NEW COMPOUNDS

Z and E Isomers of 1:1 Michael-Type Adducts from 2-Addition of Pyrroles to Dimethyl Acetylenedicarboxylate. Stereochemistry and Spectra †

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The 1:1 Michael-type adducts derived from reaction of pyrroles (1) having an open 2-position with dimethyl acetylenedicarboxylate (DMAD) in the presence of a source of active hydrogen (usually provided by their own NH groups, if present, or by sufficient acetic acid) can exist as *Z* (3) and *E* (4) stereoisomers. Both 3 and 4 were obtained from the following pyrroles, with the exceptions noted: pyrrole (1a), 1-methyl-(1b), 2-methyl-(1c), 1,2-dimethyl- (1d), 1,3-dimethyl- (1e, gave dimethyl (*Z*)-1,3-dimethyl-2-pyrrolyl-2-butenedioate (3e) but no 4e), 2,4-dimethyl- (1f), 1-butyl- (1i), 1-(1-methylpropyl)-(1j), 1-(dimethylethyl)- (1k), 1-benzyl- (1l), 1-phenyl-(1m), 1-(4-methoxyphenyl)- (1n), 1-(4-bromophenyl)-(1o), 1-(2-methylphenyl)- (1p), 1-(2,6-dimethylphenyl)-(1q and 3q only), 1-(4-nitrophenyl)- (1r, no 3r or 4r), 1-acetyl- (1s, 4s only). The stereochemistry has been determined from the NMR, UV, and IR spectra. Extensive spectral data, including mass spectra, have been tabulated and interpreted for 15 adducts of type 3 and 14 of type 4.

Discussion

This paper reports analytical data, and MS, NMR, UV, and IR spectral data, which establish the structure and stereochemistry of 29 1:1 Michael-type adducts derived from the 2-addition of pyrroles (1) to dimethyl acetylenedicarboxylate (DMAD) in the presence of a source of active hydrogen, usually provided by their own NH groups, if present, or by sufficient acetic acid. The methods of preparation of the 15 *Z* (3) and 14 *E* (4) stereoisomers are reported in detail in a companion paper (*1*). Their formation, which is probably through the zwitterionic intermediate **2** and possibly via reversible formation of the 1:1 Diels–Alder adduct **5**, is rationalized in Scheme I and discussed in more detail in the companion paper (*1*). Elemental analyses for carbon, hydrogen, nitrogen, and, where present, bromine, and high-resolution mass-spectrometric molecular ions were determined for all of the adducts and submitted for review. In all cases the elemental analyses were within 0.28% and the molecular ions within 10 ppm (except for 17.5 ppm with the *m/e* 365 peak of **3o**) of the values calculated for the structures assigned. The melting points are reported in Table I, and the detailed spectral data are reported in Tables I (MS), II (NMR), and III (UV and IR). The remainder of the paper is devoted to interpretation of the spectra.

† From the Ph.D. thesis of Chang Kiu Lee, University of Minnesota, Minneapolis, MN, Aug 1976; *Diss. Abstr. Int. B* **1977**, *38*, 1210–1.

Mass Spectra of the Michael-Type Adducts (Table I)

As shown in Table I, all of the 1:1 Michael-type adducts (**3** and **4**) have molecular ion peaks in the high-resolution mass spectra corresponding to the molecular formulas assigned. Also, with most of the 1*H*- or 1-alkylpyrroles the molecular ion (**6**, Scheme II) is either the base peak (**3a,c,f,j** and **4a–d,f,j**) or the second strongest peak (**3b,d** and **4l**). The next strongest peak, also particularly with the 1-alkyl- and 1*H*-pyrroles, results from loss of an ester group (M – $COOCH_3$), probably from the position vicinal to the pyrrole ring. This would permit the allenic conjugation with the ring shown in structure **7**. This was the base peak with four compounds (**3b,d,l** and **4l**) and the second strongest peak with another eight (**3e,f,n,q** and **4b,d,f,n**). Concomitant additional loss of a hydrogen (M – $HCOOCH_3$), probably leading to the acetylene **8**, was particularly important with the 1-aryl compounds, giving the base peak with five (**3n,o**, and **4m–o**) and the second strongest peak with three compounds (**3m,p**, and **4p**). Though never the base or second strongest peak, loss of an ester group and the elements of methanol (M – $COOCH_3$ – CH_3OH) was often a significant peak, particularly with the 1-aryl compounds, probably leading to the acetylenic acylium ion **9**, which would be conjugated with the nitrogen as shown in the cumulene resonance form **9′**.

Loss of both ester groups (M – $2COOCH_3$) was a major peak observed with all compounds (except **3l** and **4l**), probably leading to the acetylene **10**. It was, however, always accompanied by concomitant loss of those 1-alkyl substituents (the 1-butyl groups in **3l–k** and **4l–k**) which could easily be eliminated as alkenes (butylenes in these cases), giving probably the NH acetylenes (**11**) corresponding to the fragment M – $2COOCH_3$ – (R′–H). These two closely related fragments accounted for the base peak in **3m** and the second strongest peak in seven other compounds (**3a,c,j** and **4a,c,j,m**). The sole exceptions, the 1-benzyl compounds **3l** and **4l**, lost the benzyl group as the tropylium ion, C_7H_7, to give their base peak at mass 91. This just happens to correspond to the fragment M – $2COOCH_3$ – (R′–H), which would have the same integral mass number (91) in this case. Loss of one more hydrogen than in **10**, corresponding to M – $2COOCH_3$ – H, was a significant fragmentation observed with most of the compounds. It accounted for the base peak with the three 1-(methylphenyl) compounds (**3p,q** and **4p**) and the second strongest peak with **3l**. It would not be difficult to account for this hydrogen-stripping process by visualizing loss of a hydrogen from a 3- or 5-methyl or alkyl group on the pyrrole nucleus of **10** to give conjugated pyrrolinium ions such as **12** or **13**. The explanation becomes more difficult, however, when there are no substituents other than on the 1-position of the pyrrole nucleus. Loss of a hydrogen from the α carbon of the *N*-alkyl group, as in ion **14**, could account for the fragment from all of the *N*-alkyl compounds where it is

