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Synthesis and Cycloaddition Reactions of Acetylenic Iminium Compounds

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Phenyl, *tert*-butyl, and unsubstituted propiolamidium tetrafluoroborate salts, prepared from ready alkylation of acetylenic amides with triethyloxonium fluoroborate, undergo facile Diels–Alder cycloaddition with cyclopentadiene. Propiolamidium salts also react easily with tetraphenylcyclopentadienone, ethyl diazoacetate, and a mesoionic oxazolium compound. A qualitative comparison of the activation of multiple bonds toward cycloaddition by the amidium group with other known substituents is discussed.

Since electron-withdrawing substituents on acetylenes and olefins increase the rate of reaction with respect to the usual Diels–Alder addition,[2] it may be anticipated that in relation to carbonyl[3] and, in particular, nitro[4] groups, the iminium function, >C=N<$^+$, when substituted directly upon a multiple bond might exert a considerable inductive and mesomeric effect resulting in a facile Diels–Alder or 1,3-dipolar cycloaddition. The present study of iminium-activated acetylenes, previously unknown in the literature, shows that these compounds in fact rank among the best partners in Diels–Alder and 1,3-dipolar cycloaddition reactions.

Results and Discussion

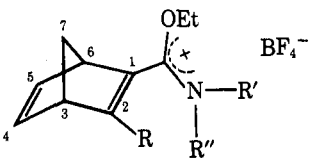
Of all the iminium-activated acetylenes represented by the general formula **1**, acetylenic iminium ethers (**1**, Z = OR‴) were the most easily accessible from phosgeneiminium salt chemistry,[5,6] and form the basis of the present study. Thus when the amide chloride of β-chlorocinnamic acid (**3**), initially formed from the condensation of acetophenone and phosgeneiminium chloride (**2**), was first hydrolyzed with saturated sodium bicarbonate yielding the β-chlorocinnamic amide **4**, followed by HCl elimination with sodium methoxide, *N,N*-dimethylphenylpropiolamide (**5**) was obtained in 76% yield. Then, treatment of **5** with triethyloxonium fluoroborate in methylene chloride at room temperature resulted in the formation of an air-stable, recrystallizable salt whose spectral and analytical data conform with the acetylenic amidium structure **6**. Analogously, *N,N*-dimethyl-*tert*-butylpropiolamide was converted into its alkylated salt **7** in 98% yield. Compound **7** is interesting in regard to *tert*-butylnitroacetylene, which was found to be much more reactive than the corresponding ester and nitrile derivatives.[4] The simplest and sterically least hindered propiolamidium tetrafluoroborate derivatives **8**–**10** were readily formed by analogous alkylation of unsubstituted propiolamides. Compounds **9** and **10** are yellow, crystalline, and isolable under an inert atmosphere. The less stable tertiary amidium **8** obtained in noncrystal-

6, R = C_6H_5; R′ = R″ = CH_3
7, R = $(CH_3)_3C$; R′ = R″ = CH_3
8, R = H; R′ = R″ = CH_3
9, R = R′ = H; R″ = CH_3
10, R = R′ = R″ = H

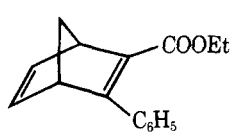
line form can be more conveniently generated in situ for use in further reactions.

A systematic comparison[7] of the ^{13}C spectra of acetylenic amides and corresponding amidium adducts indicates a considerable polarization of the amidium triple bond, i.e., a downfield shift of the β-acetylenic carbon together with an upfield shift of the α carbon, an expected result considering the conjugative effect of the iminium group. Such a polarization, explained in terms of perturbation molecular orbital theory,[8] might facilitate an unsymmetrical transition state within a cycloaddition reaction scheme, lower the energy requirements, and therefore produce a faster Diels–Alder or 1,3-dipolar cycloaddition. This has been found to be the case for acetylenic amidium compounds which exhibit a marked enhancement of reactivity when compared with their amides.

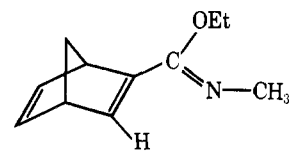
N,N-Dimethyl-*O*-ethylphenylpropiolamidium tetrafluoroborate (**6**) was treated with a slight excess of cyclopentadiene in CH_2Cl_2 at room temperature. After 24 hr the infrared absorption of the triple bond had diminished to one-half its initial intensity and after 70 hr it had completely disappeared. After evaporation of the solvent and excess diene and addition of ether, a compound whose spectral and analytical data are consistent with the norbornadiene derivative **11** was isolated. The cycloadduct **11** was characterized further by its hydrolysis to 1-carbethoxy-2-phenyl-3,6-*endo*-methylene-1,4-cyclohexadiene (**16**). The cycloadduct of cyclopentadiene and phenyl(trifluoromethanesulfonyl)acetylene occurs readily at room temperature whereas phenylpropioloyl chloride undergoes no appreciable reaction with cyclopentadiene.[2] Since an acid chloride substituent on acetylenes and olefins is more activating in cycloadditions than a nitrile, aldehyde, or ester, in that order,[2,9] it can be thus stated that *N,N*-dimethyl-*O*-ethylphenylpropiolamidium tetrafluoroborate (**6**) reacts faster than any of the corresponding carbonyl functionalized phenylacetylenes, and the amidium group activates more strongly than an acid chloride, nitrile, aldehyde, or ester group.



