-6; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3; 1-chloronapthalene, 90-13-1.

Notes

Rates of Acid-Catalyzed Geometric Isomerization of Some Compounds Containing a Carbon-Nitrogen Double Bond

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Received October 19, 1981

We recently reported on the mechanism of the hydrogen chloride catalyzed *E* to *Z* isomerization of *O*-methylbenzohydroximoyl chloride (Scheme I, 1 → 2).[2] Two mechanisms were considered for the isomerization: (a) rotation about the carbon–nitrogen double bond of the conjugate acid of 1 and (b) nucleophilic attack by chloride ion on the conjugate acid of 1 (nucleophilic catalysis). Tracer experiments with $^{36}Cl^-$ showed conclusively that the isomerization of 1 proceeds by nucleophilic catalysis (Scheme I). It was also shown in this work that para substitutents have little effect on the rate of the hydrogen chloride catalyzed isomerization of 1 ($\rho = -0.66$ with σ). The low substituent effect was rationalized in terms of offsetting ρ values for the protonation of 1 ($+\rho$) and the nucleophilic attack of chloride ion on the conjugate acid of 1 ($-\rho$).

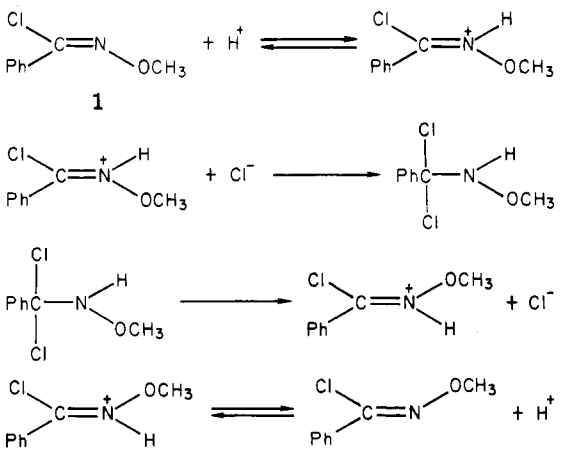
The present kinetic study was carried out to determine the effect of para substituents on the rate of hydrogen

(1) Taken in part from the M.S. Thesis of N.M.S., Texas Woman's University, May 1978.

(2) Johnson, J. E.; Silk, N. M.; Nalley, E. A.; Arfan, M. *J. Org. Chem.* 1981, *46*, 546.

0022-3263/82/1947-1958$01.25/0

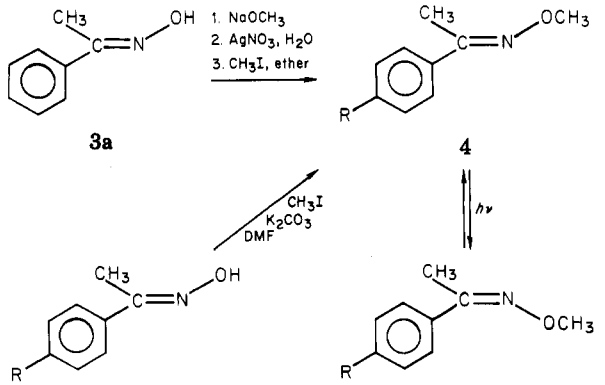
Scheme I



1

2

Scheme II[a]



3a

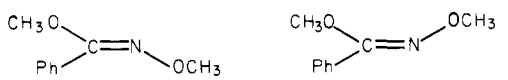
4

3b, R = OCH_3
c, R = NO_2

5

[a] 4a and 5a, R = H; 4b and 5b, R = OCH_3; 4c and 5c, R = NO_2.

chloride catalyzed geometric isomerization of acetophenone *O*-methyloximes (Scheme II, **4a–c** and **5a–c**). We have also investigated the isomerization rate of methyl *O*-methylbenzohydroximate (**6** and **7**) in order to determine the



6 7

effects on isomerization rate with changes in substututents directly attached to the carbon–nitrogen double bond.

