this sequence is that the product is an enol silyl ether of known geometry. As such, it can serve as a precursor to a variety of useful synthetic intermediates.[8]

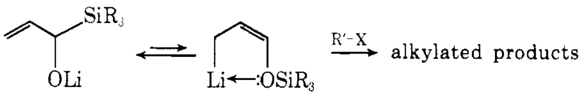
As outlined in Table I, these highly nucleophilic carbanions[9] can be alkylated by a variety of alkyl iodides and bromides.[10] Yields of aldehydes generally fall in the 80–90% range.[11] The only limitation observed thus far lies in the use of highly hindered alkylating agents. Although good yields of alkylated adducts are frequently obtained with these materials, the proportion of enol ether (**11**) in the product is unserviceably low (entry 6). Examination of other data in Table I reveals several other trends: (1) alkyl iodides give slightly better yields of **11** than do the corresponding bromides and (2) decreased halide substitution likewise leads to higher yields of terminally alkylated product.

The following experimental procedure is representative of the conversion. A solution of 2 mmol of the allyl silyl ether in 1 ml of dry tetrahydrofuran is added dropwise with stirring to a −78° solution of 2.4 mmol of *sec*-butyllithium in 10 ml of anhydrous deoxygenated tetrahydrofuran under a nitrogen atmosphere. When the addition is complete, 0.5 ml of hexamethylphosphoramide (HMPA) is added and the stirring continued for an additional 15 min. The alkyl halide (2.4 mmol) is then added. Stirring is continued for 15 min more and the solution allowed to slowly warm to room temperature. The reaction mixture is then poured into *n*-pentane, washed with saturated ammonium chloride and water (two times), and dried ($MgSO_4$). Solvent evaporation yields the crude product. Depending on the system, the product may be of sufficient purity to be used directly or may be purified by distillation.

**Acknowledgement.** The authors would like to thank Professor Gilbert Stork for his support and encouragement.

(8) These include such species as aldols (T. Mukaiyama, *et al.*, *Chem. Lett.*, 1011 (1973)), β-keto ethers (T. Mukaiyama and M. Hayashi, *ibid.*, 15 (1974)), enolates (ref 6b; G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462 (1968)), and cyclopropanols (S. Murai, T. Aya, and N. Sonoda, *J. Org. Chem.*, **38**, 4354 (1973)).

(9) Low temperature acid quenching suggests that the alkoxy silane, i, is the major anionic species in solution. Rapid equilibration with ii



and selective trapping presumably gives the observed products. Similar observations have been made with benzyl silyl ethers: A. Wright, D. Ling, P. Boudjouk, and R. West, *J. Amer. Chem. Soc.*, **94**, 4784 (1972).

(10) Chlorides and tosylates give only poor conversion to the desired products.

(11) We have also prepared ketones by this sequence. However, the starting secondary allylic ethers are metalated extremely slowly under our conditions with a corresponding low conversion to alkylated products.

**W. Clark Still,* T. L. Macdonald**
*Department of Chemistry, Columbia University*
*New York, New York 10027*

*Received May 17, 1974*

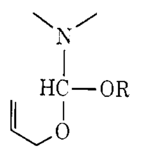
---

## Conversion of Allylic Alcohols to Homologous Amides by *N,N*-Dimethylformamide Acetals

*Sir:*

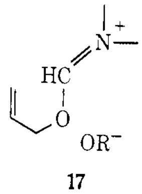
A wide variety of allylic alcohols are transformed to γ,δ-unsaturated amides when heated to approximately 160° with *N,N*-dimethylacetamide acetals.[1] We have discovered (see Table I) that certain allylic alcohols when treated similarly with *N,N*-dimethylformamide acetals are converted to homologous β,γ-unsaturated *N,N*-dimethylamides, often in synthetically useful yields. With the tertiary alcohols **1–4**, conversions were performed in xylene or collidine solutions. Slightly higher temperatures were required for the secondary alcohols **5** and **6**, and in the former case excess reagent had to be avoided because it condensed further with the amide **12** to yield a dimethylaminomethyleneamide. As judged by the behavior of geraniol (**7**), the method works poorly with γ,γ-disubstituted allylic alcohols.

After incomplete conversion the mixed amide acetals **16** were isolated from **1** and **7**. Thermolysis of the former gave the amide **8** while the latter was much more stable. Aqueous work-up regenerated geraniol (**7**). We assume that the mixed acetals, **16**, on being heated loose ethanol or neopentyl alcohol to give imidates, **17**, and then carbenes, **18**, which undergo a [2,3]sigmatropic rearrangement to produce amides. In support of this hypothesis we cite the facile formyl proton exchange in formamide acetals[2] and the previously discovered [2,3]sigmatropic rearrangement of a related carbene **19**.[3] The rate retarding effect of substituents on the double bond is attributed to nonbonding steric interactions in the transition state and/or the highly nucleophilic character of the carbene **18**.

