

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

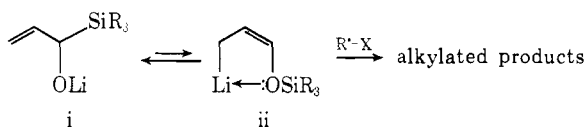
As outlined in Table I, these highly nucleophilic carbanions⁹ can be alkylated by a variety of alkyl iodides and bromides.¹⁰ Yields of aldehydes generally fall in the 80–90% range.¹¹ The only limitation observed thus far lies in the use of highly hindered alkylating agents. Although good yields of alkylated adducts are frequently obtained with these materials, the proportion of enol ether (11) in the product is unacceptably 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.

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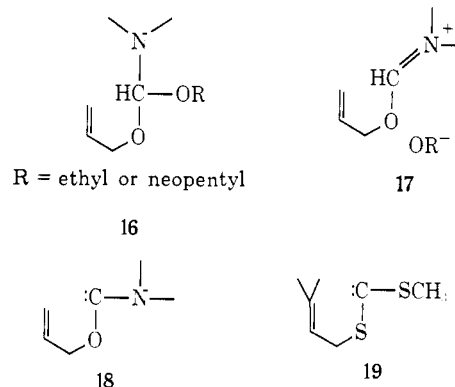
Conversion of Allylic Alcohols to Homologous Amides by *N,N*-Dimethylformamide Acetals

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 acetals² 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.

To probe the origin of amide 15 from geraniol 7, (–)-*cis*-carveol (20) [α]_D²⁵ –33.4 (*c* 5.6, $\text{C}_2\text{H}_5\text{OH}$) 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 [α]_D²⁵ –14.8 (*c* 2.6, $\text{C}_2\text{H}_5\text{OH}$) 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

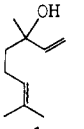
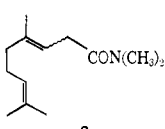
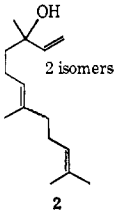
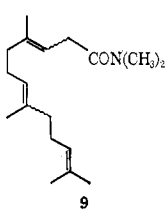

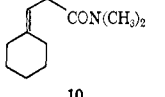

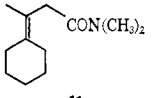
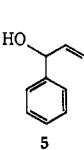
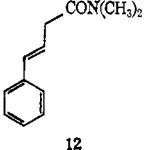
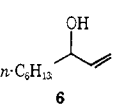
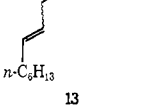
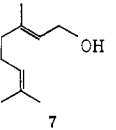
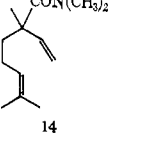
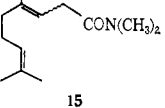
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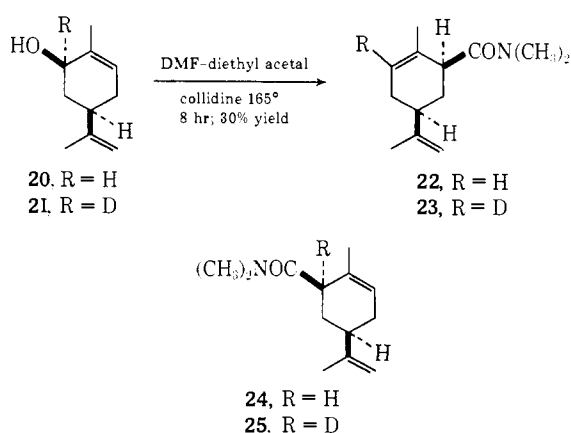
(3) J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 354 (1972).

(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.

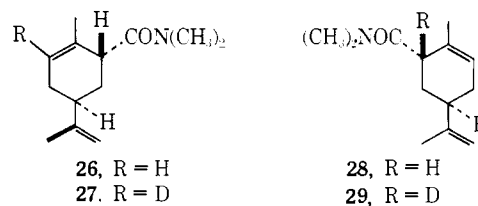
Table I

Alcohol ^a	Amide ^b	% yield (isomer ratio)	Solvent (time, hr)	Temp, °C	DMF acetal (equiv)
		70 (42:58) 75	Xylene (12) Collidine (3)	140 165	Diethyl (6) Dineopentyl (2.5)
		75 (4 isomers)	Xylene (14)	140	Diethyl (6)
		76 66	Xylene (16) Collidine (3)	140 165	Diethyl (6) Dineopentyl (2.5)
		70 70	Xylene (18) Collidine (3)	140 165	Diethyl (6) Dineopentyl (2.5)
		71 (trans only)	<i>o</i> -Dichlorobenzene (1.5)	180°	Diethyl (1.1)
		56 (89 trans:11 cis) 77 (same)	Quinoline (2) Tri- <i>n</i> -butylamine (4)	180° 180°	Diethyl (1.1) Diethyl (1.1)
		6			
			Collidine (22)	165	Dineopentyl (2.5)
		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.