The acetophenone *O*-methyloximes (**4a–c** and **5a–c**) were prepared according to the procedures outlined in Scheme II. The configurational assignments for the pairs of isomers **4b–5b** and **4c–5c** are based on their ^1H NMR spectra in analogy with the assignments made by Padwa and Albrecht for **4a** and **5a** (the $NOCH_3$ singlet absorbs farther downfield in the *E* isomer than in the *Z* isomer).[3]

The isomerizations of **5a–c** were carried out in hydrogen chloride–dioxane solutions at 39.5 °C. It was found that the isomerizations went almost entirely to the *E* isomers (**4a–c**), with the final equlibrium distributions being about 98% *E* to 2% *Z*.[4]

The isomerization rates of the *O*-methyloximes **5a–c** were found to be too fast to measure with the same acid

(3) Padwa, A.; Albrecht, F. *J. Am. Chem. Soc.* **1974**, *96*, 4849.

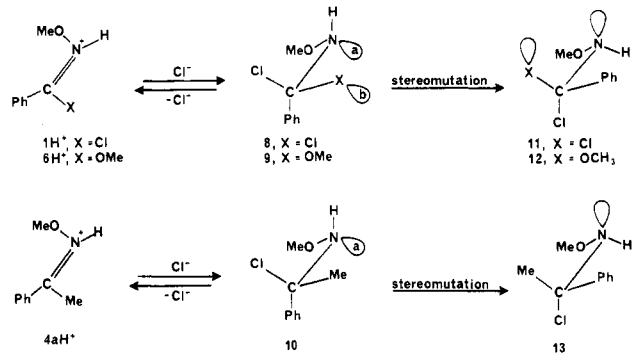
(4) Padwa and Albrecht[3] reported the equilibrium distribution of **4a** and **5a** to be 98:2 (iodine catalysis, solvent not given).

Table I. First-Order Rate Constants for the Hydrogen Chloride[a] Catalyzed Isomerization of Some Compounds Containing a Carbon–Nitrogen Double Bond in Dioxane at 39.5 °C

compd[b]	10^3k, s^{-1}	dev,[c] %
5a	2.92	4.0
5b	2.45	0.7
5c	2.18	8.4
1	0.0195	7.4
6	0.284[d]	0.7

[a] Concentration of hydrogen chloride was 0.0110 molal. [b] Concentration of the C=N compound was 0.034–0.12 molal. [c] Deviation from average of two results. [d] The equilibrium distribution of **6** and **7** is 83:17. The rate constant for isomerization was calculated from the rate equation derived for reversible first-order kinetics (see the Experimental Section).

Scheme III



concentration used in our earlier study on the isomerization of **1**. Consequently, the isomerizations of **5a–c** were carried out at an acid concentration about 10 times lower than that used earlier.

It is clear from the rate data in Table I that substituents have little effect on the rates of these isomerizations. It is likely that these isomerizations are proceeding by the same mechanism[5] (nucleophilic catalysis) as the isomerization of the hydroximoyl chloride **1** and that the lack of sensitivity to substituent effects is due to offsetting ρ values for the protonation step and the nucleophilic attack by chloride ion.

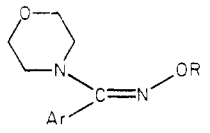
In order to determine the effect on rates of acid-catalyzed isomerization with changes in substituents on the carbon–nitrogen double bond (α-substituent effects), the isomerization rates of the hydroximoyl chloride **1** and methyl *O*-methylbenzohydroximate **6** were measured at the same acid concentration as for the oximes **5a–c**. In contrast to para substituent effects, substituent effects on the carbon–nitrogen double bond are substantial. The rate constant for isomerization of the *O*-methyl oxime **5a** is about 150 times greater than the rate constant for **1** and about 10 times greater than that for the hydroximate **6**.

Although part of the large α-substituent effect may be due to differences in polar effects on the protonation step and in steric hindrance for chloride ion attack on the conjugate acids $\mathbf{1H^+}$, $\mathbf{5aH^+}$, and $\mathbf{6H^+}$ (Scheme III), it is also possible that a significant part of the substituent effect is caused by stereoelectronic factors[6] in the tetrahedral in-