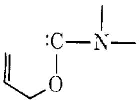


R = ethyl or neopentyl

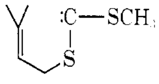
**16**



**17**



**18**



**19**

To probe the origin of amide **15** from geraniol **7**, (−)-*cis*-carveol (**20**) $[\alpha]^{25}$D −33.4 (*c* 5.6, $C_2H_5OH$) was transformed to a 88:12 mixture of diastereomeric amides **22**/**24** and **26**/**28**, both not epimerized under the reaction conditions. Intensity measurements of *N*-methyl and vinyl protons in the nmr spectrum of the major cis diastereomer $[\alpha]^{25}$D −14.8 (*c* 2.6, $C_2H_5OH$) in the presence of tris[*d,d*-dicampholylmethanato]-europium(III)[4] revealed the presence of two enantiomers in a ratio of 3:1. To determine their absolute configurations the transformation was performed on

---

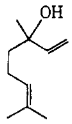
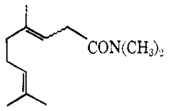
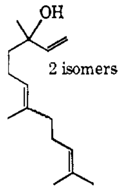
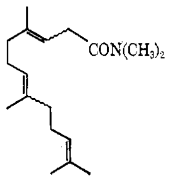
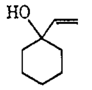
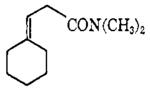
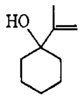
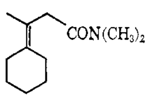
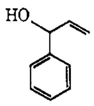
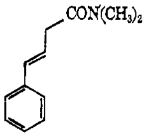
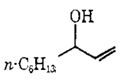
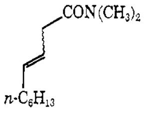
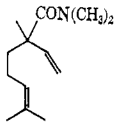
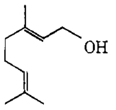
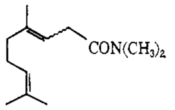
(1) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Justus Liebigs Ann. Chem.*, **641**, 1 (1961); A. E. Wick, D. Felix, K. Steen, and A. Eschenmoser, *Helv. Chim. Acta*, **47**, 2425 (1964); D. Felix, K. Gschwend-Steen, A. E. Wick, and A. Eschenmoser, *ibid.*, **52**, 1030 (1969); H. Muxfeldt, R. S. Schneider, and J. B. Mooberry, *J. Amer. Chem. Soc.*, **88**, 3670 (1966); D. F. Morrow, T. P. Culbertson, and R. M. Hofer, *J. Org. Chem.*, **32**, 361 (1967); W. Sucrow, *Angew. Chem.*, **80**, 626 (1968); D. J. Dawson and R. E. Ireland, *Tetrahedron Lett.*, 1899 (1968).

(2) G. Simchen, S. Rebsdat, and W. Kantlehner, *Angew. Chem., Int. Ed. Engl.*, **6**, 875 (1967).

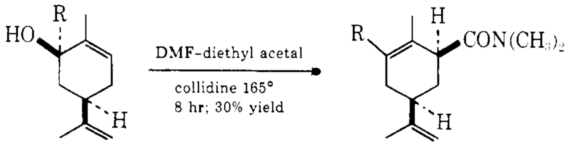
(3) J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 354 (1972).

(4) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 1038 (1974). We are grateful to Professor Whitesides for a gift of the shift reagent.

**Table I**

| Alcohol[a] | Amide[b] | % yield (isomer ratio) | Solvent (time, hr) | Temp, °C | DMF acetal (equiv) |
|---|---|---|---|---|---|
|  1 |  8 | 70 (42:58)<br>75 | Xylene (12)<br>Collidine (3) | 140<br>165 | Diethyl (6)<br>Dineopentyl (2.5) |
|  2 |  9 | 75 (4 isomers) | Xylene (14) | 140 | Diethyl (6) |
|  3 |  10 | 76<br>66 | Xylene (16)<br>Collidine (3) | 140<br>165 | Diethyl (6)<br>Dineopentyl (2.5) |
|  4 |  11 | 70<br>70 | Xylene (18)<br>Collidine (3) | 140<br>165 | Diethyl (6)<br>Dineopentyl (2.5) |
|  5 |  12 | 71 (trans only) | *o*-Dichlorobenzene (1.5) | 180[c] | Diethyl (1.1) |
|  6 |  13 | 56 (89 trans:11 cis)<br>77 (same) | Quinoline (2)<br>Tri-*n*-butylamine (4) | 180[c]<br>180[c] | Diethyl (1.1)<br>Diethyl (1.1) |
| |  14 | 6 | Collidine (22) | 165 | Dineopentyl (2.5) |
|  7 |  15 | 3 (95:5) | | | |

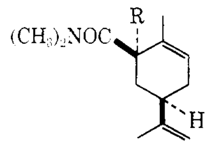
[a] Reactions were performed with 15 mmol of alcohol in 30 ml of collidine or with 5 mmol of alcohol in 20 ml of other solvents. Ethanol and neopentyl alcohol formed were removed continuously through a Claisen distillation head. [b] Satisfactory spectra were obtained for all amides. [c] The reaction mixture was heated initially at 140° for 1 hr.