11, R = C_6H_5; R′ = R″ = CH_3
12, R = $(CH_3)_3C$; R′ = R″ = CH_3
13, R = R′ = H; R″ = CH_3
14, R = R′ = R″ = H
15, R = H; R′ = R″ = CH_3



16

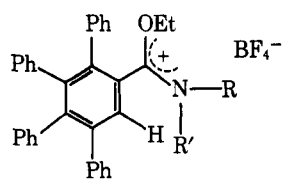


17

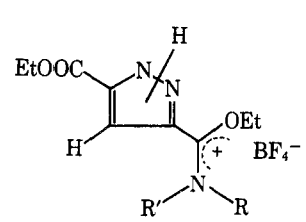
The reaction of cyclopentadiene with the *tert*-butyl acetylenic amidium compound **7** afforded after 2 weeks in methylene chloride at room temperature a stable 1:1 cycloadduct whose spectral and analytical data are consistent with its representation as **12**. In comparison with other *tert*-butyl acetylenes, the nitro-substituted derivative reacted fastest with cyclopentadiene, the completed reaction being observed after 2 hr at room temperature, but the corresponding ester and nitrile were inert to such conditions.[4] The lower reactivity of the *tert*-butyl derivative **7** toward cyclopentadiene as compared with its phenyl analogue **6** is apparently due to steric rather than electronic effects. The unsubstituted acetylenic amidium compounds **8–10** are therefore expectedly extremely reactive partners in Diels–Alder and 1,3-dipolar cycloadditions under these conditions.

Thus when the secondary propiolamidium compound **9** was initially treated in CH_2Cl_2 at room temperature with an excess of cyclopentadiene, an exothermic reaction ensued immediately upon addition. Complete disappearance of the triple bond was observed within 15 min; yet only an insoluble polymeric substance was obtained. However, when equimolar amounts of the two reactants were allowed to react, a product was isolated whose spectral characteristics are in agreement with the cycloadduct **13**. Both the ^1H and ^{13}C magnetic resonance spectra indicate that **13** exists in two forms, most likely owing to the orientation of the amidium group with respect to the norbornadiene C_1–C_2 double bond in a cis–trans arrangement. The hydrolysis of **13** with sodium carbonate produced an oil whose spectral data suggest the imino ether structure **17** since an NCH_3 resonance signal was observed at δ 3.01 and an imine absorption at 1660 cm^{-1} was recorded in the infrared spectrum. Noteworthy in the above reaction is the ease of cycloaddition reminiscent of the reactions of cyclopentadiene with dimethyl acetylenedicarboxylate[10] or propargyl aldehyde[11] at room temperature. Acetylene itself undergoes reaction[12] with cyclopentadiene only under increased pressure (1–6 atm) and at 325–435°. Even acetylacetylene requires heating at 90° for 6 hr in a sealed tube for reaction with cyclopentadiene.[13] Furthermore, the primary amidium derivative **10** was treated with cyclopentadiene at room temperature, yielding a 1:1 cycloadduct **14** in 71% yield. The NMR spectrum of **14** is easily interpretable. The H-2 olefinic proton resonated at δ 8.40 as a doublet ($J_{2,3}$ = 4.0 Hz) considerably shifted downfield with respect to the other vinylic protons H-4 and H-5 which were observed as a doublet of quartets at δ 6.92. This downfield shift is undoubtedly due to the adjacent amidium group at C-1. The allylic bridgehead protons H-3 and H-6 were found at δ 4.02 as a broad doublet and the bridge C-7 protons at δ 2.25 (bs). The NH_2 protons were nonequivalent arising at δ 8.74 and 9.17 as broad singlets and the remaining ethyl resonances were observed at δ 4.60 and 1.50. **8**, generated in situ, readily gave with cyclopentadiene the cycloadduct **15**.

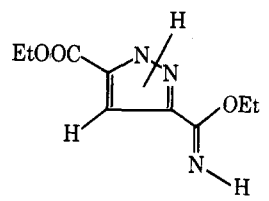
As a further example of their high reactivity, the monosubstituted acetylenic amidium derivatives **8** and **9** underwent ready cycloaddition with tetraphenylcyclopentadienone at room temperature, affording the substituted benzene derivatives **18** and **19**.