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Table I. Physical Properties and Principal High-Resolution Mass Spectral Fragments of the Dimethyl ((*Z*)-3 and (*E*)-4) 2-Pyrrolyl-2-butenedioates[g]

structure	mp, °C	M+	M − $COOCH_3$	M − $HCOOCH_3$	M − $COOCH_3$ − CH_3OH	$R'RC_6H_3N$, M − $2COOCH_3$	$R'RC_6H_2N$, M − $2COOCH_3$ − H	other
(*Z*)-3a	oil[a,b]	209[a] (100)	150[a] (47)		118[a] (57)	91[a] (65)		178[a] (18; M − CH_3O), 177[a] (44; M − CH_3OH)
(*E*)-4a	oil[a,b]	209[a] (100)	150[a] (44)		118[a] (55)	91[a] (68)		178[a] (24; M − CH_3O), 177[a] (45; M − CH_3OH)
(*Z*)-3b	67–68 (pale yellow prisms)	223 (86)	164 (100)			105 (55)	104 (25)	192 (15; M − CH_3O), 108 (22; C_6H_6NO, M − $COOCH_3$ − CH_3OH − 2C)
(*E*)-4b	oil[b]	223 (100)	164 (93)			105 (40)	104 (20)	192 (10; M − CH_3O), 108 (22; C_6H_6NO, M − $COOCH_3$ − CH_3OH − 2C)
(*Z*)-3c	110–111.5[c] (yellow prisms)	223 (100)	164 (54)		132 (45)	105 (67)	104 (43)	192 (27; M − CH_3O), 191 (59; M − CH_3OH)
(*E*)-4c	50–51.5[d] (yellow prisms)	223 (100)	164 (62)		132 (53)	105 (90)	104 (61)	192 (20; M − CH_3O), 191 (55; M − CH_3OH)
(*Z*)-3d	90–91.5[e] (yellow needles)	237 (72)	178 (100)			119 (50)	118 (56)	122 (25; C_7H_8NO, M − $COOCH_3$ − CH_3OH − 2C)
(*E*)-4d	oil[b]	237 (100)	178 (97)			119 (30)	118 (32)	122 (17; C_7H_8NO, M − $COOCH_3$ − CH_3OH − 2C)
(*Z*)-3e	oil[b]	237[f] (88)	178[f] (95)	177[f] (34)		119[f] (44)	118[f] (79)	211[f] (37), 180[f] (77), 179[f] (100), 150[f] (31), 122[f] (17), 121[f] (47), 93[f] (43)
(*Z*)-3f	oil[b]	237 (100)	178 (81)	177 (20)	146[f] (38)	119[f] (12)	118[f] (54)	206 (14; M − CH_3O), 205 (19; M − CH_3OH), 145[f] (17; M − $HCOOCH_3$ − CH_3OH), 117[f] (75; M − $2HCOOCH_3$)
(*E*)-4f	oil[b]	237 (100)	178 (79)	177 (23)	146 (38)	119 (35)	118 (65)	206 (23; M − CH_3O), 205 (23; M − CH_3OH), 145 (17; M − $HCOOCH_3$ − CH_3OH), 117 (8; M − $2HCOOCH_3$)
(*Z*)-3i	oil[b]	265 (47)	206 (100)		174 (34)	91 (R′ = H) (24)	146 (57)	178 (20), 164 (53; M − $COOCH_3$ − C_3H_6), 151 (18), 150 (25; M − $COOCH_3$ − C_4H_8), 118 (16; M − $2COOCH_3$ − C_2H_5), 118 (13; M − $COOCH_3$ − CH_3OH − C_4H_8), 105 (25; M − $2COOCH_3$ − C_3H_6), 104 (31; M − $2COOCH_3$ − C_3H_7)
(*E*)-4i	oil[b]	265 (71)	206 (100)		174 (29)	91 (R′ = H) (24)	146 (45)	178 (15; M − C_4H_7), 164 (47; M − $COOCH_3$ − C_3H_6), 151 (12; M − $COOCH_3$ − C_4H_7), 150 (17; M − $COOCH_3$ − C_4H_8), 132 (11), 118 (12; M − $2COOCH_3$ − C_2H_5), 118 (11; M − $COOCH_3$ − CH_3OH − C_4H_8), 105 (12; M − $2COOCH_3$ − C_3H_6), 104 (22; M − $2COOCH_3$ − C_3H_7)
(*Z*)-3j	oil[b]	265 (100)	206 (69)			91 (R′ = H) (76)	146 (47)	178 (48), 177 (67; M − CH_3OH − C_4H_8), 151 (33; M − $COOCH_3$ − C_4H_7), 150 (59; M − $COOCH_3$ − C_4H_8), 132 (25; M − $2COOCH_3$ − CH_3), 118 (71)
(*E*)-4j	oil[b]	265 (100)	206 (69)			91 (R′ = H) (73)	146 (40)	178 (30; M − CH_3OH − C_4H_7), 177 (57; M − CH_3OH − C_4H_8), 151 (30; M − $COOCH_3$ − C_4H_7), 150 (60; M − $COOCH_3$ − C_4H_8), 132 (28; M − $2COOCH_3$ − CH_3), 118 (66)

Table I (*Continued*)

structure	mp, °C	M+	M − $COOCH_3$	M − $HCOOCH_3$	M − $COOCH_3$ − CH_3OH	$R'RC_6H_3N$, M − $2COOCH_3$	$R'RC_6H_2N$, M − $2COOCH_3$ − H	other
(*Z*)-3k	oil[b]	265 (39)				91 (R′ = H) (40)		209 (100; M − C_4H_8), 178 (32; M − CH_3OH − C_4H_7), 177 (83; M − CH_3OH − C_4H_7), 151 (16; M − $COOCH_3$ − C_4H_7), 150 (27; M − $COOCH_3$ − C_4H_8), 147 (10; M − $HCOOCH_3$ − C_4H_{10}), 143 (23; M − $HCOOCH_3$ − CH_3OH − C_2H_6), 119 (11; M − $COOCH_3$ − CH_3OH − C_4H_7), 118 (25; M − $COOCH_3$ − CH_3OH − C_4H_8), 115 (24; M − $2HCOOCH_3$ − C_2H_6)
(*E*)-4k	oil[b]	265 (40)	206 (4)			91 (R′ = H) (45)		209 (100; M − C_4H_8), 178 (25; M − CH_3OH − C_4H_7), 177 (74; M − CH_3OH − C_4H_7), 151 (14; M − $COOCH_3$ − C_4H_7), 150 (31; M − $COOCH_3$ − C_4H_8), 147 (7; M − $HCOOCH_3$ − C_4H_{10}), 119 (11; M − $COOCH_3$ − CH_3OH − C_4H_7), 118 (30; M − $COOCH_3$ − CH_3OH − C_4H_8)
(*Z*)-3l	99–101 (pale yellow needles)	299 (14)	240 (18)			91 (C_7H_7) (100)	180 (9)	121 (27; C_8H_9O)
(*E*)-4l	oil[b]	299 (10)	240 (20)			91 (C_7H_7) (100)	180 (13)	121 (24; C_8H_9O)
(*Z*)-3m	84–85 (pale yellow prisms)	285 (19)	226 (51)	225 (92)	194 (74)	167 (100)	166 (38)	195 (10; M − $COOCH_3$ − CH_3O), 140 (11), 139 (16), 115 (11)
(*E*)-4m	oil[b]	285 (21)	226 (50)	225 (100)	194 (62)	167 (93)	166 (41)	195 (11; M − $COOCH_3$ − CH_3O), 140 (11), 139 (15), 115 (12)
(*Z*)-3n	110–113 (pale yellow needles)	315 (33)	256 (76)	255 (100)	224 (50)	197 (64)	196 (18)	209 (20), 207 (21), 182 (19; M − $2COOCH_3$ − CH_3)
(*E*)-4n	oil[b]	315 (43)	256 (75)	255 (100)	224 (49)	197 (57)	196 (22)	182 (13; M − $2COOCH_3$ − CH_3), 163 (15), 154 (17), 101 (41)
(*Z*)-3o	118–120 (pale yellow prisms)	365 (21)[f] 363 (20)[f]	306[f] (40)[f] 304[f] (39)[f]	305[f] (100)[f] 303 (96)[f]	274 (37)[f] 272 (40)[f]	247 (43)[f] 245 (46)[f]	246 (25)[f] 244[f] (18)[f]	225 (46,[f] M − $COOCH_3$ − Br), 194 (26;[f] M − $COOCH_3$ − CH_3O − Br), 167 (47;[f] M − $COOCH_3$ − $COOCH_2$ − Br), 166 (52;[f] M − $2COOCH_3$ − Br), 165 (28;[f] M − $2COOCH_3$ − H − Br), 143[f] (18[f]), 140[f] (23[f]), 139[f] (27[f]), 115[f] (32[f]), 111[f] (44[f])
(*E*)-4o	oil[b]	365 (33) 363 (37)	304[f] (52)	303[f] (100)	274 (38) 272 (36)	247 (36) 245 (37)	246 (19) 244 (16)	225 (57; M − $COOCH_3$ − Br), 194 (21; M − $COOCH_3$ − CH_3O − Br), 167 (32; M − $COOCH_3$ − $COOCH_2$ − Br), 166 (43; M − $2COOCH_3$ − Br), 165 (20; M − $2COOCH_3$ − H − Br), 149 (15), 142 (14), 140 (16), 139 (21), 115 (14)
(*Z*)-3p	119.5–121 (white prisms)	299 (33)	240 (73)	239 (96)	208 (81)	181 (55)	180 (100)	252 (8; M − CH_3OH − CH_3), 225 (19; M − $COOCH_3$ − CH_3), 179 (10; M − $2HCOOCH_3$), 178 (11; M − $2HCOOCH_3$ − H), 167 (14; M − $2COOCH_3$ − CH_2), 154 (9), 152 (12)

