Anal. Calcd for $C_{16}H_{10}NO_4$: C, 66.4; H, 6.6; N, 4.8. Found: C, 66.5; H, 6.7; N, 4.7.

Distillation of the crude dehydrogenation product at 148 °C (5×10^{-4} mm) gave only dimethyl indole-6,7-dicarboxylate: IR 1750 cm^{-1} (ν C=O); NMR δ 3.84 (s, 3), 3.85 (s, 3), 6.50 (dd, 1), 7.22 (d, 1), 7.26 (m, 1), 7.72 (d, 1).

Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.8; H, 4.75; N, 6.0. Found: C, 62.2; H, 5.2; N, 5.6.

Dimethyl 1-Methylindole-4,7-dicarboxylate. 1-Methyl-2-vinylpyrrole (0.43 g, 0.004 mol) in benzene (15 mL) was refluxed with methyl propiolate (0.67 g, 0.008 mol) and hydroquinone (0.01 g) for 2 days. The volume was reduced to 5 mL, and petroleum ether (bp 40–60 °C) was added to give the indole diester: 0.48 g (73%); mp 69–70 °C; IR 1710 cm^{-1} (ν C=O); NMR δ 3.38 (s, 3), 3.88 (s, 6), 6.98 (d, 1), 7.11 (d, 1), 7.48 (d, 1), 7.70 (d, 1).

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.1; H, 5.3; N, 5.7. Found: C, 63.6; H, 5.6; N, 6.1.

Dimethyl 1-phenylindole-4,7-dicarboxylated (yield 59%; mp 105.5 °C) was prepared by a method analogous to that used for the 1-methyl derivative: IR 1710 cm^{-1} (ν C=O); NMR δ 3.16 (s, 3), 3.98 (s, 3), 7.2–7.5 (m, 7), 7.52 (d, 1), 7.93 (d, 1).

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.9; H, 4.9; N. 4.5. Found: C, 70.0; H, 4.9; N, 4.5.

Methyl 1-*tert*-Butyl-4,5-dihydroindole-7-carboxylate. 1-*tert*-Butyl-3-vinylpyrrole (1.49 g, 0.01 mol) in benzene (10 mL) was refluxed with methyl propiolate (0.84 g, 0.01 mol) in the presence of hydroquinone (0.05 g) for 3 days. The solvent and unchanged vinylpyrrole (0.5 g) were removed under reduced pressure, and the residue was distilled to give the dihydroindole-7-carboxylic ester (0.65 g, 44% based on reacted unrecovered vinylpyrrole) as a yellow oil: bp 115–116 °C (0.05 mm); IR 1710 cm^{-1} (ν C=O); NMR δ 1.43 (s, 9), 2.0–2.5 (m, 4), 3.71 (s, 3), 5.91 (d, 1), 6.46 (t, 1), 6.73 (d, 1).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.1; H, 8.2; N, 6.0. Found: C, 71.9; H, 8.2; N, 5.85.

Methyl 1-*tert*-Butylindole-7-carboxylate. Aromatization of the 4,5-dihydroindole-7-carboxylic ester with DDQ gave methyl 1-*tert*-butylindole-7-carboxylate (78%), which was purified by elution from a column of alumina with petroleum ether (bp 40–60 °C)–diethyl ether (4:1): IR 1710 cm^{-1} (ν C=O); NMR δ 1.65 (s, 91), 3.86 (s, 3), 6.45 (d, 1), 6.98 (t, 1), 7.25 (dd, 1), 7.35 (dd, 1), 7.64 (dd, 1).

Anal. Calcd for $C_{14}H_{17}NO_2$: N, 6.1; *m/e* 231.1255 (M^+). Found: N, 6.5; *m/e* 231.1258 (M^+).

Distillation of the ester at 115 °C (0.001 mm) caused partial decomposition with the loss of the *tert*-butyl group.

