Registry No. 1a, 63436-79-3; 1b, 70867-35-5; 1c, 16308-68-2; 2 (R = Et; R′ = H; R″ = CH_2CH_2Ph), 6970-83-8; 2 (R = Me; R′ = H; R″ = CH_2CH_2Ph), 26011-68-7; 2 (R = Ph; R′ = H; R″ = CH_2CH_2Ph), 56379-81-8; 2 (R = Et; R′ = Me; R″ = CH_2Ph), 59325-17-6; 2 (R = Et; R′ = R″ = $-(CH_2)_4-$), 5470-26-8; 2 (R = Me; R′ = R″ = $-(CH_2)_4-$), 56475-80-0; 2 (R = Et; R′ = R″ = $-CH_2CH_2OCH_2CH_2-$), 6976-49-4; 2 (R = Et; R′ = R″ = —CH=NCH=CH—), 19213-72-0; 2 (R = Et; R′ = R″ = Ph), 101-99-5; 2 (R = Et; R′ = H; R″ = (1-naphthalenyl)), 19188-90-0; 2 (R = Et; R′ = H; R″ = $CH_2CH_2NH_2$), 36553-29-4; 2 (R = Et; R′ = H; R″ = $CH_2CH_2NHCO_2C_2H_5$), 818-42-8; 2 (R = Et; R′ = H; R″ = $(CH_2)_3OH$), 74877-62-6; 2 (R = Et; R′ = H; R″ = $CH(CH_3)CH_2OH$), 74877-63-7; 2 (R = Et; R′ = R″ = $-CH_2CH_2N(CH_2CH_2OH)-CH_2CH_2-$), 14000-66-9; 2 (R = Et; R′ = H; R″ = $CH(CH_2Ph)CO_2H$) (L isomer), 19887-32-2; 2 (R = Et; R′ = H; R″ = $CH(CH_2Ph)CO_2H$) (D isomer), 21488-23-3; 2 (R = Et; R′ = R″ = $-CH(CO_2H)-CH_2CH_2CH_2$) (L isomer), 5700-74-3; 3a, 74877-64-8; 3b, 74877-65-9; 3c, 74877-66-0; phenethylamine, 64-04-0; *N*-methylbenzenemethanamine, 103-67-3; pyrrolidine, 123-75-1; morpholine, 110-91-8; 1*H*-imidazole, 288-32-4; benzeneamine, 62-53-3; 1-naphthalenamine, 134-32-7; 1,2-ethanediamine, 107-15-3; 3-amino-1-propanol, 156-87-6; 2-amino-1-propanol, 78-91-1; 1-piperazineethanol, 103-76-4; L-phenylalanine, 63-91-2; D-phenylalanine, 673-06-3; L-proline, 147-85-3; ethyl chloroformate, 541-41-3; bis[(carbomethoxy)methyl]-mercury, 3600-21-3; methyl chloroformate, 79-22-1; phenyl chloroformate, 1885-14-9.

(22) Baker, J. C.; Ough, C. S. *J. Agric. Food Chem.* **1976**, *24*, 528.

Reactions of [3-(Dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium Chloride with Methyl Ketones, Primary Amines, and Unsubstituted Amides

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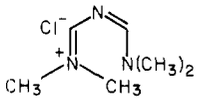
Received April 29, 1980

Considerable interest has recently developed concerning the preparation[1] and utilization[2] of preformed imminium salts. In 1960 Gold[3] described the preparation of a novel imminium salt, [3-(dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium chloride (1), but little has been done since then to clarify its synthetic utility and mode of reaction.



1

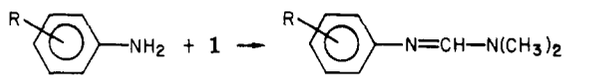
Gold has shown that 1 can be prepared in quantitative yield from cyanuric chloride and *N,N*-dimethylformamide (see Experimental Section) and that this reagent can be reacted with hydrazines to yield 1,2,4-triazoles. In this investigation it was also found that amidines[4] reacted with 1 to give either 2-monosubstituted or 2,4-disubstituted

(1) (a) A. Eschenmosher, J. Schreiber, H. Magg, and N. Hashimoto, *Angew. Chem., Int. Ed. Engl.*, **10**, 330 (1971); (b) T. A. Bryson, G. H. Bonitz, C. J. Reichel, and R. E. Dardis, *J. Org. Chem.*, **45**, 524 (1980).