18, R = R′ = CH_3
19, R = H; R′ = CH_3



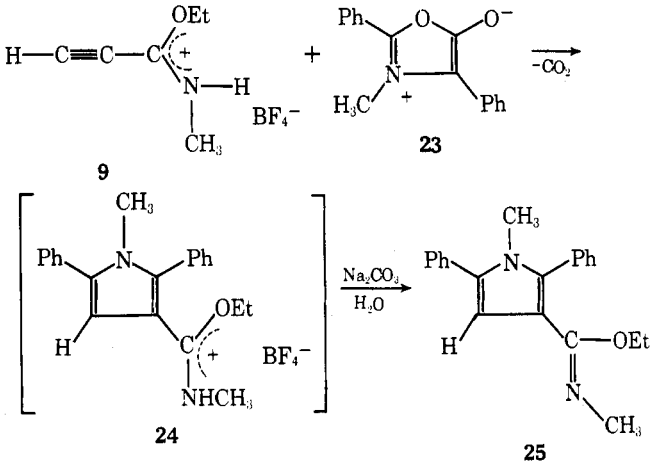
20, R = H; R′ = CH_3
21, R = R′ = H



22

Derivatives **9** and **10** also underwent a facile 1,3-dipolar cycloaddition at room temperature. With ethyl diazoacetate and **9** or **10**, an exothermic reaction occurred and the amidium pyrazoles **20** and **21** were formed, respectively. Basic hydrolysis of **21** gave the imino ether derivative **22**. The 1,3 relationship between the carbethoxy and amidium groups is the expected[14] directiospecificity in such 1,3-dipolar cycloadditions.

Reaction of **9** with the azomethine 1,3-dipole contained in the oxazolium mesoionic compound[21] munchnone (**23**) afforded in a facile manner the imino ether pyrrole **25** via basic hydrolysis of the intermediate **24**.



The inability of **9** to undergo cycloaddition with anthracene or with tosyl azide gives an indication of the limits of reactivity of the monosubstituted acetylenic amidium derivatives.

When methyl propiolate as a reference and **8** and **9** were compared in reactivity to tetraphenylcyclopentadienone, only the acetylenic amidium salts reacted. Thus the monosubstituted acetylenic compounds are more reactive than the corresponding ester derivatives. In contrast to these highly reactive amidium salts, the corresponding propiolamides were unreactive under these conditions. Preliminary results on phenylpropiolamidinium perchlorate compounds (**1**, R = C_6H_5; Z = NHR; X = ClO_4) obtained by aminolysis of **3**, elimination of HCl, and protonation by perchloric acid, indicate that these derivatives are not very reactive in cycloadditions. The synthesis of less sterically hindered acetylenic amidinium compounds as well as other representative iminium-activated acetylenes (**1**, Z = H, alkyl, Cl) is currently under investigation and will be reported at a later date.

Experimental Section

Spectral characterizations were carried out on the following instrumentation: infrared spectra, Perkin-Elmer Model 257 spectrophotometer; NMR spectra, Varian DP-60, T-60, XL-100, and CFT-20 spectrometers, using Me_4Si as internal standard; mass spectra, Varian MAT-311 mass spectrometer at 70 eV. Melting points are uncorrected and were determined in capillaries in a "Dr. Tottoli" apparatus and all evaporations were carried out using a Rotovap apparatus. Microanalyses were performed by the Institüt für Organische Chemie, Universität Wien, Vienna, Austria, and Instranal Laboratories, Rensselaer, N.Y.

Preparation of *N,N*-Dimethylphenylpropiolamide (5). To a stirred solution of *N,N*-dimethyl-β-chlorocinnamamide[6] (**4**) in dry methanol was added a methanolic solution of excess sodium methoxide at room temperature. After 5 min of stirring, the reaction was quenched with a small amount of water, solvent was evaporated, and the solid residue was extracted with CH_2Cl_2–H_2O. The organic layer was separated, dried over Na_2SO_4, and evaporated. **5** was recrystallized from cyclohexane as colorless needles (76%): mp 96–98° (lit.[15] mp 99, 101, 92°); ir ($CHCl_3$) 2220 (C≡C), 1625 cm^{-1} (CO); NMR ($CDCl_3$) δ 3.08, 3.33 [2 s, 6, $N(CH_3)_2$], 7.22–7.80 (m, 5, aromatic); mass spectrum *m/e* 173 ($M^{\cdot+}$), 129 (M − 44).

***N,N*-Dimethyl-*O*-ethylphenylpropiolamidium Tetrafluoroborate (6).** **5** (1.67 g, 0.01 mol) and triethyloxonium fluoroborate[16] (1.84 g, 0.01 mol) were stirred at room temperature in dry CH_2Cl_2 (20 ml) for 24 hr. The solvent was evaporated and the residue digested in anhydrous ether. Filtration, washing with ether, and drying afforded 2.39 g (85%) of a colorless, air-stable solid which could be recrystallized as colorless needles from ethanol (technical), but the recovery of **6** was low, possibly indicating reaction with solvent: mp 113–115°; ir (CH_2Cl_2) 2205 (C≡C), 1640 (amidium), 1060 cm^{-1} (BF_4^-); NMR ($CDCl_3$) δ 1.58 (t, *J* = 7.5 Hz, 3, OCH_2CH_3), 3.48, 3.73 [2 s, 6, $N(CH_3)_2$], 4.90 (q, 2, OCH_2CH_3), 7.34–8.08 (m, 5, aromatic).