Dimethyl 1-*tert*-Butylindole-4,7-dicarboxylate. 1-*tert*-Butyl-3-vinylpyrrole (0.45 g, 0.003 mol) and methyl propiolate (0.8 g, 0.01 mol) in benzene (10 mL) were heated under reflux in the presence of hydroquinone (0.05 g) for 4 days. Removal of the solvent and chromatographic purification of the residual oil gave the thermally unstable dimethyl 1-*tert*-butylindole-4,7-dicarboxylate: 0.57 g (66%); NMR δ 1.64 (s, 9), 3.86 (s, 3), 3.88 (s, 3), 6.77 (d, 1), 7.20 (d, 1), 7.45 (d, 1), 7.70 (d, 1).

Anal. Calcd for $C_{16}H_{19}NO_4$ (M^+): *m/e* 289.1314. Found: *m/e* 289.1325.

Distillation of the diester at ca. 150 °C (5×10^{-4} mm) caused considerable decomposition with the loss of the *tert*-butyl group.

Kinetic Measurements. The ^1H NMR spectra of equimolar equivalents of 1-methyl-2-vinylpyrrole and the appropriate dienophile in $CDCl_3$, containing 1,2-dichlorobenzene as a standard, were measured periodically. The average of ten integration values for the vinyl signals at 4.50 and 5.42 ppm and a suitable signal characteristic of the cycloadducts were normalized by comparison with the intensity of the aromatic signals for the standard.

Registry No. 1a, 2540-06-9; **1b**, 74304-92-0; **2**, 74304-93-1; **5**, 74809-21-5; **6**, 74809-22-6; **7**, 74809-23-7; **9** (R = Me), 74825-03-9; **9** (R = Ph), 74809-24-8; **10**, 74809-25-9; **11**, 74809-26-0; **12**, 74809-27-1; 2-formyl-1-methylpyrrole, 1192-58-1; 2-formyl-1-phenylpyrrole, 30186-39-1; 1-*tert*-butyl-3-formylpyrrole, 30186-46-0; maleic anhydride, 108-31-6; 1-methyl-4,5,6,7-tetrahydroindole-*cis*-4,5-dicarboxylic anhydride, 74809-28-2; 1-phenyl-4,5,6,7-tetrahydroindole-*cis*-4,5-dicarboxylic anhydride, 74809-29-3; 1-*tert*-butyl-4,5,6,7-tetrahydroindole-*cis*-6,7-dicarboxylic anhydride, 74809-30-6; dimethyl 1-methyl-4,5,6,7-tetrahydroindole-*cis*-4,5-dicarboxylate, 74809-31-7; dimethyl maleate, 624-48-6; maleonitrile, 928-53-0; *cis*-4,5-dicyano-1-methyl-4,5,6,7-tetrahydroindole, 74809-32-8; *trans*-4,5-dicyano-1-methyl-4,5,6,7-tetrahydroindole, 74809-33-9; fumaronitrile, 764-42-1; methyl 1-methyl-4,5,6,7-tetrahydroindole-4-carboxylate, 74809-34-0; methyl acrylate, 96-33-3; 4-cyano-1-methyl-4,5,6,7-tetrahydroindole, 74809-35-1; acrylonitrile, 107-13-1; dimethyl acetylenedicarboxylate, 762-42-5; dimethyl 1-methyl-6,7-dihydroindole-4,5-dicarboxylate, 74809-36-2; dimethyl 1-phenyl-6,7-dihydroindole-4,5-dicarboxylate, 74809-37-3; dimethyl 1-methylindole-4,5-dicarboxylate, 74809-38-4; dimethyl 1-phenylindole-4,5-dicarboxylate, 74809-39-5; methyl propiolate, 922-67-8; methyl 1-*tert*-butyl-4,5-dihydroindole-7-carboxylate, 74809-25-9.