(2) (a) S. Danishefsky, T. Kitahara, R. McKee, and P. F. Shuda, *J. Am. Chem. Soc.*, **98**, 6715 (1976); (b) S. Danishefsky, P. F. Shuda, T. Kitahara, and S. J. Etheredge, *ibid.*, **99**, 6066 (1977); (c) J. Hooz and J. N. Bridson, *ibid.*, **95**, 602 (1973); (d) C. C. Poulter, J. L. Roberts, and P. S. Borromeo, *Tetrahedron Lett.*, 1299 (1977); (e) G. Kunst and L. F. Tietze, *Angew. Chem., Int. Ed. Engl.*, **15**, 239 (1976); (f) N. L. Holy and Y. F. Wang, *J. Am. Chem. Soc.*, **99**, 944 (1977).

(3) H. Gold, *Angew. Chem.*, **72**, 956 (1960); *Chem. Abstr.*, **57**, 4542*d* (1962).

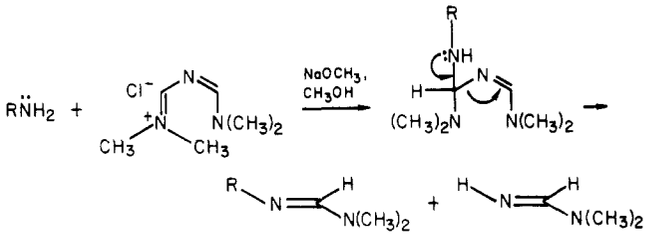
Table I



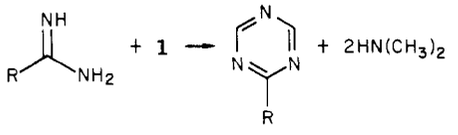
entry	R	% yield[a]	bp or mp, °C
1	4-Me	74	177 (30 mm) [lit.[5] 163 (30 mm)]
2	2-Me[b]	97	85 (3 mm)
3	4-NO_2	84	74-75 (lit.[6] 82-83)
4	4-Br[c]	86	118 (3 mm)
5	2-NH_2[d]	76	169-171 (lit.[7] 172-174)

[a] The yields reported refer to isolated products and nonoptimized conditions. All reaction products, with the exception of benzimidazole, were synthesized independently by the reaction of the appropriate amine with *N,N*-dimethylformamide dimethyl acetal.[8] An authentic sample of benzimidazole was obtained from Nutritional Biochemicals of Cleveland, OH. All reaction products gave NMR and IR spectra and TLC behavior identical with those of the authentic samples. [b] NMR ($CDCl_3$) δ 2.26 (s, 3 H), 2.98 (s, 6 H), 6.98 (m, 4 H), 7.38 (s, 1 H); IR ($CHCl_3$) 1640, 1600, 1480, 1370, 730 cm^{-1}; UV (EtOH) 253 (ε 10 400), 235 nm (10 200); mass spectrum, *m/e* (relative intensity) 162 (76), 147 (47), 118 (100). [c] For spectral data, see the experimental section. [d] The product of this reaction was benzimidazole.

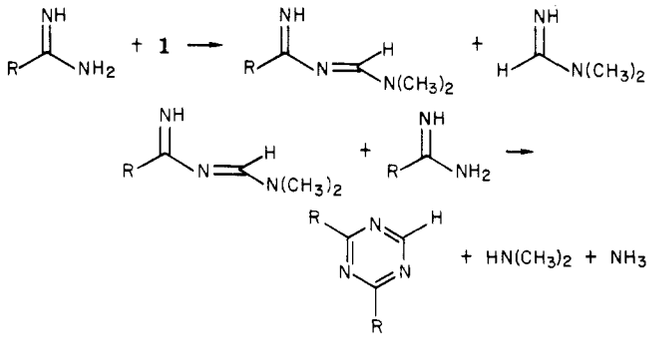
Scheme I



Scheme II



Scheme III



(4) Benzamidine and guanidine were the amidines studied.