Table I (*Continued*)

structure	mp, °C	M+	M − $COOCH_3$	M − $HCOOCH_3$	M − $COOCH_3$ − CH_3OH	$R'RC_6H_3N$, M − $2COOCH_3$	$R'RC_6H_2N$, M − $2COOCH_3$ − H	other
(*E*)-4p	oil[b]	299 (43)	240 (85)	239 (95)	208 (85)	181 (66)	180 (100)	252 (10; M − CH_3OH − CH_3), 225 (20; M − $COOCH_3$ − CH_3), 179 (9; M − $2HCOOCH_3$), 178 (10; M − $2HCOOCH_3$ − H), 167 (16; M − $2COOCH_3$ − CH_2), 154 (11), 152 (10)
(*Z*)-3q	98–99 (pale yellow prisms)	313 (48)	254 (76)	253 (21)	222 (59)	195 (35)	194 (100)	282 (12; M − CH_3O), 266 (12; M − CH_3OH − CH_3), 240 (10; M − $COOCH_3$ − CH_2), 239 (17; M − $COOCH_3$ − CH_3), 193 (11; M − $2HCOOCH_3$), 181 (16; M − $2COOCH_3$ − CH_2), 180 (15; M − $2COOCH_3$ − CH_3), 170 (19; M − $2COOCH_3$ − H − 2C), 168 (11; M − $2COOCH_3$ − C_2H_3)
(*E*)-4s	45–48 (pale yellow prisms)	251 (23)				91 (R′ = H) (42)		209 (100; M − CH_2CO), 185 (21), 184 (34), 178 (21; M − CH_3O − CH_2CO), 177 (50; M − CH_3OH − CH_2CO), 156 (17), 153 (28), 151 (12), 150 (26), 125 (13), 118 (28; M − CH_3OH − $COOCH_3$ − CH_2CO)

[a] Reference 2. [b] Oils were yellow in color. [c] Literature mp, 111 °C (*3a,b*). [d] Literature mp, 52 °C (*3b*). [e] Literature mp, 92 °C (*4*). [f] From a low-resolution mass spectrum. [g] For brevity, high-resolution masses (at 200 °C, 70 eV; with relative intensities in parentheses) are given as *m/e* to the nearest whole mass numbers, although the found values were within at least 15 ppm of those calculated as determined by a computer program. When no assignments are given, the found values did not fit reasonable formulas for the fragment calculated within that limit. In general, ^{13}C isotopic peaks have been excluded.

observed. (It is not a significant fragment with the NH (**3a**, **4a**), *N*-*tert*-butyl (**3k**, **4k**), or *N*-acetyl (**4s**) compounds.) Such an explanation, however, cannot account for the significance of this fragment with all of the *N*-aryl compounds (**3m–q**, **4m–p**), particularly with those lacking 2-methyl groups. For these, the allenic carbenium ion **15** is suggested, for want of a better explanation. Interestingly, the 1-butylpyrroles which lost butylene in the formation of the M − $2COOCH_3$ − C_4H_8 fragment (**11**) do not lose the 1-butyl substituent during formation of the M − $2COOCH_3$ − H fragment (**12–15**). This suggests that the two pathways may not have a common ultimate precursor (**10**), although they could have.

With the 1-butyl compounds (**3l–k**, **4l–k**), the usual fragmentations observed in this series are accompanied by varying degrees of fragmentation of the butyl groups (as described in Table I under "other" peaks). This becomes particularly prominent with the 1-*tert*-butyl compounds (**3k**, **4k**), where loss of isobutylene, M − C_4H_8, becomes the base peak. With the 1-(4-bromophenyl) compounds (**3o**, **4o**), the usual fragmentations are frequently accompanied by loss of the bromine atom. With the 1-(4-methoxyphenyl) (**3n**, **4n**) and 1-(2-methylphenyl) (**3p,q**, **4p**) compounds, the usual fragmentations were also frequently accompanied by loss of methyl groups. With the 1-acetyl compound (**4s**), loss of the elements of ketene was facile and gave the base peak (M − CH_2CO). Consistent with this, most of the usual fragmentations were also observed, but in each case the fragment had also lost the elements of ketene (such as *m/e* 91, M − $2COOCH_3$ − CH_2CO).

NMR Spectra of the Michael-Type Adducts (Table II)

The proton NMR data presented in Table II show that the most characteristic chemical shift differences between the *Z* and *E* isomers of the 1:1 Michael adducts occur with the vinyl proton singlet. The significant additional magnetic anisotropy of the ester carbonyl group cis to the vinyl proton in the *E* isomers should lead to greater deshielding than in the *Z* isomers, as is calculated from the additivity rules (*5a*). Thus, the calculated chemical shifts for the vinyl proton in the *E* and *Z* isomers are δ 6.97 and 6.37, respectively. The calculations do not take into account additional resonance shielding which could come from electron release from the pyrrole nitrogen. These values provide a basis for NMR assignment of stereochemistry to the isomers **4** and **3**. The observed ranges are δ 5.85–6.98 (average 6.64) for the downfield isomer set (now designated as the *E*, structure **4**) and δ 5.07–6.13 (average 5.64) for the upfield isomer set (now designated as the *Z*, structure **3**).