Facile and Efficient Carboalkoxylation and Carboaryloxylation of Amines

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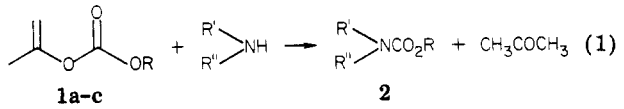
Recently, we demonstrated the synthesis of alkyl and aryl isopropenyl carbonates (1) and their carboalkoxylating and carboaryloxylating capacity in the reaction with amines (eq 1).[1] They react with amines in the absence



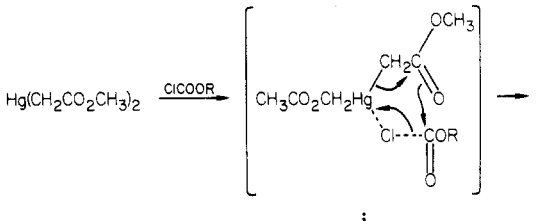
(1)

1a-c 2

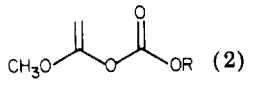
a, R = C_2H_5; b, R = CH_3; c, R = C_6H_5

of base or catalyst to give the corresponding N-carboalkoxylated and N-carboaryloxylated compounds (2) in good yields and acetone is the single side product. These characteristics should make them interesting reagents, but their reactivity is not strong enough, especially in the reaction with weakly basic amines. We now report potentially efficient reagents, α-methoxyvinyl carbonates (3), which can react with various types of amines including weakly basic amines in quantitative yields under extremely mild conditions and can be handled under ordinary conditions.[2]

The unknown reagents 3 were prepared by the reaction of bis[(carbomethoxy)methyl]mercury[3] as the enolate equivalent[4] with alkyl and aryl chloroformates (eq 2). The



i



(2)

3a, R = C_2H_5
b, R = CH_3
c, R = C_6H_5

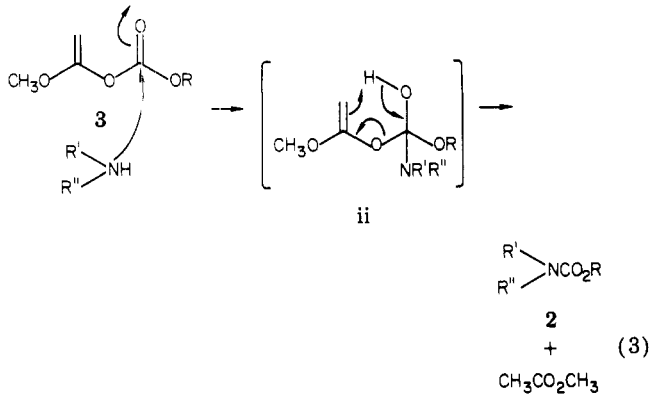
(1) Tamura, Y.; Haruta, J.; Okuyama, S.; Kita, Y. *Tetrahedron Lett.* 1978, 3737.

(2) These reagents are very soluble in common organic solvents and stable enough to be allowed to stand at room temperature for a few weeks or to be stored in the refrigerator for more than several months after the reagent bottle is flushed with nitrogen.

(3) Bis[(carbomethoxy)methyl]mercury was readily prepared by the passage of ketene into mercury(II) oxide and mercury(II) acetate in absolute methanol: Lutsenko, I. F.; Foss, V. L.; Ivanova, N. L. *Dokl. Akad. Nauk SSSR* 1961, *141*, 1107; *Chem. Abstr.* 1961, *56*, 12920*d*.

0022-3263/80/1945-4519$01.00/0

reaction of the carbonates (**3a–c**) with amines is generally carried out by employing equivalent amounts of the reagent **3** and amine (except for the case of an aromatic amine) in a solvent such as methylene chloride or carbon tetrachloride and proceeds completely at low temperature for a short period to give the desired N-carboalkoxylated or N-carboaryloxylated compound (**2**) accompanied by the volatile methyl acetate (bp 56.9 °C) as a single side product (eq 3). However, under the same conditions, the reaction



ii

$$\begin{matrix} R' \\ R'' \end{matrix}\!\!>\!NCO_2R \quad \mathbf{2} \quad + \quad CH_3CO_2CH_3 \qquad (3)$$

with weakly basic amines such as aromatic amines took many hours to go to completion. By the use of 5 equiv of **3** the reaction time was shortened. Evaporation of the reaction mixture gave almost pure desired **2**, which was purified by microdistillation, recrystallization, or column chromatography. The reaction was performed with various types of amines. Selective N-monocarboalkoxylation of diamino compounds was observed by the use of equivalent amounts of **3a** and complete N,N'-dicarboalkoxylations were done by the use of 3 equiv of **3a**. Although we have not as yet investigated the limitations imposed on the reaction by the presence of other functional groups in detail, weakly basic groups such as the hydroxyl group, were found not to cause interference. Thus, an amino alcohol readily reacts with **3a** to give the corresponding N-carboethoxylated compound as the sole product in a high yield. As indicated in Table I, the conditions were extremely mild and the yields were uninformly high compared with the previously reported method.[1]