(5) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Justus Liebigs Ann. Chem.*, **641**, 1 (1961).

(6) H. Bredereck, F. Effenberger, and T. Brendle, *Angew. Chem.*, **78**, 147 (1966).

(7) "Aldrich Handbook of Fine Chemicals", Aldrich Chemical Co., Milwaukee, WI, 1980, p 91.

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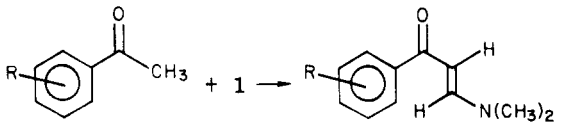
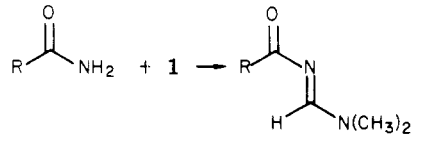
Table II



entry	R	% yield[a]	bp or mp, °C
6	H	83	88–89 (lit.[5] 90)
7	4-NO_2[b]	56	142–143
8	4-Br[c]	74	75–76
9	4-OCH_3[d]	90	89–90

[a] The yields reported refer to isolated products and nonoptimized conditions. All reaction products were synthesized independently by the reaction of the appropriate ketone with *N,N*-dimethylformamide dimethyl acetal.[8] All reaction products gave NMR and IR spectra and TLC behavior identical with those of authentic samples. [b] NMR ($CDCl_3$) δ 3.18 (br s, 6 H), 5.70 (d, J = 12 Hz, 1 H), 7.83 (d, J = 12 Hz, 1 H), 8.00 (d, J = 8 Hz, 2 H), 8.23 (d, J = 8 Hz, 2 H); IR ($CHCl_3$) 1635, 1600, 1545, 1420, 1340, 850 cm^{-1}; UV (EtOH) 363 (ε 12 000), 271 nm (16 900); mass spectrum, *m/e* (relative intensity) 220 (49), 219 (3), 205 (9), 204 (16), 203 (100). Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 60.00; H, 5.50; N, 12.72. Found: C, 58.95; H, 5.46; N, 12.55. [c] For spectral data, see the experimental section. [d] The yield for this reaction is based on recovered starting material: NMR ($CDCl_3$) δ 2.96 (s, 6 H), 3.76 (s, 3 H), 5.50 (d, J = 13 Hz, 1 H), 6.75 (d, J = 8 Hz, 2 H), 7.45 (d, J = 13 Hz, 1 H), 7.78 (d, J = 8 Hz, 2 H); IR ($CHCl_3$) 1645, 1580, 1555, 1430, 1350, 900 cm^{-1}; UV (EtOH) 337 (ε 29 000), 267 nm (ε 13 500); mass spectrum, *m/e* (relative intensity) 205 (49), 204 (5), 190 (8), 189 (14), 188 (100). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.26; H, 7.32; N, 6.83. Found: C, 69.91; H, 7.34; N, 6.75.

Table III



entry	R	% yield[a]	bp or mp, °C
10	phenyl	91	71–73 (lit.[9] 73–75)
11	4-nitrophenyl	81	132–135 (lit.[9] 141–143)
12	3-pyridyl	89	60–62 (lit.[9] 64–66)

[a] The yields reported refer to isolated products and nonoptimized conditions. All reaction products were characterized by NMR, IR, and TLC behavior.

1,3,5-triazines, depending on the nature of the reaction conditions.

To further examine the behavior of 1 we have studied its reaction with primary arylamines, aryl methyl ketones, and unsubstituted arylamides. Amines were found to produce *N,N*-dimethylamidines (Table I), ketones were found to produce *N,N*-dimethylenamino ketones (Table II), and amides were found to produce *N'*-acyl-*N,N*-dimethylformamidines (Table III).

Scheme I depicts a possible mechanism to account for the reaction of 1 with primary amines.[10]

Apparently, *N,N*-dimethylformamidine is a better leaving group than the *N,N*-dimethylamino moiety under the reaction conditions studied.[11] This mode of reaction may explain why Gold observed both 2-monosubstituted (Scheme II) and 2,4-disubstituted (Scheme III) 1,3,5-triazines in his reaction of 1 with amidines.