(-)-*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-



nism.⁵ In agreement with this the trans diastereomer **26/28** had negligible optical rotation $[\alpha]_D^{25} + 2^{\circ}$ (*c* 0.6, C₂H₅OH) 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 CH₂=C(C₆H₅)-CH₂OH in *o*-dichlorobenzene at 175° with 2.5 equiv of dimethylformamide dineopentyl acetal during 4 hr gave CH₂=C(C₆H₅)CH₂CON-(CH₃)₂ in 55% yield.

(6) National Institutes of Health Postdoctoral Fellow, 1973-present.

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Photochemical Cleavage of the Quadruple Bond in [Re₂Cl₈]²⁻

Sir:

The thermal chemistry of [Re₂Cl₈]²⁻ has been extensively investigated in recent years.¹⁻⁶ The quadruply bonded Re₂ unit has proved to be exceptionally inert, although occasionally monomeric products have been obtained.^{3,4} We now report that bond cleavage has been achieved by ultraviolet irradiation of CH₃CN solutions of [Re₂Cl₈]²⁻, providing a very convenient synthetic route to monomeric chloro complexes of Re(III).

The absorption spectrum of [(*n*-C₄H₉)₄N]₂[Re₂Cl₈] (**1**) in CH₃CN 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 6×10^{-5} M solution of **1** in CH₃CN 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 Re₂ unit, has been cleaved. Confirmation of Re₂ dissociation is provided by the observation that two mono-

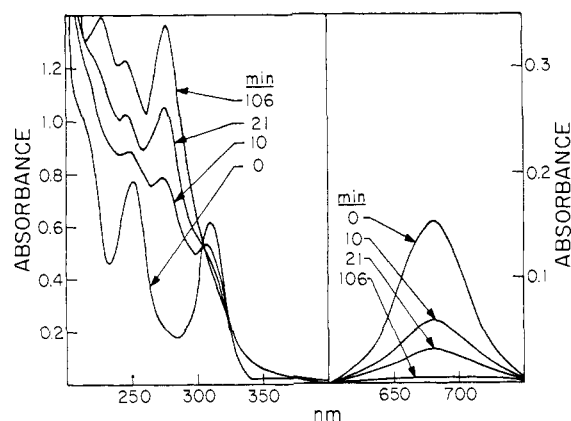


Figure 1. Pyrex-filtered irradiation of a 6×10^{-5} M acetonitrile solution of [(*n*-C₄H₉)₄N]₂[Re₂Cl₈].

meric products are isolated from a preparative scale photolysis.¹⁰ The most abundant is an orange solid, [ReCl₃(CH₃CN)₃]¹¹ (**2**). The magnetic moment of **2**, 1.60 BM, accords well with values obtained¹²⁻¹⁴ for monomeric Re(III) complexes. Complex **2** should be a valuable starting material for the preparation of related [ReCl₃L₃] 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*-C₄H₉)₄N][ReCl₄(CH₃CN)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 [(CH₃)₃NH][ReCl₄(CH₃CN)₂].¹⁵ The disappearance quantum yield of [Re₂Cl₈]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 CH₃CN 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.

As it is difficult to visualize the one-step conversion **1** \rightarrow **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).

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(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*-C₄H₉)₄N]₂[Re₂Cl₈] 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 CH₃CN. 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)₂.

(10) Pyrex-filtered light was used to photolyze a solution containing 1 g of [(*n*-C₄H₉)₄N]₂[Re₂Cl₈] in 75 ml of spectroquality CH₃CN. 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 CH₂Cl₂ as eluent. Evaporation of the CH₂Cl₂ eluent solution, followed by recrystallization of the resultant solid from CH₂Cl₂-C₄H₁₀O, gave analytically pure **2**. Continued CH₃CN-elution from the same column, followed by evaporation, gave **3**.

(11) *Anal.* Calcd for [ReCl₃(CH₃CN)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 [(CH₃)₃NH][ReCl₄(CH₃CN)₂]¹² (**4**) in CH₃CN yields a tan compound, **5**, also analyzing for [(CH₃)₃NH][ReCl₄(CH₃CN)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**.