The application of the above method to amino acids was briefly examined. Carboethoxylation with **3a** simply requires stirring a dioxane–water or methanol solution of amino acid with equivalent amounts of **3a** and a 50% excess of triethylamine at room temperature for a short period.

The reaction using **3** presumably occurs by initial addition of the amine to the carbonyl carbon of the reagent (**3**), subsequent decomposition proceeding with an inter- or intramolecular proton tranfer, e.g., ii, and is undoubtedly accelerated by the favorable enol–keto transformation.[5]

Experimental Section[6]

General Preparation of Alkyl and Aryl α-Methoxyvinyl Carbonates (3a–c). Ethyl chloroformate (0.5 mol) was added dropwise with stirring to a previously warmed solution of bis[(carbomethoxy)methyl]mercury (0.1 mol) in dry benzene or toluene (50 mL) at 80 °C over 1 h and stirring was continued at the same temperature for 2 days. After removal of the solvent, the residual liquid was extracted with *n*-pentane (250 mL) and the extract was concentrated. Distillation gives a 43–54% yield of **3a**: bp 88–90 °C (26 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3 H), 3.63 (s, 3 H), 3.72 (d, 1 H), 3.92 (d, 1 H), 4.23 (q, 2 H); IR ($CHCl_3$) 1765, 1675 cm^{-1}; exact mass calcd for $C_6H_{10}O_4$ 146.0578, found 146.0575. Anal. Calcd for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.45; H, 7.00.

Similarly, other carbonates (**3b,c**) were prepared; **3b**: 36% yield; bp 75–76 °C (35 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3 H), 3.74 (d, 1 H), 3.80 (d, 3 H), 3.92 (d, 1 H); IR ($CHCl_3$) 1775, 1680 cm^{-1}; exact mass calcd for $C_5H_8O_4$ 132.0422, found 132.0427. **3c**: 18% yield; bp 41 °C (0.06 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 3.82 (d, 1 H), 4.07 (d, 1 H), 7.15–7.45 (m, 5 H); IR ($CHCl_3$) 1775, 1670 cm^{-1}; exact mass calcd for $C_{10}H_{10}O_4$ 194.0577, found 194.0574.

General Procedure for Conversion of Amine into *N*-(Carboalkoxy)- or *N*-(Carboaryloxy)amine. To a solution of phenethylamine (1 mmol) in carbon tetrachloride (5 mL), cooled in ice, was added **3a** (1.1 mmol). After 1 min the solvent was removed in vacuo and the residue was distilled to give *N*-(carboethoxy)phenethylamine, identical in all respects with an authentic sample.[7]

General Procedure for Conversion of Amino Acid into *N*-(Carboalkoxy)amino Acid. To a solution of L-phenylalanine (1 mmol) in methanol (2 mL) was added triethylamine (1.5 mmol). After the mixture was stirred at room temperature for 30 min, a solution of **3a** (1 mmol) in methanol (0.5 mL) was added, and the mixture was stirred at room temperature for 3 h, acidified by 5% methanolic citric acid, and concentrated. The residue was extracted with chloroform, and the extract was concentrated in vacuo to give a solid, which was recrystallized from a 25% aqueous methanol to give pure *N*-(carboethoxy)-L-phenylalanine, identical in all respects with an authentic sample.[8]