Although "Gold's reagent" (1) produces products identical with those obtained from *N,N*-dimethylformamide dimethyl acetal, it appears to have some advantages in terms of cost, ease of preparation, long-term stability, and mild reaction conditions. It should also be advantageous since it can react with anions, whereas the reaction of anions with amide acetals has not been reported and would seem to be an unlikely prospect.[8] For the compounds studied so far (Tables I–III), imminium salt 1 and *N,N*-dimethylformamide dimethyl acetal form products in the same yield range. We are continuing to investigate the reactions of 1 with other nucleophiles which may lead to synthetically useful transformations.

Experimental Section[12]

The following procedures are typical of the experimental conditions used for the reaction of amines, ketones, and amides with [3-(dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium chloride.

[3-(Dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium Chloride (1). To a solution of cyanuric chloride (148 g, 0.803 mol) in dioxane (800 mL) at 25 °C was added 386 g (5.28 mol) of *N,N*-dimethylformamide. The mixture was stirred and heated at 65 °C for 0.75 h at which point a vigorous, exothermic reaction ensued with evolution of carbon dioxide. The reaction temperature was maintained between 65 and 85 °C for 2–3 h, during which a mineral oil bubbler was used to monitor gas evolution. At this point gas evolution was minimal and the reaction mixture was cooled to room temperature with subsequent crystallization of the product. The solid was rapidly filtered and dried in vacuo overnight to yield 339 g (86%) of a tan solid: mp 94–96 °C (lit.[3] mp 101–103 °C); NMR ($CDCl_3$) δ 3.22 (s, 3 H), 3.40 (s, 3 H), 9.07 (s, 1 H); IR ($CHCl_3$) 3300, 1600, 1410, 1345, 1120, 1050 cm^{-1}; UV (EtOH) 286, 242 nm.

***N,N*-Dimethyl-*N'*-*p*-bromophenylformamidine.** A solution of sodium methoxide in methanol was prepared by the addition of 1.4 g (0.060 mol) of sodium metal to 100 mL of absolute methanol. After all of the sodium had reacted, the solution was cooled to room temperature and 8.6 g (0.060 mol) of *p*-bromoaniline was added in one portion. After the solution had stirred for several minutes, 10.6 g (0.065 mol) of [3-(dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium chloride was added and the resulting mixture was refluxed with stirring overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The residue was taken up in chloroform (100 mL) and extracted twice with an aqueous solution of sodium bicarbonate (30 mL portions). The resulting chloroform phase was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo to afford 13.3 g of a dark brown oil. The material was distilled (Kugelrohr) to yield 9.8 g (86% yield) of the amidine as a yellow oil: bp 145–155 °C (4 mm); NMR ($CDCl_3$) δ 2.93 (s, 6 H), 6.72 (d, J = 8 Hz, 2 H), 7.25 (d, J = 8 Hz, 2 H),

(8) R. F. Abdulla and R. S. Brinkmeyer, *Tetrahedron Lett.*, 1675 (1979).
(9) Y. Lin, S. A. Lang, M. F. Lovell, and N. A. Perkinson, *J. Org. Chem.*, 44, 4160 (1979).
(10) Mechanistically, ketones and amides should react in a similar manner except that the attacking nucleophile is an anion.
(11) When phenylhydrazine was reacted with 1 in the presence of $NaOCH_3$ and CH_3OH, 1-phenyl-1,2,4-triazole was produced. This data would seem to rule out *N,N*-dimethylformamide dimethyl acetal as a potential intermediate. In addition, NMR absorptions corresponding to *N,N*-dimethylformamidine could be observed in the crude reaction mixtures (reported in Table I) prior to extraction with aqueous sodium bicarbonate.
(12) Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrophotometer, using either CCl_4 or $CHCl_3$ as the solvent. NMR spectra were obtained in CCl_4, $CDCl_3$, or Me_2SO-d_6 solutions [$(CH_3)_4Si$ internal standard] at 60 MHz with a Varian T-60 spectrometer. Ultraviolet spectra were obtained with a Perkin-Elmer 552 spectrophotometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. TLC analysis was carried out, utilizing Merck silica GF-254 (type 60). All boiling points and melting points are uncorrected and melting points were recorded on a Fisher-Johns melting-point apparatus.