(5) It appears that most acid-catalyzed isomerizations of imines proceed by a nucleophilic catalysis mechanism analogous to the mechanism outlined in Scheme I: (a) Reference 2. (b) Jennings, W. B.; Al-Showiman, S.; Tolley, M. S.; Boyd, D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1535. (c) Conlon, P. R.; Sayer, J. M. *J. Org. Chem.* **1979**, *44*, 262. An exception to this generalization is the isomerization of benzamidoximes **14** which isomerize by rotation about the carbon–nitrogen bond of the conjugate acid.[8]

termediates 8–10. In order for the acid-catalyzed isomerization of 1, 5a, or 6 to occur, the tetrahedral intermediates 8–10 must undergo stereomutation (via nitrogen inversion, proton exchange, and C–N bond rotation) to conformations in which the $NOCH_3$ and phenyl groups are anti to each other (11–13). Loss of chloride ion from the tetrahedral intermediates 8–10 to reform, $1H^+$, $5aH^+$, and $6H^+$ is competitive with stereomutation, and if the rates are large enough, these reverse reactions will lower the overall rates of the isomerizations. Our kinetic data suggest that loss of chloride ion from the tetrahedral intermediates 8 and 9 is more important than in the tetrahedral intermediate 10. This inference is explicable in terms of the theory of stereoelectronic control because in 8 and 9 two nonbonded electron pairs (a and b) are antiperiplanar to the leaving chloride ion while only one nonbonded pair is antiperiplanar to the leaving chloride ion in 10.

Benzamidoximes 14, which have been shown to isomerize by rotation about the carbon–nitrogen bond of the conjugate acid,[7] isomerize much faster[8] than the compounds investigated in this study. Benzamidoximes represent a special case because delocalization of the positive charge in the conjugate acid of 14 is especially important, and as a consequence the equilibrium constant for protonation of 14 is large ($pK_a \simeq 4$ for 14).[7] The C=N bond order is reduced by this delocalization to the extent that rotation is faster than the rate of nucleophilic attack by the acid counterion.



14

Experimental Section

General Methods. All inorganic chemicals were reagent grade. The dioxane was obtained from Burdick and Jackson (distilled in glass) and was used without further purification. The hydroximoyl chlorides 1 and 2 and the hydroximates 6 and 7 were prepared according to published procedures[9,10] and were purified for the kinetic experiments by preparative gas–liquid chromatography followed by micromolecular distillation. The *O*-methyloximes 4a and 5a were prepared according to the procedure of Padwa and Albrecht.[3] ^1H NMR spectra were obtained on either a Varian A-60A or a Varian EM-390 NMR spectrometer. The infrared spectra were obtained with a Perkin-Elmer Model 225 or a Pye-Unicam SP1100 spectrophotometer. Solid samples were determined as Nujol mulls between sodium chloride plates, and liquid samples were run as thin films of the neat liquids between sodium chloride plates. The gas–liquid chromatography (GLC, analytical and preparative) was carried out with a column (30 ft ×0.375 in.) consisting of 20% silicon gum rubber (SE-30) on 45–60-mesh Chromosorb W. Analyses using thin-layer chromatography (TLC) were accomplished with silica gel sheets containing fluorescent indicator (Eastman Chromatograph Sheet No. 13181, Eastman Kodak Co.) and 10% ether–hexane as the developing solvent. Column chromatrographic separations were carried out with 5% ether–hexane as the eluting solvent on a 50 cm × 25 mm column packed with silica gel (0.2-mm grain size, Makerey, Nagel and Co.). High-performance liquid chromatography (HPLC) was carried out on a Corasil column with hexane–chloroform as the eluant. Microanalyses were carried out at Atlantic Microlab, Atlanta, GA.