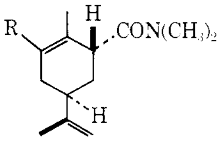
20, R = H
21, R = D

22, R = H
23, R = D

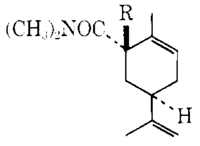
(−)-*cis*-carveol-2-$d_1$ (**21**). The ratio of products **23** and **25** determined by integration of the cyclic vinyl and methine protons in the nmr spectrum was 4 : 1, suggesting that the major products **22** and **23**, respectively, arise from a concerted rearrangement. The minor enantiomers **24** and **25** and the minor diastereomers **26**/**28** and **27**/**29** result from a dissociation–recombination mecha-



24, R = H
25, R = D



26, R = H
27, R = D



28, R = H
29, R = D

nism.[5] In agreement with this the trans diastereomer **26**/**28** had negligible optical rotation $[\alpha]^{25}\text{D}$ +2° ($c$ 0.6, $C_2H_5OH$) and in compounds **27**/**29** from deuterated carveol **21** the label was distributed equally between vinyl and methine positions.[5a]

**Acknowledgments.** We are indebted to the National Institutes of Health Grant No. GM 09686 and to Firmenich SA Geneva for generous financial support.

[5] Review: U. Schöllkopf, *Angew. Chem.*, **82**, 795 (1970); J. E. Baldwin, J. DeBernardis, and J. E. Patrick, *Tetrahedron Lett.*, 353 (1970), and earlier papers; V. Rautenstrauch, *J. Chem. Soc.*, *Chem. Comm.*, 4 (1970).

[5a] NOTE ADDED IN PROOF. Condensation of $CH_2{=}C(C_6H_5)CH_2OH$ in *o*-dichlorobenzene at 175° with 2.5 equiv of dimethylformamide dineopentyl acetal during 4 hr gave $CH_2{=}C(C_6H_5)CH_2CON(CH_3)_2$ in 55% yield.

[6] National Institutes of Health Postdoctoral Fellow, 1973–present.

**George Büchi,* Mark Cushman,[6] Hans Wüest**
*Department of Chemistry, Massachusetts Institute of Technology*
*Cambridge, Massachusetts 02139*

*Received June 10, 1974*

---

## Photochemical Cleavage of the Quadruple Bond in $[Re_2Cl_8]^{2-}$

*Sir:*

The thermal chemistry of $[Re_2Cl_8]^{2-}$ has been extensively investigated in recent years.[1-6] The quadruply bonded $Re_2$ unit has proved to be exceptionally inert, although occasionally monomeric products have been obtained.[1,3,4] We now report that bond cleavage has been achieved by ultraviolet irradiation of $CH_3CN$ solutions of $[Re_2Cl_8]^{2-}$, providing a very convenient synthetic route to monomeric chloro complexes of Re(III).

The absorption spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ (**1**) in $CH_3CN$ is shown in Figure 1 ("0" min). A detailed polarized single crystal electronic absorption spectral study of **1** and several closely related complexes has established that the 680-nm band is attributable to a $\delta \rightarrow \delta^*$ transition,[7,8] and has further suggested that the low intensity band at 370 nm represents a $\sigma \rightarrow \delta^*$ excitation.[8] Irradiation of a $6 \times 10^{-5}$ $M$ solution of **1** in $CH_3CN$ with a 1000-W Hg–Xe lamp equipped with a Pyrex filter results in the spectral changes shown in Figure 1.[9] The decrease in intensity of the 680-nm band suggests that the δ bond, and possibly the entire $Re_2$ unit, has been cleaved. Confirmation of $Re_2$ dissociation is provided by the observation that two monomeric products are isolated from a preparative scale photolysis.[10] The most abundant is an orange solid, $[ReCl_3(CH_3CN)_3]$[11] (**2**). The magnetic moment of **2**, 1.60 BM, accords well with values obtained[12-14] for monomeric Re(III) complexes. Complex **2** should be a valuable starting material for the preparation of related $[ReCl_3L_3]$ compounds. A tan compound, **3**, was isolated in very small yield. Although an insufficient amount of **3** was obtained to allow an elemental analysis, spectroscopic data suggest formulation as $[(n\text{-}C_4H_9)_4N][ReCl_4(CH_3CN)_2]$. The ir spectrum of **3** establishes that tetrabutylammonium is present, and the uv–visible and ir spectra attributable to the anionic component are identical with analogous features measured on a known sample of $[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$.[15] The disappearance quantum yield of $[Re_2Cl_8]^{2-}$ upon 313 nm excitation, determined by monitoring the decrease in absorbance at 680 nm, was found to be 0.017 ± 0.005. Irradiation of **3** in $CH_3CN$ results in a rapid conversion to **2**, but the spectral similarity of **2** and **3** precluded a quantum-yield determination for this photolysis. However, the quantum yield appears to be at least an order of magnitude greater than that for the disappearance of **1**. Infrared and electronic absorption spectral data of **1**–**3** are set out in Table I.