7.36 (s, 1 H); IR ($CHCl_3$) 1630 (C=N), 1580, 1480 (aromatic C=C), 1370 (aromatic C—N), 830 cm^{-1} (aromatic CH); UV (EtOH) 268 nm (ϵ 7600); mass spectrum, m/e (relative intensity) 228 (82), 226 (100), 213 (57), 211 (61), 186 (46), 184 (71).

β-(Dimethylamino)vinyl *p*-Bromophenyl Ketone. A solution of sodium methoxide in methanol was prepared by the addition of 1.5 g (0.065 mol) of sodium metal to 100 mL of absolute methanol. After all of the sodium had reacted, the solution was cooled to room temperature and 10.0 g (0.050 mol) of *p*-bromoacetophenone was added in one portion. After the solution had stirred for several minutes, 10.6 g (0.065 mol) of [3-(dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium chloride was added and the resulting mixture was refluxed with stirring overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The residue was taken up in chloroform (100 mL) and extracted twice with an aqueous solution of sodium bicarbonate (30-mL portions). The resulting chloroform phase was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo to afford 13.5 g of a dark brown solid. This material was stirred with 50 mL of a 10% carbon tetrachloride/hexane mixture and filtered to give 9.4 g (74% yield) of the enamino ketone as a light brown solid: mp 75–76 °C; NMR ($CDCl_3$) δ 2.98 (s, 6 H), 5.68 (d, J = 13 Hz, 1 H), 7.45 (d, J = 9 Hz, 2 H), 7.72 (d, J = 9 Hz, 2 H), 7.72 (d, J = 13 Hz, 1 H); IR ($CHCl_3$) 1640 (C=O), 1575 (C=C), 1535, 1420 (aromatic C=C), 1353 (C—N), 900 cm^{-1} (aromatic CH); UV (EtOH) 343 (ϵ 21 900), 248 nm (ϵ 13 000). Anal. Calcd for $BrC_{11}H_{12}NO$: C, 51.99; H, 4.76; N, 5.51. Found: C, 51.61; H, 4.76; N, 5.44; mass spectrum, m/e (relative intensity) 255 (28), 254 (8), 253 (39), 252 (4), 240 (6), 239 (10), 238 (99), 237 (12), 236 (100).

N′-(*p*-Nitrobenzoyl)-*N*,*N*-dimethylformamidine. A solution of sodium isopropoxide in isopropyl alcohol was prepared by the addition of 1.4 g (0.060 mol) of sodium metal to 100 mL of absolute isopropyl alcohol. After all of the sodium had reacted, the solution was cooled to room temperature and 8.3 g (0.050 mol) of *p*-nitrobenzamide was added in one portion. After the solution had stirred for several minutes, 10.6 g (0.065 mol) of [3-(dimethylamino)-2-azaprop-2-en-1-ylidene]dimethylammonium chloride was added and the resulting mixture was refluxed with stirring overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The residue was taken up in chloroform (100 mL) and extracted twice with an aqueous solution of sodium bicarbonate (30-mL portions). The resulting chloroform phase was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo to afford 13.1 g of a yellow solid. This material was recrystallized from 10:1 carbon tetrachloride–chloroform to give 8.9 g (81% yield) of a white solid: mp 132–135 °C (lit.[9] mp 141–143 °C); NMR ($CDCl_3$) δ 3.20 (s, 6 H), 8.12 (d, J = 9 Hz, 2 H), 8.34 (d, J = 9 Hz, 2 H), 8.31 (s, 1 H); IR ($CHCl_3$) 1630 (C=O), 1600 (C=N), 1580 (aromatic NO_2), 1470 (aromatic C=C), 1330 (aromatic NO_2), 830 cm^{-1} (aromatic CH).

Acknowledgment. This research was supported in part by grants from the Research Corporation and the University of Central Florida, Division of Sponsored Research. We also thank the Foods Division of Coca-Cola Company, Plymouth, FL, for the gift of the mass spectrometer and Mr. Garry Kiefer of L.S.U. for obtaining the combustion analyses and some of the mass spectra. We would also like to thank Dr. John P. Idoux for helpful discussions during the course of this work.