(*E*)-*p*-Methoxyacetophenone *O*-Methyloxime (4b). A mixture of *p*-methoxyacetophenone oxime[11] (33.0 g, 0.200 mol), anhydrous potassium carbonate (44.3 g, 0.321 mol), and methyl iodide (56.8 g, 0.400 mol) in dimethylformamide (200 mL) was stirred for 72 h. After an initial exothermic reaction causing a rise in temperature to 40 °C, the temperature of the reaction mixture stabilized at 30 °C. The precipitate was filtered by vacuum filtration, and salt water (400 mL) was added to the filtrate. The organic material was extracted with ether (200 mL followed by 3 × 50 mL). The ether extracts were combined and washed with salt water (3 × 30 mL) and then with distilled water (3 × 30 mL). The ether was evaporated by means of rotary evaporation. Water (100 mL) was added to the residual liquid, and the aqueous mixture was cooled and acidified by slow addition of 12 N hydrochloric acid. The crude product was extracted with ether (4 × 100 mL). The acidic material was removed from the ether extract with 3 N sodium hydroxide (6 × 50 mL). The ether extract was then washed with water (4 × 50 mL), dried with anhydrous magnesium sulfate, and filtered. The ether was removed by means of rotary evaporation, and the crude product was analyzed by TLC and found to contain *p*-methoxyacetophenone, *p*-methoxyacetophenone oxime, and (*E*)-*p*-methoxyacetophenone *O*-methyloxime. Column chromatography of the crude product gave in the first fractions (*E*)-*p*-methoxyacetophenone *O*-methyloxime: 10.2 g (28%); mp 50–54 °C. Recrystallization from methanol–water gave white crystals: 10.1 g, mp 50–52 °C; IR (Nujol) 1614 cm^{-1} (s, C=N); NMR ($CDCl_3$) δ 2.19 (s, 3, CH_3), 3.82 (s, 3, $ArOCH_3$), 3.96 (s, 3, $NOCH_3$), 6.89 (d, J = 9 Hz, 2, aromatic H), 7.62 (d, J = 9 Hz, 2, aromatic H).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.16; H, 7.36; N, 7.92.

(*Z*)-*p*-Methoxyacetophenone *O*-Methyloxime (5b). A hexane (50 mL) solution of (*E*)-*p*-methoxyacetophenone *O*-methyloxime (0.90 g, 0.005 mol) was irradiated in a Rayonet photochemical reactor equipped with 2537-Å lamps. The reaction mixture was analyzed by TLC during the course of the irradiation, after 2.5 h the reaction was stopped, and the hexane was evaporated by means of rotary evaporation. The crude product contained a mixture of the *E* and *Z* isomers 4b and 5b along with some *p*-methoxyacetophenone and *p*-methoxyacetophenone oxime. The crude product from this reaction was combined with that from a similar reaction. Column chromatography of this combined material gave in the first fractions (*E*)-*p*-methoxyacetopheone *O*-methyloxime (0.85 g, 47%). Later fractions gave the *Z* isomer (0.65 g, 36%). Recrystallization of the *Z* isomer from methanol–water gave the analytical sample: mp 37–38 °C; IR (Nujol) 1607 cm^{-1} (s, C=N); NMR ($CDCl_3$) δ 2.19 (s, 3, CH_3), 3.83 (s, 3, $ArOCH_3$), 3.87 (s, 3, $NOCH_3$), 6.93 (d, J = 9 Hz, 2, aromatic H), 7.58 (d, J = 9 Hz, 2, aromatic H).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.99; H, 7.34; N, 7.82.

(*E*)-*p*-Nitroacetophenone *O*-Methyloxime (4c). The *O*-methyloxime 4c was prepared by reacting *p*-nitroacetophenone oxime[12] (38.8 g, 0.215 mol), anhydrous potassium carbonate (44.3 g, 0.321 mol), and methyl iodide (56.8 g, 0.400 mol) in dimethyl formamide (200 mL) as previously described for the preparation of the *O*-methyloxime 4b. The crude product was recrystallized from methanol to give 19.2 g (46%) of 4c, mp 107–110 °C. Further recrystallizations gave the analytical sample: 15.7 g (38%); mp 110–112 °C; IR (Nujol) 1602 and 1589 cm^{-1} (2 s, C=N); NMR ($CDCl_3$) δ 2.26 (s, 3, CH_3), 4.06 (s, 3, $NOCH_3$), 7.86 (d, J = 9 Hz, 2, aromatic H), 8.26 (d, J = 9 Hz, 2, aromatic H).

Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.67; H, 5.19; N, 14.43. Found: C, 55.62; H, 5.20; N, 14.40.

(*Z*)-*p*-Nitroacetophenone *O*-Methyloxime (5c). Ultraviolet irradiation of a benzene (50 mL) solution of (*E*)-*p*-nitroacetophenone *O*-methyloxime (0.97 g, 0.005 mol) for 3 h gave a mixture of the *Z* and *E* isomers which were separated by column chro-

(6) (a) Deslongchamps, P. *Heterocycles* **1977**, *7*, 1271. (b) *Pure Appl. Chem.* **1975**, *43*, 351. (c) *Tetrahedron* **1975**, *31*, 2463.