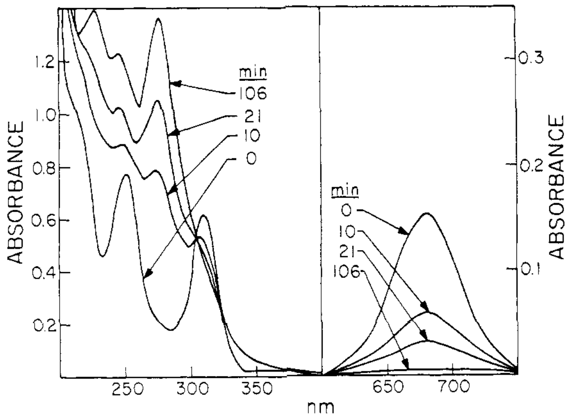


**Figure 1.** Pyrex-filtered irradiation of a $6 \times 10^{-5}$ $M$ acetonitrile solution of $[(n\text{-}C_4H_9)_4N_2[Re_2Cl_8]$.

As it is difficult to visualize the one-step conversion **1** → **2**, we prefer the reaction pathway outlined in Scheme I. The initial photoproduct under Pyrex-

---

(1) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

(2) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

(3) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967).

(4) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, **6**, 929 (1967).

(5) F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).

(6) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

(7) C. D. Cowman and H. B. Gray, *J. Amer. Chem. Soc.*, **95**, 8177 (1973).

(8) C. D. Cowman, Ph.D. dissertation, California Institute of Technology, 1973.

(9) $[(n\text{-}C_4H_9)_4]N]_2[Re_2Cl_8]$ was prepared by the method of Cotton *et al.* (F. A. Cotton, N. F. Curtis, B. F. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965)]. Photolysis was conducted in 1-cm quartz cuvettes thermostated at 25° using MC and B spectroquality $CH_3CN$. Spectral data were obtained using Cary 17 and Perkin-Elmer 225 spectrophotometers. Magnetic susceptibility measurements were performed on a Princeton Applied Research FM-1 vibrating sample magnetometer calibrated with $HgCo(SCN)_4$.

(10) Pyrex-filtered light was used to photolyze a solution containing 1 g of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in 75 ml of spectroquality $CH_3CN$. A continuous argon purge was maintained throughout the photolysis. After the solution had turned from blue to orange (typically 24–48 hr), the irradiation was discontinued and the solution was concentrated by evaporation. The resultant solution and precipitate were chromatographed on silica gel with $CH_2Cl_2$ as eluent. Evaporation of the $CH_2Cl_2$ eluent solution, followed by recrystallization of the resultant solid from $CH_2Cl_2$–$C_4H_{10}O$, gave analytically pure **2**. Continued $CH_3CN$-elution from the same column, followed by evaporation, gave **3**.

(11) *Anal.* Calcd for $[ReCl_3(CH_3CN)_3]$: Re, 44.80; Cl, 25.59; C, 17.32; N, 10.11; H, 2.17. Found: Re, 44.50; Cl, 25.53; C, 16.99; N, 10.46; H, 2.32.

(12) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 489 (1968).

(13) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 993 (1967).

(14) B. F. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 152 (1964).

(15) Photolysis of orange $[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$[12] (**4**) in $CH_3CN$ yields a tan compound, **5**, also analyzing for $[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$. Calcd: Re, 39.60; Cl, 30.20; N, 8.93; C, 17.86; H, 3.40. Found: Re, 40.37; Cl, 30.48; N, 8.71; C, 17.69; H, 3.51. Presumably, **4** and **5** are cis and trans isomers and ir evidence suggests that **4** is cis. The spectral properties of the anion of **3** are identical with those of the anion of **5**.