Registry No. 1, 20353-93-9; cyanuric chloride, 108-77-0; *N*,*N*-dimethylformamide, 68-12-2; *p*-toluidine, 106-49-0; *o*-toluidine, 95-53-4; *p*-nitroaniline, 100-01-6; *p*-bromoaniline, 106-40-1; *o*-phenylenediamine, 95-54-5; *N*,*N*-dimethyl-*N*′-*p*-methylphenylformamidine, 7549-96-4; *N*,*N*-dimethyl-*N*′-*o*-methylphenylformamidine, 10278-71-4; *N*,*N*-dimethyl-*N*′-*p*-nitrophenylformamidine, 1205-59-0; *N*,*N*-dimethyl-*N*′-*p*-bromophenylformamidine, 13181-50-5; benzimidazole, 51-17-2; acetophenone, 98-86-2; *p*-nitroacetophenone, 100-19-6; *p*-bromoacetophenone, 99-90-1; *p*-methoxyacetophenone, 100-06-1; β-(dimethylamino)vinyl phenyl ketone, 1201-93-0; β-(dimethylamino)vinyl *p*-nitrophenyl ketone, 68760-11-2; β-(dimethylamino)-vinyl *p*-bromophenyl ketone, 73387-60-7; β-(dimethylamino)vinyl *p*-methoxyphenyl ketone, 18096-70-3; benzamide, 55-21-0; *p*-nitrobenzamide, 619-80-7; nicotinamide, 98-92-0; *N*′-benzoyl-*N*,*N*-dimethylformamidine, 41876-75-9; *N*′-(*p*-nitrobenzoyl)-*N*,*N*-dimethylformamidine, 65675-91-4; *N*′-nicotinoyl-*N*,*N*-dimethylformamidine, 71565-88-3.

Communications

Effect of Substituents on the Structure and Catalytic Activity of Arene Chromium Tricarbonyls

Summary: Heteroatom substituents induce a strong perturbation in the six-electron ligand–metal bond of arene $Cr(CO)_3$ compounds, which enhance their catalytic activity.

Sir: The use of chromium tricarbonyl compounds as catalysts for the regioselective 1,4-hydrogenation of dienes to monoenes is of special interest in view of the high cis stereospecificity of products attained in the reaction.[1] The simple monoarenes thermally catalyze the reaction at high pressures (50 atm) and high temperatures (150–175 °C).[2] It has been reported that electron-withdrawing substituents in the arene accelerated the reaction while electron-donating group (CH_3) inhibited, to a large extent, the efficiency of the catalyst.[3] It has been suggested that the true catalytic species in a coordinating solvent (L) was $L_3Cr(CO)_3$.[4] These properties were related to the changes in the total metal–arene bond strength. However, this simple scheme does not account for the new substituent effects shown here that allow catalytic hydrogenation under surprisingly mild conditions (70 °C).[5]

All the complexes were prepared by using slight modifications of Pauson's procedure[6] and the catalytic experiments were carried out in a Burton Corblin A.F.P. 305 magnet drive autoclave.

The hydrogenation of methyl sorbate into methyl 3-hexenoate in THF has been studied as a test reaction. Some characteristic results are listed in Table I. The following comments can be made. (1) The catalytic efficiency of arene complexes bearing heterosubstituents is

(1) For a review, see M. Cais and D. Fraenkel, *N.Y. Acad. Sci.*, in press.
(2) M. Cais, E. N. Frankel, and A. Rejoan, *Tetrahedron Lett.*, 1919 (1968).
(3) E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, 34, 3930 (1969).
(4) Y. Eden, O. Fraenkel, M. Cais, and E. A. Halevi, *Isr. J. Chem.*, 15, 223 (1976).
(5) The possibility of decreasing the reaction temperature in these systems is important in order to favor cheap, clean, and selective reactions (G. Yagupsky and M. Cais, *Inorg. Chim. Acta*, 12, 127 (1975)). Consequently, pressure conditions may also be diminished (e.g., 70 °C and 6 atm).
(6) C. A. Mahaffy and P. L. Pauson, *Inorg. Synth.*, 19, 154 (1979).

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