In the NH compounds the vinyl proton in the *E* isomer appears significantly upfield from that calculated and from that observed in all cases with an *N*-alkyl or *N*-phenyl substituent. This is the primary reason that the chemical shift differences between the *E* and *Z* isomers of the NH compounds are quite small: in **4a** − **3a**, δ 5.97 − 5.92, $\Delta\delta$ 0.05; **4c** − **3c**, δ 5.93 − 5.78, $\Delta\delta$ 0.15; **4f** − **3f**, δ 5.85 − 5.53, $\Delta\delta$ 0.32. For the remaining, *N*-substituted compounds, with the *E* isomers the alkyl vs. phenyl nature of the N substituent makes little difference, and the chemical shifts of the vinyl proton are δ 6.91 for the six *N*-alkyl and 6.74 for the four *N*-phenyl compounds, and 6.84 overall. With the *Z* isomers, however, there is a significant difference, with values of δ 5.88 for the seven *N*-alkyl and 5.24 for the five *N*-phenyl compounds, and 5.62 overall. Clearly, in these cases, the upfield shift over that calculated from the additivity rules (*5a*) is far greater in the *Z* isomers than in the *E* isomers, suggesting the possibility of greater resonance shielding in the *Z* isomers. Resonance shielding may also account for the relative upfield shift of the vinyl proton in the *E*

Table II. Proton Nuclear Magnetic Resonance (NMR) Chemical Shifts in the Dimethyl ((*Z*)-3 and (*E*)-4) 2-Pyrrolyl-2-butenedioates[b]