(4) For reports on the use of bis(keto)mercurials as the enolate equivalents, see: (a) Nesmeyanov, A. N.; Lutsenko, I. F.; Khomutov, R. M.; Dubovitskii, V. A. *Zh. Obshch. Khim.* **1959**, *29*, 2817; *Chem Abstr.* **1960**, *54*, 12048*b*. (b) Murahashi, S.; Nozakura, S.; Fuji, S.; Kikukawa, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1905. (c) Lutsenko, I. F.; Foss, V. L.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1966**, *169*, 117; *Chem. Abstr.* **1966**, *65*, 13533*g*. (d) Lutsenko, I. F.; Baukov, Yu. I.; Burlachenko, G. S.; Khasapov, B. N. *J. Organomet. Chem.* **1966**, *5*, 20. (e) Kruglaya, O. A.; Baukov, Yu. I.; Petrov, B. I.; Vyazankin, N. S. *Zh. Obshch. Khim.* **1971**, *41*, 1408; *Chem. Abstr.* **1971**, *75*, 88734. (f) Chauzov, V. A.; Vodolazskaya, V. M.; Kitaeva, N. S.; Baukov, Yu. I. *Zh. Obshch. Khim.* **1973**, *43*, 597; *Chem. Abstr.* **1973**, *79*, 41775. (g) House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514. (h) Novikova, Z. S.; Sadovnikov, N. P.; Zdorova, S. N.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1974**, *44*, 2233; *Chem. Abstr.* **1975**, *82*, 43519. (i) Olofson, R. A.; Bauman, B. A.; Wancowicz, D. J. *J. Org. Chem.* **1978**, *43*, 752. Exclusive formation of O-acylated products in α-mercurialkanones is explained by either shielding of the α carbon atom by mercury atom or the involvement of a transition state, such as i, in which the mercury atom acts as an intermolecular catalyst.

(5) Analogous types of useful reagents using enol–keto transformation have been reported. Silylating agent: Kita, Y.; Haruta, J.; Segawa, J.; Tamura, Y. *Tetrahedron Lett.* **1979**, 4311. Acylating agent: (a) Wasserman, H. H.; Wharton, P. S. *Tetrahedron* **1958**, *3*, 321; (b) Wasserman, H. H.; Wharton, P. S. *J. Am. Chem. Soc.* **1960**, *82*, 661; (c) van Melick, J. E. W.; Wolters, E. T. M. *Synth. Commun.* **1972**, *2*, 83; (d) Banks, G. R.; Cohen, D. *Proc. Chem. Soc.* **1963**, 83. Phosphorylating agent: (e) Pudovik, A. N. *Zh. Obshch. Khim*, 1956, *26*, 2238; *Chem. Abstr.* **1957**, *51*, 1827a; (f) Pudovik, A. N.; Biktimirova, L. G. *Zh. Obshch. Khim*, **1957**, *27*, 1708; *Chem. Abstr.* **1958**, 52, 3714*b*; (g) Lichtenthaler, F. W. *Chem. Rev.* **1961**, *61*, 607; (h) Wasserman, H. H.; Cohen, D. *J. Org. Chem.* **1963**, *29*, 1817.

(6) IR absorption spectra were recorded on a Hitachi EPI-G2 spectrometer, ^{1}H NMR spectra on a Hitachi R-20A spectrometer with tetramethylsilane as an internal standard, and mass spectra on a Hitachi RMU-6MG mass spectrometer at 20 eV.

(7) Métayer, M. *Bull. Soc. Chim. Fr.* **1951**, 802.

(8) Kanao, S. *J. Pharm. Soc. Jpn.* **1946**, *66*, 6; *Chem. Abstr.* **1951**, *45*, 7957*d*.