(7) (a) Dignam, K. J.; Hegarty, A. F. *J. Chem. Soc., Chem. Commun.* **1976**, 863. (b) Dignam, K. J.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1437.

(8) We found the isomerization of (*Z*)-*N*,*N*-tetramethylenebenzamide *O*-methyloxime in hydrogen chloride–dioxane solution too fast to follow by using conventional techniques.

(9) Johnson, J. E.; Nalley, E. A.; Weidig, C.; Arfan, M. *J. Org.* Chem. **1981**, *46*, 3623.

(10) Johnson, J. E.; Nalley, E. A.; Kunz, Y. K.; Springfield, J. R. *J. Org. Chem.* **1976**, *41*, 252. The configurational assignments made for the hydroximoyl chlorides in this paper must be reversed.[2]

(11) von-Auwers, K.; Lechner, M.; Bundesmann, J. *Ber.* **1925**, *58*, 36.

(12) Posner, T.; *Justus Leibigs Ann. Chem.* **1912**, *398*, 1.

matography. The *Z* isomer (0.41 g, 42%; mp 92–95 °C) was recrystallized from methanol to give the analytical sample: mp 93.5–95.5 °C; IR (Nujol) 1601 cm^{-1} (s, C=N); NMR ($CDCl_3$) δ 2.24 (s, 3, CH_3), 3.86 (s, 3, $NOCH_3$), 7.64 (d, J = 9 Hz, 2, aromatic H, 8.26 (d, J = 9 Hz, 2, aromatic H).

Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.67; H, 5.19; N, 14.43. Found: C, 55.57; H, 5.19; N, 14.45.

Kinetic Method. The isomerizations were followed by either GLC (**1**, **5a**, and **6**) or HPLC (**4b**,**c**). The details of the techniques used for following the kinetics have been described previously.[2] The rate constant for the isomerization of **6** to **7** was calculated from the equation derived from reversible first-order kinetics and the equilibrium constant for **6** $\rightleftarrows$ **7**.[13] Since the equilibrium favored the *E* isomer (**6**), the isomerization of **7** to **6** was followed.

Acknowledgment. We gratefully acknowledge support of this work by a grant from the Robert A. Welch Foundation and by a Texas Woman's University Institutional Research Grant.

Registry No. (*E*)-**1**, 41071-34-5; (*Z*)-**2**, 41071-35-6; **3b**, 2475-92-5; **3c**, 10342-64-0; (*E*)-**4a**, 15754-20-8; (*E*)-**4b**, 80965-21-5; (*E*)-**4c**, 80965-22-6; (*Z*)-**5a**, 15754-21-9; (*Z*)-**5b**, 80965-23-7; (*Z*)-**5c**, 80965-24-8; (*E*)-**6**, 41071-40-3; (*Z*)-**7**, 41071-39-0.

(13) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; p 186.

Total Synthesis of Pallescensin A

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Received September 14, 1981

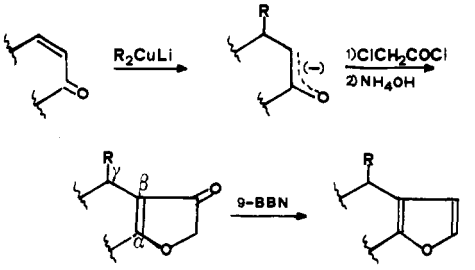
In recent papers[1,2] we have described a new method for the construction of fused furan rings and its application to the synthesis of some natural compounds.