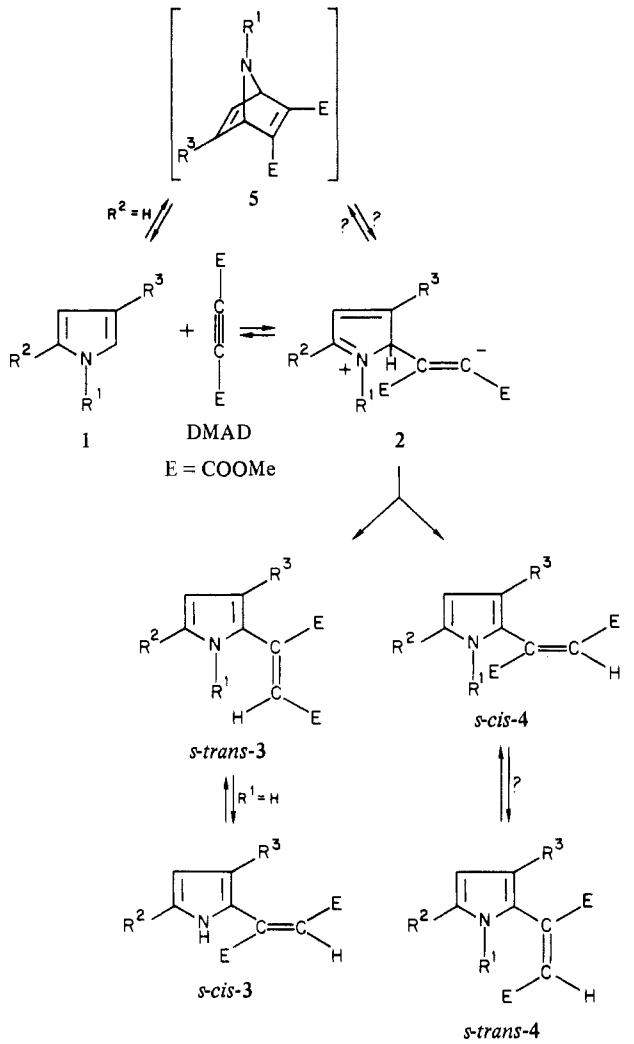
compd	vinyl H (s, 1 H)	N-R	$2COOCH_3$ (2 s of 3 H)		other
(*Z*)-3a	5.92[a]	12.61[a] (NH) (br s, 1 H)	3.73[a]	3.83[a]	6.27[a] (m, 1 H, 4-H), 6.72[a] (m, 1 H, 3-H), 6.98[a] (m, 1 H, 5-H)
(*E*)-4a	5.97[a]	9.03[a] (NH) (br s, 1 H)	3.68[a]	3.90[a]	6.17[a] (m, 1 H, 4-H), 6.42[a] (m, 1 H, 3-H), 6.82[a] (m, 1 H, 5-H)
(*Z*)-3b	5.95	3.70 (CH_3) (s, 3 H)	3.73	3.93	6.13 (dd, 1 H, 4-H, $J_{4,3}$ = 3.5, $J_{4,5}$ = 2), 6.43 (dd, 1 H, 3-H, $J_{3,4}$ = 3.5, $J_{3,5}$ = 1.5), 6.73 (dd, 1 H, 5-H, $J_{5,3}$ = 1.5, $J_{5,4}$ = 2)
(*E*)-4b	6.98	3.47 (CH_3) (s, 3 H)	3.67	3.83	6.15 (m, 2 H, 3- and 4-H), 6.70 (m, 1 H, 5-H)
(*Z*)-3c	5.78	12.33 (NH) (brs, 1 H)	3.77	3.83	2.33 (s, 3 H, 5-CH_3), 6.00 (d, 1 H, 4-H, $J_{4,3}$ = 4), 6.60 (d, 1 H, 3-H, $J_{3,4}$ = 4)
(*E*)-4c	5.93	9.40 (NH) (br s, 1 H)	3.68	3.92	2.27 (s, 3 H, 5-CH_3), 5.93 (m, 1 H, 4-H), 6.33 (m, 1 H, 3-H)
(*Z*)-3d	5.90	3.65 (CH_3) (s, 3 H)	3.75	3.92	2.27 (s, 3 H, 5-CH_3), 5.97 (d, 1 H, 4-H, $J_{4,3}$ = 4), 6.37 (d, 1 H, 3-H, $J_{3,4}$ = 4)
(*E*)-4d	6.85	3.28 (CH_3) (s, 3 H)	3.58	3.78	2.22 (s, 3 H, 5-CH_3), 5.87 (d, 1 H, 4-H, $J_{4,3}$ = 4), 6.10 (d, 1 H, 3-H, $J_{3,4}$ = 4)
(*Z*)-3e	5.88	3.55 (CH_3) (s, 3 H)	3.77	3.83	2.10 (s, 3 H, 3-CH_3), 5.98 (d, 1 H, 4-H, $J_{4,5}$ = 2.5), 6.60 (d, 1 H, 5-H, $J_{5,4}$ = 2.5)
(*Z*)-3f	5.53	12.05 (NH) (br s, 1 H)	3.73	4.17	2.00 (s, 3 H, 3-CH_3), 2.28 (s, 3 H, 5-CH_3), 5.82 (m, 1 H, 4-H)
(*E*)-4f	5.85	8.67 (NH) (br s, 1 H)	3.68	3.88	2.10 (s, 3 H, 3-CH_3), 2.17 (s, 3 H, 5-CH_3), 5.77 (m, 1 H, 4-H)
(*Z*)-3i	5.70	0.90–2.00 (m, 7 H, $CH_3CH_2CH_2$), 3.73 (t, 2 H, NCH_2)	3.60	3.70	5.97 (m, 1 H, 4-H), 6.17 (m, 1 H, 3-H), 6.63 (m, 1 H, 5-H)
(*E*)-4i	6.77	0.80–1.80 (m, 7 H, $CH_3CH_2CH_2$), 3.60 (t, 2 H, NCH_2)	3.58	3.67	5.90 (m, 2 H, 3- and 4-H), 6.55 (m, 1 H, 5-H)
(*Z*)-3j	5.87	0.75 (t, 3 H, CH_3CH_2, J = 7), 1.40 (d, 3 H, CH_3CH, J = 7), 1.72 (m, 2 H, CH_3CH_2CH), 4.27 (m, 1 H, NCH)	3.75	3.88	6.20 (dd, 1 H, 4-H, $J_{4,3}$ = 3, $J_{4,5}$ = 2), 6.38 (dd, 1 H, 3-H, $J_{3,4}$ = 3, $J_{3,5}$ = 1.5), 6.77 (dd, 1 H, 5-H, $J_{5,4}$ = 2, $J_{5,3}$ = 1.5)
(*E*)-4j	6.98	0.75 (t, 3 H, CH_3CH_2, J = 7), 1.35 (d, 3 H, CH_3CH, J = 7), 1.68 (m, 2 H, CH_3CH_2CH), 3.82 (m, 1 H, NCH)	3.62	3.78	6.05 (dd, 1 H, 4-H, $J_{4,3}$ = 3.5, $J_{4,5}$ = 1.5), 6.17 (dd, 1 H, 3-H, $J_{3,4}$ = 3.5, $J_{3,5}$ = 2), 6.78 (dd, 1 H, 5-H, $J_{5,4}$ = 1.5, $J_{5,3}$ = 2)
(*Z*)-3k	6.13	1.58 (C_4H_9) (s, 9 H)	3.77	3.80	6.17 (m, 2 H, 3- and 4-H), 6.97 (m, 1 H, 5-H)
(*E*)-4k	6.93	1.48 (C_4H_9) (s, 9 H)	3.55	3.68	5.85 (m, 1 H, 4-H), 6.07 (m, 1 H, 3-H), 6.87 (m, 1 H, 5-H)
(*Z*)-3l	5.75	5.22 (s, 2 H, CH_2), 7.03–7.27 (m, 5 H, C_6H_5)	3.67	3.82	6.23 (dd, 1 H, 4-H, $J_{4,3}$ = 4, $J_{4,5}$ = 2.5), 6.50 (dd, 1 H, 3-H, $J_{3,4}$ = 4, $J_{3,5}$ = 1.5), 6.80 (dd, 1 H, 5-H, $J_{5,4}$ = 2.5, $J_{5,3}$ = 1.5)
(*E*)-4l	6.95	4.90 (s, 2 H, CH_2), 7.18 (m, 5 H, C_6H_5)	3.62	3.65	6.13 (m, 1 H, 4-H), 6.17 (m, 1 H, 3-H), 6.70 (m, 1 H, 5-H)
(*Z*)-3m	5.30	7.33 (m, 5 H, C_6H_5)	3.61	3.77	6.28 (dd, 1 H, 4-H, $J_{4,3}$ = 4, $J_{4,5}$ = 2.5), 6.55 (dd, 1 H, 3-H, $J_{3,4}$ = 4, $J_{3,5}$ = 2), 6.93 (dd, 1 H, 5-H, $J_{5,4}$ = 2.5, $J_{5,3}$ = 2)
(*E*)-4m	6.78	7.28 (m, 5 H, C_6H_5)	3.42	3.65	6.28 (m, 1 H, 4-H), 6.43 (m, 1 H, 3-H), 6.97 (m, 1 H, 5-H)
(*Z*)-3n	5.30	3.60 (s, 3 H, OCH_3), 6.93 and 7.20 (AB q, 4 H, C_6H_4, J = 9)	3.70	3.85	6.30 (dd, 1 H, 4-H, $J_{4,3}$ = 4, $J_{4,5}$ = 3), 6.55 (dd, 1 H, 3-H, $J_{3,4}$ = 4, $J_{3,5}$ = 2), 6.83 (dd, 1 H, 5-H, $J_{5,4}$ = 3, $J_{5,3}$ = 2)
(*E*)-4n	6.75	3.45 (s, 3 H, OCH_3), 6.87 and 7.17 (AB q, 4 H, C_6H_4, J = 9)	3.65	3.78	6.32 (m, 2 H, 3- and 4-H), 6.87 (m, 1 H, 5-H)
(*Z*)-3o	5.40	7.30 and 7.70 (AB q, 4 H, C_6H_4, J = 9)	3.60	3.70	6.35 (dd, 1 H, 4-H, $J_{4,3}$ = 4, $J_{4,5}$ = 2.5), 6.58 (dd, 1 H, 3-H, $J_{3,4}$ = 4, $J_{3,5}$ = 1.5), 7.10 (dd, 1 H, 5-H, $J_{5,4}$ = 2.5, $J_{5,3}$ = 1.5)
(*E*)-4o	6.80	7.10 and 7.47 (AB q, 4 H, C_6H_4, J = 8)	3.48	3.67	6.35 (m, 2 H, 3- and 4-H), 6.93 (m, 1 H, 5-H)
(*Z*)-3p	5.13	2.00 (s, 3 H, CH_3), 7.27 (m, 4 H, C_6H_4)	3.58	3.75	6.32 (dd, 1 H, 4-H, $J_{4,3}$ = 4, $J_{4,5}$ = 2.5), 6.53 (dd, 1 H, 3-H, $J_{3,4}$ = 4, $J_{3,5}$ = 1.5), 6.77 (dd, 1 H, 5-H, $J_{5,4}$ = 2.5, $J_{5,3}$ = 1.5)
(*E*)-4p	6.65	2.18 (s, 3 H, CH_3), 7.17 (m, 4 H, C_6H_4)	3.42	3.68	6.28 (dd, 1 H, 4-H, $J_{4,3}$ = 3.5, $J_{4,5}$ = 2.8), 6.45 (dd, 1 H, 3-H, $J_{3,4}$ = 3.5, $J_{3,5}$ = 2), 6.82 (dd, 1 H, 5-H, $J_{5,4}$ = 2.8, $J_{5,3}$ = 2)
(*Z*)-3q	5.07	2.00 (s, 6 H, $2CH_3$), 7.20 (m, 3 H, C_6H_3)	3.57	3.75	6.37 (dd, 1 H, 4-H, $J_{4,3}$ = 4, $J_{4,5}$ = 2), 6.52 (dd, 1 H, 3-H, $J_{3,4}$ = 4, $J_{3,5}$ = 1.5), 6.66 (dd, 1 H, 5-H, $J_{5,3}$ = 1.5, $J_{5,4}$ = 2)
(*E*)-4s	6.87	2.52 ($COCH_3$) (s, 3 H)	3.63	3.77	6.28 (m, 2 H, 3- and 4-H), 7.17 (m, 1 H, 5-H)

[a] Reference 2. [b] δ (multiplicity, relative proton areas, J in Hz) in $CDCl_3$ containing 1% tetramethylsilane as an internal standard; br = broad, s = singlet, m = multiplet, d = doublet, t = triplet, q = quartet.

isomers of the NH compounds since the small, hydrogen substituent on nitrogen should provide the maximum opportunity in the *E* series for coplanarity and resonance overlap of the adjacent vinyl group with the pyrrole ring.