Anal. Calcd for $C_{13}H_{16}NOBF_4$: C, 54.01; H, 5.58, N, 4.85. Found: C, 53.82; H, 5.40; N, 4.99.

***N,N*-Dimethyl-*O*-ethyl-*tert*-butylpropiolamidium Tetrafluoroborate (7).** Similarly, *N,N*-dimethyl-*tert*-butylpropiolamide[17] (0.95 g, 0.0062 mol) and triethyloxonium fluoroborate (1.2 g, 0.0063 mol) at room temperature in CH_2Cl_2 (25 ml) afforded an ether-insoluble product recrystallized as colorless prisms from ethanol–ether (1.32 g, 98%): mp 72–73°; ir (CH_2Cl_2) 2220 (C≡C), 1645 (amidium), 1060 cm^{-1} (BF_4^-); NMR ($CDCl_3$) δ 1.43 [s, 9, $C(CH_3)_3$], 1.52 (t, *J* = 7.0 Hz, 3, OCH_2CH_3), 3.41, 3.51 [2 s, 6, $N(CH_3)_2$], 4.70 (q, 2, OCH_2CH_3).

Anal. Calcd for $C_{11}H_{20}NOBF_4$: C, 49.09; H, 7.49; N, 5.21. Found: C, 48.87; H, 7.64; N, 5.37.

***N,N*-Dimethyl-*O*-ethylpropiolamidium Tetrafluoroborate (8).** *N,N*-Dimethylpropiolamide[18] (0.55 g, 0.006 mol) and triethyloxonium fluoroborate (1.20 g, 0.006 mol) were stirred in dry CH_2Cl_2 (15 ml) at room temperature for 19 hr. Solvent was removed in vacuo and the orange residual oil treated with anhydrous ether. After washing and decanting (all operations carried out under N_2) the oil was dried successively on water and oil vacuum pumps: yield 1.13 g (93% crude); ir (CH_2Cl_2) 3270 (HC≡C), 2120 (C≡C), 1655 (amidium), 1060 cm^{-1} (BF_4^-); NMR (CD_2Cl_2) δ 1.53 (t, *J* = 7.0 Hz, 3, OCH_2CH_3), 3.40, 3.63 [2 s, 6, $N(CH_3)_2$], 4.83 (q, 2, OCH_2CH_3), 4.93 (s, 1, HC≡C).

***O*-Ethyl-*N*-methylpropiolamidium Tetrafluoroborate (9).** *N*-Methylpropiolamide[18] (0.41 g, 0.005 mol) and Meerwein's reagent (0.94 g, 0.005 mol) were similarly allowed to react. After removal of solvent and addition of anhydrous ether, continued agitation produced a crystalline, yellow solid which was isolated (N_2 atmosphere) and dried under reduced pressure: yield 0.83 g (84%); ir (CH_2Cl_2) 3270 (HC≡C), 3220 (NH), 2130 (C≡C), 1665 (amidium), 1075 cm^{-1} (BF_4^-); NMR (CD_2Cl_2) δ 1.57 (t, *J* = 7.0 Hz, 3, OCH_2CH_3), 3.22 (d, *J* = 5.2 Hz, 3, $NHCH_3$), 4.70 (s, 1, HC≡C), 4.88 (q, 2, OCH_2CH_3), 10.2 (bs, 1, $NHCH_3$).

***O*-Ethylpropiolamidium Tetrafluoroborate (10).** Propiolamide[19] (0.66 g, 0.01 mol) and triethyloxonium fluoroborate (1.82 g, 0.01 mol) in dry CH_2Cl_2 (15 ml) were stirred overnight at room temperature. A light yellow oil insoluble in CH_2Cl_2 was formed. Solvent was evaporated and the oily residue was washed with anhydrous ether causing crystallization. The product (1.44 g, 82%) was dried under oil-pump vacuum. Owing to its insolubility spectral characterization could not be carried out.

1-(*N,N*-Dimethyl-*O*-ethylcarboxamidium)-2-phenyl-3,6-*endo*-methylene-1,4-cyclohexadiene Tetrafluoroborate (11). *N,N*-Dimethyl-*O*-ethylphenylpropiolamidium tetrafluoroborate (**6**, 0.2 g, 0.0007 mol) in CH_2Cl_2 (15 ml) was stirred at room temperature with an excess (~2 ml) of freshly distilled cyclopentadiene. After 70 hr the ir triple bond absorption had completely disappeared. The excess diene and solvent were evaporated and anhydrous ether added to the residual oil. Crystallization was induced by scratching after adding a trace of ethyl acetate, and recrystallization from ethyl acetate afforded colorless prisms (0.21 g, 85%): mp 122–123° dec; ir (CH_2Cl_2) 1645 (amidium), 1055 cm^{-1} (BF_4^-); NMR ($CDCl_3$) δ 1.31 (t, *J* = 7.0 Hz, 3, OCH_2CH_3), 2.20–2.56 (m, 2, H_7), 3.13, 3.41 [2 s, 6, $N(CH_3)_2$], 3.90–4.20 (m, 4, OCH_2CH_3, H_3 and H_6), 6.96–7.60 (m, 7, aromatic, H_4 and H_5).