An enolate anion was generated by conjugate addition of lithium dimethylcuprate to an α,β-unsaturated ketone and was quenched with chloroacetyl chloride. Then, base-promoted intramolecular ring closure afforded a β-furanone, which was easily reduced to the furan (Scheme I). By this route, only alkyl (R = Me or other) γ-substituted furans could be synthesized, whose occurrence in natural compounds is very limited.[3]

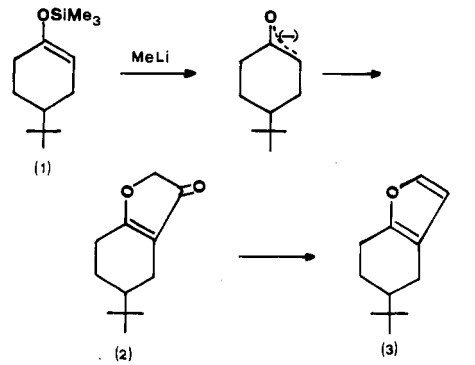
If the enolate anion had been directly generated from the corresponding saturated ketone, by the same procedure, γ-unsubstituted (R = H) furan compounds, which are more widespread in nature, should have been obtained.

A very simple substrate, i.e., 4-*tert*-butyl cyclohexanone, was first submitted to the described reaction sequence in order to check its applicability, with its trimethylsilyl enol ether[4] as a carbanion source. Compound **1** was reacted with methyllithium until disappearance of the starting material, and then the lithium enolate obtained was quenched with chloroacetyl chloride. Weak base (iced ammonia) extraction of the reaction mixture afforded **2**

Scheme I



Scheme II



in 82% yield (Scheme II). After 9-BBN reduction,[1] the furan compound **3** was isolated in excellent yield.

The same method was then applied for the synthesis of racemic pallescensin A (**4**), a furan sesquiterpenoid of unusual skeleton, which has been isolated by Cimino et al.[5] from the marine sponge *Disidea pallescens* and recently synthesized by Nasipuri and Das[6] by following a biomimetic scheme.

Ketone **5** was synthesized by starting from 2-methylcyclohexane-1,3-dione (in 38% overall yield) and following the procedure of Welch and Rao.[7]

Treatment of **5** with trimethylchlorosilane according to standard procedures[4] led to very poor yields of **6**, whereas ethyl (trimethylsilyl)acetate together with tetra-*n*-butylammonium fluoride[8] (Scheme III) successfully performed the transformation (73% yield).

After the above-described procedure, compound **6** afforded the β-furanone **7** in 81% yield. Smooth reduction of **7** gave pure racemic **4** in almost quantitative yield which proved to be identical with natural pallescensin A.[5]

Other classical methods for direct enolate formation by strong bases from **5** (e.g., LDA in THF) always failed, producing insignificant amounts of **7**.

Taking into account the well-known regioselectivity in trimethylsilyl enol ether formation[9] and the good yields of the subsequent steps, the above described method would seem to be promising in the field of the synthesis of natural furan compounds.

Experimental Section

^1H and ^{13}C NMR were recorded with a Varian XL-100 instrument (tetramethylsilane as an internal standard). IR spectra were registered on a Perkin-Elmer 257 spectrophotometer. Mass spectra were taken on a Varian Mat 112 spectrometer (DIS, 71-eV acceleration potential).

(1) S. Bernasconi, M. Ferrari, P. Gariboldi, G. Jommi, M. Sisti, and R. Destro, *J. Chem. Soc., Perkin Trans. 1*, 1994 (1981); S. Bernasconi, P. Gariboldi, G. Jommi, S. Montanari, and M. Sisti, *ibid.*, 2394 (1981).
(2) S. Bernasconi, P. Gariboldi, G. Jommi, M. Sisti, and P. Tavecchia, *J. Org. Chem.*, **46**, 3719 (1981).
(3) T. K. Devon and A. I. Scott, "Handbook of Naturally Occurring Compounds", Vol. II, Academic Press, New York and London, 1972.
(4) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
(5) G. Cimino, S. De Stefano, A. Guerriero, and L. Minale, *Tetrahedron Lett.*, 1417, 1421, 1425, 3723 (1975).
(6) D. Nasipuri and G. Das, *J. Chem. Soc.*, Perkin *Trans. 1*, 2776 (1979).
(7) S. C. Welch and A. S. C. P. Rao, *Tetrahedron Lett.*, 505 (1977).
(8) E. Nakamura, T. Murofushi, M. Shimuzu, and I. Kuwajima, *J. Am. Chem. Soc.*, **98**, 2346 (1976).
(9) G. H. Posner and C. M. Lentz, *J. Am. Chem. Soc.*, **101**, 934 (1979).

0022-3263/82/1947-1961$01.25/0