Another factor which may contribute to the upfield shift of the vinyl proton in the *E* isomers of the NH compounds could be intramolecular hydrogen bonding (through a six-membered ring) of the NH proton with the ester carbonyl cis to the vinyl proton (with **4** in the *s*-cis conformation). This would diminish the double bond character of the carbonyl group and thus diminish its anisotropic effect on the vinyl proton (though in this case there would probably be some offsetting resonance deshielding). Alternatively, if the *E* isomer were in the *s*-trans conformation (which seems less probable), intramolecular hydrogen bonding (through a seven-membered ring) of the NH proton might occur with the ester carbonyl geminal to the vinyl proton, which might have a similar, but weaker, effect. The most favorable case for intramolecular hydrogen bonding, however, would be with the *Z* isomers in the *s*-cis (but not the *s*-trans) conformation, since steric interaction between the 3-proton on the pyrrole nucleus and a coplanar ester group (such as would be present in the *E* isomers) would be absent

Scheme I[a]



	R¹	R²	R³
1a, 3a,[b] 4a[b]	H	H	H
1b, 3b, 4b	Me	H	H
1c, 3c, 4c	H	Me	H
1d, 3d,[c] 4d	Me	Me	H
1e, 3e	Me	H	Me
1f, 3f, 4f	H	Me	Me
1g, 3g,[d] 4g[d]	H	Me	H (R⁴ = Me)
1h, 3h[d]	H	Me	Me (R⁴ = Me)
1i, 3i, 4i	*n*-Bu	H	H
1j, 3j, 4j	*sec*-Bu	H	H
1k, 3k, 4k	*t*-Bu	H	H
1l, 3l, 4l	CH_2Ph	H	H
1m, 3m, 4m	Ph	H	H
1n, 3n, 4n	4-(MeOPh)	H	H
1o, 3o, 4o	4-(BrPh)	H	H
1p, 3p, 4p	2-(MePh)	H	H
1q, 3q	2,6-(diMePh)	H	H
1s, 4s	COMe	H	H

[a] The numbering and lettering of compounds corresponds to that used in (ref *1*). [b] Reference *2*. [c] Reference *4*. [d] Reference *3b*.

in this case. Consistent with greater hydrogen bonding in the *Z* isomers is the fact that the NH protons appear significantly downfield (**3a**, δ 12.61; **3c**, 12.33; **3f**, 12.05; average 12.33) from those in the *E* isomers (**4a**, δ 9.03; **4c**, 9.40; **4f**, 8.67; average 9.03), while the NH proton in pyrrole itself (**1a**) appears at δ 7.70 (*5b*).

The significant upfield shift of the vinyl proton in the *Z* isomers of the *N*-phenyl relative to the *N*-alkyl compounds is probably due to shielding by the phenyl ring (in the *s*-trans conformation of **3**). The pyrrole and phenyl rings are probably not coplanar, as a result of distortion caused by steric interaction of the ortho substituents (hydrogen or larger) of the phenyl ring with the ortho substituents of the pyrrole ring (5-hydrogen or substituents of the 2-vinyl group). The angle of distortion and consequent shielding of the vinyl proton should increase with increasing size of ortho substituents on either ring. This trend is observed in the chemical shift of the vinyl proton as the 2-substituent on the phenyl ring is varied from hydrogen (δ 5.30) to 2-methyl (δ 5.13) to 2,6-dimethyl (δ 5.07). In the absence of such steric effects, variation of the substituents (in the para position) on the phenyl ring does not appear to have any significant effect on the chemical shift of the vinyl proton in either the *Z* (H, δ 5.30; CH_3O, 5.30; Br, 5.40) or the *E* isomers (H, 6.78; CH_3O, 6.75; Br, 6.80). This is as might be expected if there is steric inhibition of resonance between the phenyl and pyrrole rings (and, thus, on subsequent transmission to the vinyl group). There may also be some steric inhibition by the phenyl group of resonance between the vinyl group and the pyrrole ring.

1,3-Dimethylpyrrole (**1e**) has two open nonequivalent 2- (or 5-) positions. Thus, Michael-type addition could conceivably occur either at the sterically favored position meta to the *C*-methyl group or at the electronically activated position ortho to the *C*-methyl group. While the data may be inconclusive, the NMR chemical shift and coupling constant data in Table II favor the latter alternative, which would give structure **3e** (or **4e**). The downfield (5-) proton at δ 6.60 has a chemical shift somewhat upfield from but reasonably consistent with the average of 6.81 for the 5-proton in 22 adducts (excluding **4s**) or of 6.77 in the selected group of 12 most closely related *N*-alkylpyrrole adducts. The upfield proton at δ 5.98 has a chemical shift different from the average of 6.40 for the 3-proton in 20 adducts. It is in reasonable agreement, however, with the average of δ 6.12 for the 4-proton in 22 adducts, and in better agreement with the average of 5.89 for the 4-proton in the six adducts having a methyl group ortho (5- or 3-) to the proton.

The averages for the coupling constants which could be identified for the pyrrole protons in the adducts in Table II are $J_{3,4}$ = 3.8 (13 values), $J_{3,5}$ = 1.7 (9 values), and $J_{4,5}$ = 2.4 (9 values) Hz. The coupling constant for the two pyrrole protons in **3e** is 2.5 Hz, in good agreement with $J_{4,5}$. Only a single 1:1 Michael-type adduct was isolated in this case (from 1,3-dimethylpyrrole, **1e**). Its NMR (vinyl proton), UV, and IR data are more consistent with the *Z* isomer (**3e**, to which it is assigned) than with the *E* isomer (**4e**). Furthermore, the *E* isomer would be expected to be very sterically hindered, because of side-chain interaction with the 1- and 3-methyl groups, whether it is in the *s*-cis or the *s*-trans conformation, which is consistent with the fact that it was not isolated. A possibly analogous situation occurs with 2,3,4-trimethylpyrrole (**1h**), although here, being only from one side, the steric hindrance should be somewhat less. Only a single adduct has been isolated (*3b*), which, because of its high melting point (137–138 °C) and expected lesser steric hindrance, is now assumed to be the *Z* isomer (**3h**). The analogy breaks down, however, with 2,4-dimethylpyrrole (**1f**) and 1,2-dimethylpyrrole (**1d**), which should be even somewhat less sterically hindered, since these compounds form both *E* and *Z* isomers.