Anal. Calcd for $C_{18}H_{22}NOBF_4$: C, 60.86; H, 6.24; N, 3.94. Found: C, 61.19; H, 5.96; N, 3.94.

Hydrolysis of 11. From **6** (0.2 g) and excess cyclopentadiene as described above was obtained the 1:1 cycloadduct **11** which was treated at room temperature with a saturated solution of potassium carbonate in H_2O with stirring and simultaneous extraction with ether. After all the solid had dissolved, the ether layer was isolated, the aqueous layer extracted once more with ether, and the ether extracts combined, dried ($MgSO_4$), and evaporated, leaving a light yellow oily residue which was distilled (horizontal bulbs,

130°, 0.1 mm) affording 1-carbethoxy-2-phenyl-3,6-*endo*-methylene-1,4-cyclohexadiene (**16**, 0.12 g, 72%): ir (film) 1700 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.18 (t, J = 7.0 Hz, 3, OCH_2CH_3), 2.12 (m, 2, H_7), 3.95 (m, 2, H_3 and H_6), 4.08 (q, 2, OCH_2CH_3), 6.70–7.67 (m, 7, aromatic, H_4 and H_5); mass spectrum *m/e* 240 ($M^{\cdot+}$), 211 (M − Et·), 196 (M − CH_3CHO), 195 (M − EtO·), 175 (M − C_5H_5·), 129 ($PhC{\equiv}C{-}CO^+$).

1-(*N,N*-Dimethyl-*O*-ethylcarboxamidium)-2-*tert*-butyl-3,6-*endo*-methylene-1,4-cyclohexadiene Tetrafluoroborate (12). Over the period of 2 weeks was formed from **7** (0.5 g, 0.0018 mol) and excess cyclopentadiene in CH_2Cl_2 (15 ml) at room temperature, after evaporation and trituration with ether, a colorless solid recrystallized from ethyl acetate as colorless prisms (0.2 g, 32%): mp 135–140° dec; ir (CH_2Cl_2) 1655 (amidium), 1055 cm^{-1} (BF_4^-); NMR ($CDCl_3$) δ 1.08 (s, 9, *tert*-butyl), 1.45 (t, J = 7.0 Hz, 3, OCH_2CH_3), 1.90–2.26 (m, 2, H_7), 3.04, 3.33, 3.40, 3.43 [4 s, 6, $N(CH_3)_2$], 3.74–4.17 (m, 2, H_3 and H_6), 4.47 (q, 2, OCH_2CH_3), 6.66–7.23 (m, 2, H_4 and H_5).

Anal. Calcd for $C_{16}H_{26}NOBF_4$: C, 57.33; H, 7.82; N, 4.18. Found: C, 57.67; H, 7.87; N, 4.23.

1:1 Adduct of 9 and Cyclopentadiene. The secondary unsubstituted yneamidium compound **9** (0.65 g, 0.0033 mol) in dry CH_2Cl_2 (10 ml) was treated with an equivalent amount of freshly distilled cyclopentadiene (0.22 g, 0.0033 mol) at room temperature with stirring. After the reaction was followed by ir spectroscopy, solvent was evaporated 30 min later and the residue washed thoroughly (N_2 atmosphere) with anhydrous ether. The ether was decanted and the semisolid residue of 1-(*N*-methyl-*O*-ethylcarboxamidium)-3,6-*endo*-methylene-1,4-cyclohexadiene tetrafluoroborate (**13**) was dried under reduced pressure: ir (CH_2Cl_2) 3290, 3220 (NH), 1645 (amidium), 1060 cm^{-1} (BF_4^-); NMR (CD_2Cl_2) δ 1.46 (t, J = 7.0 Hz, 3, OCH_2CH_3), 2.38 (m, 2, H_7), 3.10, 3.26 (dd, J = 5.5 Hz, 3, $NHCH_3$), 3.95 (m, 2, H_3 and H_6), 4.50 (m, 2, OCH_2CH_3, nonequivalent methylene protons presented as a ten-line multiplet), 6.88 (m, 2, H_4 and H_5), 7.96 (m, 1, H_2), 9.05 (bs, 1, $NHCH_3$).

Hydrolysis of 13. Treatment of **13** (0.13 g, 0.0005 mol) with a saturated solution of Na_2CO_3, extraction with ether, drying, and evaporation afforded a crude orange oil whose spectral data were in accord with the norbornadienyl imino ether **17**: ir (film) 3000 region (CH aliphatic), 1660 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.25 (t, J = 7.0 Hz, 3, OCH_2CH_3), 1.92–2.17 (m, 2, H_7), 3.01 (s, 3, NCH_3), 3.55–3.92 (m, 2, H_3 and H_6), 3.96 (q, 2, OCH_2CH_3), 6.59–7.08 (m, 3, H_2, H_4, and H_5); mass spectrum *m/e* 177 ($M^{\cdot+}$).