(9) Shriner, R. L.; Child, R. G. *J. Am. Chem. Soc.* **1952**, *74*, 549.
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(11) Joullié, M. M.,; Day, A. R. *J. Am. Chem. Soc.* **1954**, *76*, 2990.
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(17) Laakso, T. M.; Reynolds, D. D. *J. Am. Chem. Soc.* **1957**, *79*, 5717.
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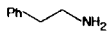
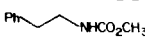
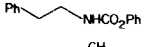
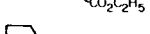
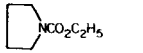
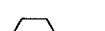
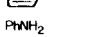
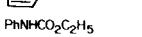
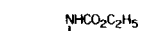
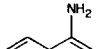
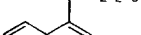
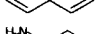
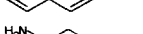
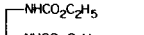
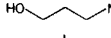
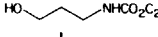
(19) Najer, H.; Chabrier, P.; Giudicelli, R. *Bull. Soc. Chim. Fr.* **1959**, 1611.
(20) Foye, W. O.; Fedor, L. R., Jr. *J. Am. Pharm. Assoc.* **1959**, *48*, 412.
(21) Schuller, W. H.; Niemann, C. *J. Am. Chem. Soc.* **1951**, *73*, 1644.

Table I. Preparation of N-Carboalkoxylated and N-Carboaryloxylated Amines

amine	product 2[a]	reagent 3: reaction conditions	reagent 3: yield, %[b]	reagent 3: bp,[c] °C (torr) [mp,[c] °C (recryst solvent)]	reagent 1: reaction conditions[d]	reagent 1: yield, %[b]
		1 equiv of **3a**, CCl_4, 0 °C, 1 min	96 (75)	116–117 (3)[e]	5 equiv of **1a**, 65 °C, 6 h	90
		1 equiv of **3b** CH_2Cl_2, 20 °C, 15 min	94 (73)	137–138 (0.9)[f]	5 equiv of **1b**, 55 °C, 6 h	95
		1 equiv of **3c** CH_2Cl_2, 0 °C, 1 min	85 (76)	[89–90 (*n*-hexane)][g]	5 equiv of **1c**, 40 °C, 3 h	83
		1 equiv of **3a**, CH_2Cl_2, 20 °C, 10 min	97 (84)	97–98 (2)[h]	5 equiv of **1a**, 65 °C, 2 days	88
		1 equiv of **3a**, CH_2Cl_2, 0 °C, 1 min	96 (77)	61–62 (3)[i]	5 equiv of **1a**, 55 °C, 6 h	95
		1 equiv of **3b**, CH_2Cl_2, 0 °C, 1 min	88 (82)	79–80 (13)[j]	5 equiv of **1b**, 55 °C, 6 h	91
		1 equiv of **3a**, CH_2Cl_2, 0 °C, 1 min	95 (82)	72–73 (5)[k]	5 equiv of **1a**, 55 °C, 6 h	83
		1 equiv of **3a**, CH_2Cl_2, 20 °C, 2 h	87 (75)	71–72 (6)[l]	5 equiv of **1a**,[m] 55 °C, 2 days	84
$PhNH_2$	$PhNHCO_2C_2H_5$	5 equiv of **3a**, CCl_4, 60 °C, 3 h	80 (71)	[51–52 (H_2O)][n]	5 equiv of **1a**,[m] 65 °C, no reaction	
		5 equiv of **3a**, CCl_4, 60 °C, 30 min	97 (70)	[75–76 (Et_2O)][o]	5 equiv of **1a**,[m] 65 °C, no reaction	
		1 equiv of **3a**, CCl_4, 20 °C, 10 min	97 (71)	106–107 (2)[p]		
		3 equiv of **3a**, CCl_4, 20 °C, 10 min	97 (71)	[108–109 (EtOH)][q]		
		1 equiv of **3a**, CH_2Cl_2, 20 °C, 5 min	99 (71)	124–125 (3)[r]		
		1 equiv of **3a**, CH_2Cl_2, 20 °C, 5 min	99 (76)	105–106 (2.5)[s]		
		1 equiv of **3a**, CH_2Cl_2, 20 °C, 20 min	99 (70)	132–133 (3)[t]		
		1 equiv of **3a**, MeOH or dioxane–H_2O, 20 °C, 3 h	97 (85)	[79.5–81.5 (MeOH–H_2O)][u]		
		1 equiv of **3a**, MeOH, 20 °C, 3 h	85 (83)	[80–81 (MeOH)][v]		
		1 equiv of **3a**, MeOH, 20 °C, 30 min	85 (83)	[57–58 (petroleum ether)][w]		