UV Spectra of the Michael-Type Adducts (Table III)

The UV data presented for the longest-wavelength K bands in Table III show no very consistent pattern of difference in wavelength between the *Z* (average 340 nm) and *E* (average 346 nm, excluding **4s**) isomers. On average, the *Z* isomers have maxima at slightly lower wavelengths (6 nm) than the *E* isomers, but the intensities of the *Z* bands (average log ϵ 4.20) are ~4 times greater than the *E* bands (average log ϵ 3.61). All of the *Z* bands have intensities greater than log ϵ 4.0, except for the sterically hindered *N*-*tert*-butyl (**3k**) case, which has a

Table III. Characteristic Ultraviolet (UV) and Infrared (IR) Bands of the Dimethyl (*Z*)-3 and (*E*)-4 2-Pyrrolyl-2-butenedioates

compd	UV λ max, nm, CH_3OH (log ε)	IR,[q] cm^{-1} NH	C=O	C=C	other
(*Z*)-3a	346[a] (4.17)	3260[a] m	1735[a] s, 1690[a] s	1582[a] s	1450 ms, 1438 ms, 1291[a] s, 1261 s, 1234[a] s, 1212[a] s, 1137 s, 1100[a] s, 1042[a] ms, 755[a] m
(*E*)-4a	335[a] (4.06)	3350[a] m	1740[a] s, 1712[a] s	1602[a] s	1234[a] s, 1200[a] s, 1170[a] s, 732[a] m
(*Z*)-3b	334[b] (4.37)		1739 s, 1702 s	1597 vs	1416 s, 1261 s, 1223 s, 1195 s, 1174 s, 760 m
(*E*)-4b	341 (3.45)		1730 vs	1625 m	1360 m, 1260 vs, 1235 s, 1216 s, 1168 ms, 1037 ms, 730 s
(*Z*)-3c	356 (4.33)	3180 mw	1727 s, 1679 ms	1568 s	1252 s, 1211 s, 1174 s, 1044 s, 800 m
(*E*)-4c	353[c] (4.47)	3322 ms	1740 s, 1685 s	1605 s	1250 s, 1200 s, 1183 s, 1044 ms, 775 ms
(*Z*)-3d	350[p] (4.36)		1730 s, 1700 s	1590 vs	1336 s, 1262 s, 1217 s, 1200 s, 1172 s, 1147 s, 770 m
(*E*)-4d	376[d] (3.50)		1728 s	1617 m	1438 ms, 1255 s, 1218 ms, 1175 ms, 1150 m, 1050 ms, 1025 ms, 760 m
(*Z*)-3e	346[e] (4.01)		1733 s, 1715 s	1590 ms	1438 m, 1273 s, 1232 ms, 1210 ms, 1198 ms, 1168 s, 738 mw
(*Z*)-3f	374 (4.25)	3190 mw	1735 s, 1680 m	1568 ms sh, 1550 s	1273 s, 1235 s, 1201 vs, 1182 s, 1039 ms
(*E*)-4f	362 (4.30)	3350 ms	1720 s, 1685 s sh	1590 s, 1568 s	1433 s, 1230 s, 1196 s, 1165 s
(*Z*)-3i	336 (4.02)		1735 s, 1722 s	1630 m, 1600 ms	1265 s, 1218 s, 1170 s, 755 m
(*E*)-4i	353 (3.33)		1727 s	1630 w	1440 m, 1259 s, 1024 ms, 722 m
(*Z*)-3j	337[f] (4.14)		1745 vs, 1723 vs	1603 s	1251 s, 1224 s, 1170 vs, 735 m
(*E*)-4j	343 (3.37)		1730 vs	1622 m	1254 vs, 1208 m, 1025 m, 723 m
(*Z*)-3k	337 (3.73)		1727 vs	1630 mw	1436 m, 1250 s, 1216 s, 1196 ms, 1168 s, 715 m
(*E*)-4k	351 (3.08)		1728 vs	1640 m	1440 ms, 1259 vs, 1140 ms, 1024 ms, 725 ms
(*Z*)-3l	332[g] (4.27)		1738 s, 1710 s	1605 s	1264 s, 1228 s, 1201 s, 1175 s, 762 ms
(*E*)-4l	354[h] (3.28)		1725 s	1630 m	1436 ms, 1285 ms, 1260 s, 1240 s, 725 m
(*Z*)-3m	331[i] (4.12)		1732 s, 1701 s	1610 s	1227 s, 1200 ms, 1191 ms, 1168 s, 765 ms
(*E*)-4m	336 (3.40)		1730 vs	1630 w, 1600 m	1505 s, 1260 s, 1210 s, 1168 m, 1024 m, 728 m
(*Z*)-3n	331[j] (4.26)		1750 s, 1720 s	1600 s, 1520 ms	1425 m, 1292 m, 1260 s, 1237 s, 1171 s, 852 m, 770 m
(*E*)-4n	332[k] (3.70)		1729 s	1612 ms, 1518 s	1265 s, 1043 s, 1024 s, 840 s, 729 ms
(*Z*)-3o	331[l] (4.18)		1740 s, 1717 s	1600 s	1232 s, 1175 s, 768 m
(*E*)-4o	326[m] (3.57)		1730 s	1628 m, 1596 m	1500 s, 1262 s br, 1167 s, 840 ms, 728 ms
(*Z*)-3p	331[n] (4.30)		1748 s, 1716 s, 1706 s	1600 vs	1420 s, 1235 s, 1200 s, 1171 vs, 768 m
(*E*)-4p	337 (3.47)		1728 vs	1628 m, 1588 mw	1502 s, 1499 s, 1471 s, 1437 s, 1260 vs, 1230 s sh, 1205 s, 1168 s, 1021 s, 770 s, 722 m
(*Z*)-3q	331[o] (4.45)		1745 s, 1717 s	1602 s	1282 ms, 1230 ms, 1200 ms, 1172 s, 790 ms
(*E*)-4s	315 (3.34)		1720 vs	1637 m	1438 ms, 1404 ms, 1351 ms, 1315 s, 1299 s, 1264 vs, 1168 ms

[a] Reference 2. Additional bands at (*b*) 274 sh (3.48), (*c*) 260 sh (3.39), (*d*) 278 (3.04), 310 sh (3.07), 328 sh (3.19), 346 sh (3.39), (*e*) 282 (3.57), (*f*) 275 wsh (3.32), (*g*) 235 sh (3.70), 269 (3.40), (*h*) 267 sh (3.11), (*i*) 221 sh (4.03), 272 (3.52), (*j*) 228 (4.26), 287 sh (3.81), (*k*) 226 sh (4.29), 280 sh (3.67), (*l*) 228 (4.22), 271 sh (3.76), (*m*) 242 (4.20), (*n*) 271 sh (3.58), (*o*) 274 (3.71). [p] Literature λ max 350 in CH_3OH (*4*). [q] In KBr pellets for solids and neat for oils; sh = shoulder, br = broad; intensities: m = medium, s = strong, w = weak.

markedly lower intensity (log ε 3.73). It also provides the lowest-intensity member (**4k**) of the *E* series (log ε 3.08). The bands of the *E* series all occur at intensities of log ε 3.7 or below (average 3.42, without **4a,c,f,s**), except for the NH compounds **4a** (4.06), **4c** (4.47), and **4f** (4.30), where the intramolecular hydrogen bonding already suggested in the NMR discussion may increase the probability of the transition. The greater intensity of the bands in the latter two *E* isomers (**4c,f**) leads to a reversal of the usual relative intensities, so that these bands have greater intensities than those of the corresponding members of the *Z* series (**3c**, log ε 4.33; **3f**, 4.25).