1-(*O*-Ethylcarboxamidium)-3,6-*endo*-methylene-1,4-cyclohexadiene Tetrafluoroborate (14). To a suspension of the primary amidium compound **10** (0.74 g, 0.004 mol) in dry CH_2Cl_2 (20 ml) was added cyclopentadiene (0.27 g, 0.0041 mol) with stirring at room temperature. The initially insoluble **10** reacted gradually into solution (0.5 hr). After 3 hr the reaction mixture was filtered, the solvent evaporated, and dry ether added, effecting the crystallization of an air-stable cream solid (0.72 g, 71%): mp 120–123° dec; ir (CH_2Cl_2) 3440, 3180 (NH), 1680 (amidium), 1050 cm^{-1} (BF_4^-); NMR ($CDCl_3$) δ 1.50 (t, J = 7.5 Hz, 3, OCH_2CH_3), 2.25 (bs, 2, H_7), 4.02 (bd, 2, H_3 and H_6), 4.60 (q, 2, OCH_2CH_3), 6.92 (dq, J = 3.0, 14.0 Hz, 2, H_4 and H_5), 8.40 (d, $J_{2,3}$ = 4.0 Hz, 1, H_2), 8.74, 9.17 (2 bs, 2, NH_2).

1-(*N,N*-Dimethyl-*O*-ethylcarboxamidium)-3,6-*endo*-methylene-1,4-cyclohexadiene Tetrafluoroborate (15). To triethyloxonium fluoroborate (1.0 g, 0.0052 mol) in dry CH_2Cl_2 (20 ml) was added *N,N*-dimethylpropiolamide[18] (0.51 g, 0.0052 mol) with stirring. After 5 min at room temperature, cyclopentadiene (0.35 g, 0.0053 mol) was introduced. Solvent was evaporated after 20 min, and the residue was washed thoroughly with anhydrous ether and dried under reduced pressure (0.1 mm), yield 1.28 g (87%) of an orange oil contaminated by a small amount of Meerwein's reagent: ir (CH_2Cl_2) 1650 (amidium), 1600 (C=C), 1050 cm^{-1} (BF_4^-); NMR (CD_2Cl_2) δ 1.42 (t, 3, OCH_2CH_3), 2.04–2.40 (m, 2, H_7), 3.25, 3.33 [2 s, 6, $N(CH_3)_2$], 3.84–4.16 (m, 2, H_3 and H_6), 4.30 (q, 2, OCH_2CH_3), 6.84–7.17 (m, 2, H_4 and H_5), 7.60–7.73 (m, 1, H_2).

***N,N*-Dimethyl-*O*-ethyl-2,3,4,5-tetraphenylbenzamidium Tetrafluoroborate (18).** After triethyloxonium fluoroborate (1.25 g, 0.0066 mol) and **8** (0.64 g, 0.0066 mol) were stirred in dry CH_2Cl_2 (20 ml) for 10 min, tetraphenylcyclopentadienone (2.33 g, 0.0061 mol) was introduced and stirring continued for 18 hr. The solvent was then evaporated, anhydrous ether added, and crystallization induced by scratching, and **18** was recrystallized as colorless, irregular prisms from acetonitrile–ether (3.1 g, 83%): mp 248–250° dec (with gas evolution); ir (CH_2Cl_2) 1660 (amidium), 1060 cm^{-1} (BF_4^-); NMR (Me_2SO-d_6) δ 1.27 (t, J = 7.0 Hz, 3, OCH_2CH_3), 3.20, 3.40 [2 s, 6, $N(CH_3)_2$], 4.36 (m, 2, OCH_2CH_3), 6.96 (bs, 10, aromatic), 7.25 (s, 10, aromatic), 8.00 (s, 1, H_6).

Anal. Calcd for $C_{35}H_{32}NOBF_4$: C, 73.82; H, 5.67; N, 2.46. Found: C, 74.50; H, 5.26; N, 2.54.

***N*-Methyl-*O*-ethyl-2,3,4,5-tetraphenylbenzamidium Tetrafluoroborate (19).** **9** (0.5 g, 0.0025 mol) and tetracyclone (0.97 g, 0.0025 mol) were stirred in dry CH_2Cl_2 (20 ml) overnight. Solvent was evaporated and ether added, precipitating a solid, which was digested by agitation, filtered, and recrystallized from ethanol as colorless prisms (1.31 g, 94%): mp 209–211° dec (with gas evolution); ir ($CHCl_3$) 1665 (amidium), 1080 cm^{-1} (BF_4^-); NMR ($CDCl_3$) δ 1.18 (t, J = 7.0 Hz, 3, OCH_2CH_3), 2.88 (d, J = 5.0 Hz, 3, $NHCH_3$), 4.24 (q, 2, OCH_2CH_3), 6.50–7.34 (3 bs, 20, aromatic), 7.67 (s, 1, H_6), 9.92 (bs, 1, $NHCH_3$).

Anal. Calcd for $C_{34}H_{30}NOBF_4$: C, 73.52; H, 5.44; N, 2.52. Found: C, 73.68; H, 5.49; N, 2.49.