[a] All known products were identified by comparison with authentic samples. New compounds were characterized by ^1H NMR, IR, exact mass, and analytical data. [b] Isolated yields were based on amine and purity of the products (>95%) was determined by GLC. Distilled or recrystallized yields carried out on a 6–8-mmol scale of amine are given in parentheses. [c] Uncorrected boiling point and melting point are given. [d] Reactions were performed without any solvent. [e] Lit.[7] bp 145–148 °C (13 torr). [f] Lit.[9] bp 118–124 °C (0.5 torr). [g] Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.62; H, 6.08; N, 6.04. [h] Lit.[10] bp 100–101 °C (2.5 torr). [i] Lit.[11] bp 63 °C (2 torr). [j] Lit.[12] bp 42 °C (0.2 torr). [k] Lit.[10] bp 60 °C (1 torr). [l] Lit.[13] bp 105–107 °C (16 torr). [m] A catalytic quantity of *p*-toluenesulfonic acid or concentrated sulfuric acid was added. [n] Lit.[14] mp 53 °C. [o] Lit.[15] mp 79 °C. [p] Lit.[16] bp 128–130 °C (4 torr). [q] Lit.[17] mp 110 °C. [r] Lit.[18] bp 140–142 °C (5 torr). [s] Lit.[19] bp 128 °C (5 torr). [t] Lit.[20] bp 190–192 °C (20 torr). [u] Lit.[8] mp 81 °C, lit.[21] mp 85 °C. [v] Lit.[21] mp 85 °C. [w] Lit.[22] mp 62–63 °C.

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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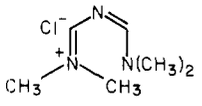
Received April 29, 1980

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

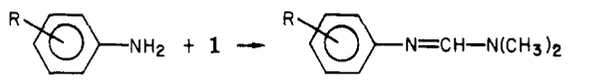
Gold has shown that 1 can be prepared in quantitative yield from cyanuric chloride and *N,N*-dimethylformamide (see Experimental Section) and that this reagent can be reacted with hydrazines to yield 1,2,4-triazoles. In this investigation it was also found that amidines[4] reacted with 1 to give either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

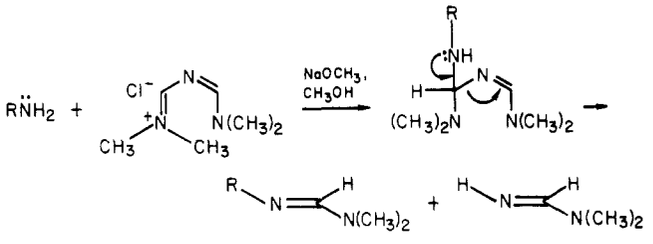
Table I



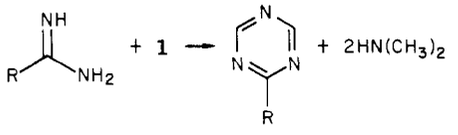
entry	R	% yield[a]	bp or mp, °C
1	4-Me	74	177 (30 mm) [lit.[5] 163 (30 mm)]
2	2-Me[b]	97	85 (3 mm)
3	4-NO_2	84	74-75 (lit.[6] 82-83)
4	4-Br[c]	86	118 (3 mm)
5	2-NH_2[d]	76	169-171 (lit.[7] 172-174)

[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.

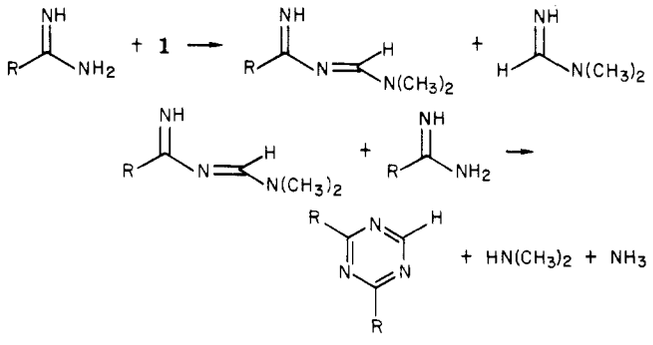
Scheme I



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).

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

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