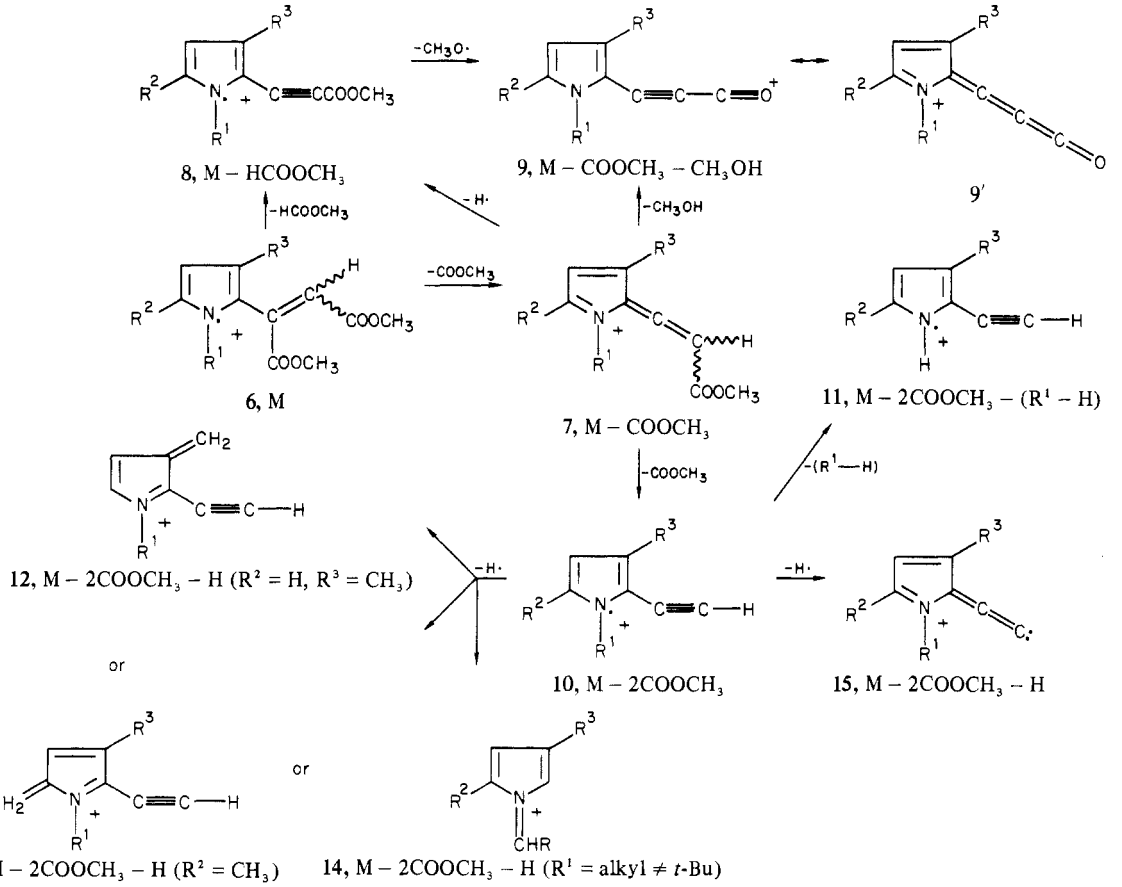
All five *N*-phenyl-substituted compounds in the *Z* series (**3m–q**) have the same wavelength of their K band, 331 nm, regardless of the nature or position of their phenyl substituents, strongly suggesting that there is no conjugation with the pyrrole nucleus, because of steric inhibition of resonance, as already suggested in the NMR discussion. Similarly, with the corresponding *N*-phenyl *E* isomers (**4m–p**) there is also no consistent variation in wavelength, with a range of 326–337 and an average of 333 nm.

IR Spectra of the Michael-type Adducts (Table III)

The IR data presented in Table III shows that the *Z* isomers, except for **3k**, have two strong carbonyl stretching bands of comparable intensity, at average positions of 1738 and 1706 cm^{-1}. (In the case of **3p**, the lower-frequency carbonyl band is finely split into two peaks, at 1716 and 1706 cm^{-1}, but the average position of 1711 cm^{-1} has been used.) The normal, higher-frequency unsaturated ester band is assigned to the α carbonyl, and the lower-frequency band to the β carbonyl, which is evidently conjugated with the pyrrole nucleus. The exception is the *N-tert*-butyl compound (**3k**), which has a single, very strong carbonyl band at 1727 cm^{-1}. The absence of the lower-frequency band is attributed to steric inhibition (by the adjacent *N-tert*-butyl group) of resonance of the maleate group with the pyrrole ring, so that the β carbonyl now also behaves largely as part of a simple maleate ester system. With the *E* isomers, except for the NH compounds, there is also only one broad, strong carbonyl band at an average position of 1728 cm^{-1}. This is similarly attributed to steric inhibition (by the N substituent) of resonance, so that both carbonyl groups behave largely as parts of a simple fumarate ester system. With the NH compounds in the *E* series (**4a,c,f**), there are two strong carbonyl bands at average positions of 1733 and 1694 cm^{-1}, much as with the *Z* series. This suggests that, with the small adjacent hydrogen substituent on nitrogen, resonance of the fumarate group with the pyrrole ring is not largely sterically inhibited and can occur in much the same manner as in the *Z* series.

The other most characteristic feature of the IR spectra is the carbon double-bond stretching band. With the *Z* isomers, except for **3k**, and with the conjugated NH members of the *E* series (**4a,c,f**), this band is strong (comparable in intensity to the carbonyl bands) and appears at an average position of 1595 cm^{-1}, indicating that it is conjugated, as has already been seen from the frequency of the β-carbonyl group with which it is conjugated. In contrast, with the largely pyrrole-unconjugated

Scheme II



compounds, which include the sterically hindered *tert*-butyl compound **3k** in the *Z* series and all of the *N*-alkyl, *N*-phenyl, and 1-acyl members of the *E* series, the highest-frequency major carbon double-bond band appears at an average position of 1625 cm^{-1} and is of medium to weak intensity. It is also significant that the out-of-plane bending band of the hydrogens in the pyrrole ring occurs at higher frequency in the *Z* series (average 764 cm^{-1}) than in the *E* series (average 734 cm^{-1}), except for the *N*-*tert*-butyl isomers, where this trend is reversed (**3k**, *Z*, 715; **4k**, *E*, 725 cm^{-1}).

With the NH compounds, the NH stretching frequency is lower in the *Z* isomers (average 3210 cm^{-1}) than in the *E* isomers (average 3341 cm^{-1}). This is consistent with the conclusion from the NH chemical shifts in the NMR that intramolecular hydrogen bonding is more important in the *Z* than in the *E* isomers.

Experimental Section

Melting points were determined on a calibrated Thomas Hoover capillary melting-point apparatus. Electron-impact mass spectra (MS) were determined on an AEI MS-30 spectrometer at 70 eV and 200 °C by Dr. Roger A. Upham (to whom we are indebted for helpful discussions), Edmund A. Larka, and Philip Price. Nuclear magnetic resonance spectra (NMR) were determined on Varian Associates T-60 or A-60 60-MHz spectrometers. Ultraviolet spectra (UV) were determined on a Cary Model 11 recording spectrophotometer. Infrared spectra (IR) were determined on a Beckman IR-18A or on a Perkin-Elmer Model 257 recording spectrophotometer. Elemental microanalyses were performed by M-H-W Laboratories, Garden City, MI (now Phoenix, AZ), except for the microanalysis of **4m** which was performed by the Institute of Physical and Chemical Research, Wako-shi, Saitama-ken, Japan.

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