3-(*N*-Methyl-*O*-ethylcarboxamidium)-5-carbethoxypyrazole Tetrafluoroborate (20). A solution of ethyl diazoacetate (0.45 g, 0.004 mol) in CH_2Cl_2 (5 ml) was added dropwise to a stirred solution of the acetylenic amidium compound **9** (0.79 g, 0.004 mol). An exothermic reaction ensued and after stirring was continued for 1 hr, solvent was evaporated, anhydrous ether was added, and the resultant viscous oil was washed and vacuum dried (1.04 g, 84%): ir (CH_2Cl_2) 3200–3300 (b, NH), 1735 (CO), 1660 (amidium), 1080 cm^{-1} (BF_4^-); NMR (CD_2Cl_2) δ 1.00–1.92 (m, 6, OCH_2CH_3), 3.34 (d, J = 5.0 Hz, 3, $NHCH_3$), 4.42 (q, 2, $COOCH_2CH_3$), 5.05 (q, 2, OCH_2CH_3), 7.62 (s, 1, H_4), 9.75 (bm, 1, $NHCH_3$), 12.1 (bs, 1, ring NH).

3-(*O*-Ethylcarboxamidium)-5-carbethoxypyrazole Tetrafluoroborate (21). To a suspension of **10** (1.44 g, 0.0078 mol) suspended in dry CH_2Cl_2 (15 ml) was added dropwise ethyl diazoacetate (0.89 g, 0.0078 mol) with stirring at room temperature. After 30 min all starting material had reacted and stirring was continued for an additional 1 hr. The reaction mixture was filtered and evaporated and the residue digested in dry ether, yielding an air-stable light yellow solid (1.77 g, 76%): mp 80–83° dec; ir (CH_2Cl_2) 3000–3400 (NH, CH aliphatic, broad), 1740 (CO), 1690 (amidium), 1640 (CN), 1065 cm^{-1} (BF_4^-); NMR (Me_2SO-d_6) δ 1.38, 1.52 (2 t, 6, OCH_2CH_3), 4.45, 4.69 (2 q, 4, OCH_2CH_3), 7.79 (s, 1, H_4), NH not observed but addition of CF_3COOD yielded a peak of approximate integration of three protons.

Hydrolysis of 21. In the usual manner **21** (1.0 g, 0.0033 mol) was hydrolyzed with saturated Na_2CO_3–H_2O affording the imino ether **22** as light orange needles from ethyl acetate (0.6 g, 85%): mp 148–150°; ir (CH_2Cl_2) 3600 (NH), 3410 (NH), 1730 (CO), 1650 cm^{-1} (CN); NMR ($CDCl_3$) δ 1.38 (dt, 6, OCH_2CH_3), 4.38 (q, 4, OCH_2CH_3), 7.03 (s, 1, H_4), 10.1 (bs, 2, NH); mass spectrum *m/e* 211 ($M^{\cdot+}$), 210 (M − H·), 196 (M − CH_3·), 183 (M − CO).

Anal. Calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found: C, 50.99; H, 5.92; N, 19.85.

Reaction of 9 with Munchnone.[21] To **9** (0.36 g, 0.0018 mol) in CH_2Cl_2 (15 ml) was added in small portions the oxazolium mesoionic compound **23** (0.46 g, 0.0018 mol) whereupon an immediate evolution of gas was observed (CO_2). After 1 hr of stirring at room temperature, solvent was evaporated but the oily residue could not be induced to crystallize and was directly hydrolyzed with saturated Na_2CO_3–H_2O in the usual manner, affording the imino ether pyrrole **25** as colorless needles from cyclohexane (0.51 g, 89%): mp 94–98° dec; ir (CH_2Cl_2) 1670 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.12 (t, J = 7.0 Hz, 3, OCH_2CH_3), 2.90 (s, 3, NCH_3), 3.52 (s, 3, NCH_3), 4.08 (q, 2, OCH_2CH_3), 6.40 (s, 1, H_4), 7.17–7.59 (m, 10, aromatic); mass spectrum *m/e* 318 ($M^{\cdot+}$), 317 (M − H·), 303 (M − CH_3·), 298 (M − CO), 289 (M − Et·), 273 (M − EtO·), 105 ($PhC{\equiv}O^+$), 77 (Ph^+).

Anal. Calcd for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.97; N, 8.80. Found: C, 79.22; H, 6.98; N, 9.04.

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Registry No.—**4**, 40233-44-1; **5**, 26218-50-8; **6**, 56676-94-9; **7**, 56676-96-1; **8**, 56676-98-3; **9**, 56724-30-2; **10**, 56724-28-8; **11**, 56677-00-0; **12**, 56713-52-1; **13**, 56724-34-6; **14**, 56724-32-4; **15**, 56677-02-2; **16**, 57273-96-8; **17**, 56724-33-5; **18**, 57273-98-0; **19**, 57274-00-7; **20**, 57274-02-9; **21**, 57274-04-1; **22**, 57274-03-0; **23**, 13712-75-9; **25**, 57274-05-2; sodium methoxide, 124-41-4; triethyloxonium fluoroborate, 368-39-8; *N,N*-dimethyl-*tert*-butylpropiolamide, 56677-03-3; *N,N*-dimethylpropiolamide, 2682-34-0; *N*-methylpropiolamide, 2682-32-8; propiolamide, 7341-96-0; cyclopentadiene, 542-92-7; tetraphenylcyclopentadienone, 479-33-4.

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Bridgehead Nitrogen Systems. X. Cycloadditions with Thiazolium *N*-Ylides[1]

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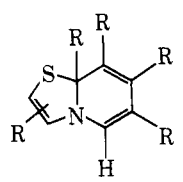
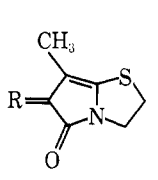
The thiazolium ylides, derived from 3-(2-aryl-2-oxoethyl)-4-methylthiazolium bromides and triethylamine, gave with dimethyl acetylenedicarboxylate and dibenzoylacetylene derivatives of the 1*H*-pyrrolo[2,1-*c*][1,4]thiazine system that were formed by rearrangement of the intermediate 5,7a-dihydropyrrolo[2,1-*b*]thiazole system. With ethyl propiolate a 1,2 adduct was formed by further reaction of a hydroxyl substituent in the thiazine system with ethyl propiolate and, in one instance, dibenzoylacetylene gave a dihydrothiazolo[3,2-*a*]azepine derivative. *N*-Phenylmaleimide also formed an adduct of the above pyrrolo[2,1-*b*]thiazole system but with phenyl isocyanate and phenyl isothiocyanate, ring closure of the initially formed 1,5-dipolar intermediate did not occur, these betaines being readily isolated.

Thiazole and its alkyl derivatives[2] undergo condensation with dimethyl acetylenedicarboxylate, giving 1:2 adducts. In contrast to the reaction of pyridine with acetylenic dienophiles, reactions of this type have recently been shown[3–5] to lead to isomeric rearrangement products such as **1**. Δ^2-Thiazolines also react[6] with acetylenic esters and an interesting variation occurs when 2-ethyl-Δ^2-thiazoline and the acetylenic ester react in the presence of 1 mol of an unsaturated compound such as methyl vinyl ketone. In this case the pyrrolo[2,1-*b*]thiazole derivative **2** was formed, with the ethylenic compound being involved in a transient quaternization of the thiazoline nitrogen atom.[7] Other 2-alkylthiazoles, converted into 3-acetonyl- and 3-phenacyl-2-alkylthiazolium salts, are cyclized with sodium acetate in aprotic solvents into pyrrolo[2,1-*b*]thiazoles.[8] Thiazole itself reacted[9] with tetracyanoethylene oxide to form the ylide **3** which, with dimethyl acetylenedicarboxylate, gave **4**. The ready quaternization of thiazoles suggested that deprotonation and subsequent 1,3-dipolar cycloaddition of the resulting ylide with dipolarophiles would be an attractive and versatile route to pyrrolo[2,1-*b*]thiazole derivatives with a variety of functional groups in the 6 and 7 positions. Our efforts to obtain these products, intermediates in the synthesis of analogues of the thieno[3,4-*c*]pyrrole system,[10] are described below.

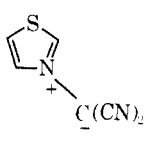


1



2

R = CH_3OOCCH



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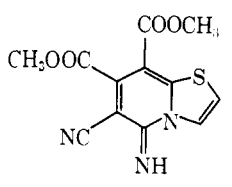
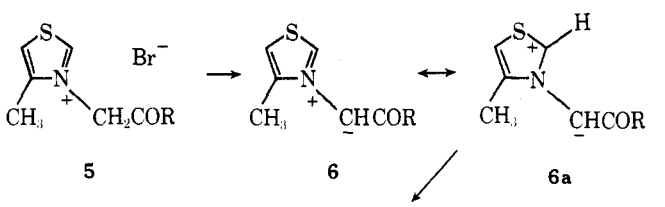
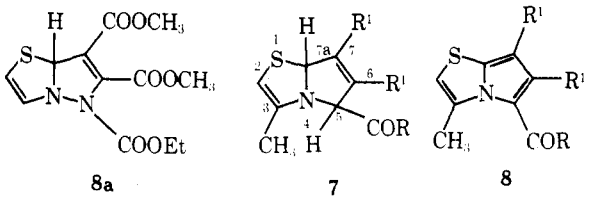


4

4-Methylthiazole and 2-bromoacetophenone, as well as 2,4′-dibromoacetophenone, reacted readily in boiling ethanol, giving the corresponding thiazolium salt **5** (R = Ph, *p*-BrC_6H_4, respectively). Similarly, ethyl bromoacetate in ether at room temperature gave the corresponding salt **5** (R = OEt). In the reactions described below the ylide **6** was generated in situ from the salt **5** and triethylamine in the



5 **6** **6a**



8a **7** **8**