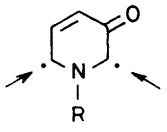
1,3-Dipolar Character of Six-membered Aromatic Rings. Part 56.† The Cycloadditions of Acetylenes and 3-Oxidopyridinium Betaines

Christina Y. Ishag,*[a] Keith J. Fisher,[b] Badr Eldin Ibrahim,[b] George M. Iskander,[a] and Alan R. Katritzky[c]

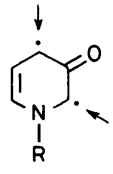
[a] *Department of Chemistry, University of Khartoum, Sudan*
[b] *Faculty of Education, University of Khartoum, Sudan*
[c] *Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.*

Cycloaddition of dimethyl acetylenedicarboxylate with a variety of 1-substituted 3-oxidopyridinium betaines yields novel furan cycloadducts. Methyl phenylpropiolate reacts similarly with the activated 1-[1',2-di(*p*-nitrophenyl)vinyl]-3-oxidopyridinium betaine, but phenylacetylene adds to activated betaines to give azabicyclo[3.2.1]octene adducts.

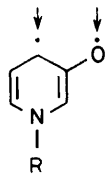
The 3-oxidopyridinium betaines (**2**), derived from 3-hydroxypyridinium salts (**1**), are versatile cycloaddition components capable of undergoing four different kinds of cycloaddition. They can act as 4π components (adding 2π[1] or 6π[2] addends across the 2,6-positions), 2π/6π components (adding thermally 4π[3] or photochemically 2π/6π[4] addends across the 2,4-positions), or as 8π[5] components (adding 2π addends across the exocyclic oxygen and C-4, or across the oxygen and C-2). In this way a large number of new systems have been synthesized.



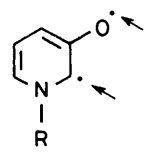
4 π component



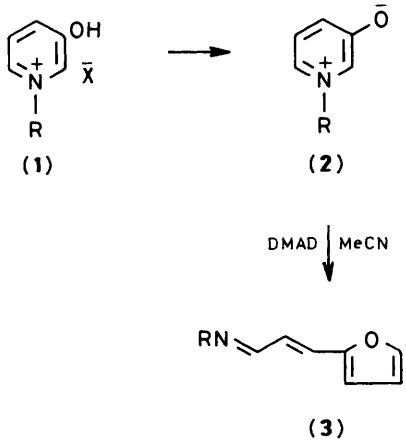
2π/6π component



8 π component



8 π component



a; R = Me, X = I
b; R = CH_2Ph, X = Cl
c; R = Ph, X = Cl
d; R = 1-(*p*-Nitrophenyl)-2-(*m*-nitrophenyl)vinyl, X = Cl
e; R = 1,2-Di(*p*-nitrophenyl)vinyl, X = Cl
f; R = 5,6-Diphenyl-1,2,4-triazin-3-yl, X = Cl
g; R = *trans*-(4-Chlorophenyl)-3-oxoprop-1-enyl, X = Cl

Scheme 1.

In this paper we describe the formation of a novel system by cycloadditions of the 2π addend dimethyl acetylenedicarboxylate (DMAD) adding across the oxygen and C-2 of 3-oxidopyridinium betaines (**2a**, **b**, **c**, **d**, or **e**) which act as 8π components.

In our preliminary communication,[6] 1,3-dipolar cycloaddition of DMAD with 3-oxido-1-phenylpyridinium betaine (**2c**) was shown to form the unusual furan adduct (**3c**) by the cycloaddition of DMAD across the oxygen and C-2 with concomitant opening of the pyridinium ring (Scheme 1). We have now found that DMAD cycloadducts are easily obtained from a variety of 3-oxidopyridinium betaines (**2a**—**e**) (Table 1). The much less reactive methyl phenylpropiolate reacted, at high temperature, only with betaine (**2e**) to give a furan cycloadduct (for unknown regiochemistry) in 23% yield. Phenylacetylene reacted only with the betaines (**2c** and **e**) and gave the 8-azabicyclo[3.2.1]oct-3-en-2-one adducts (**4a**)[7] and (**4b**), in 60 and 24% yield respectively.

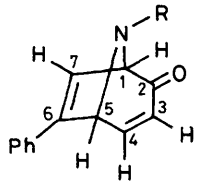
Reactions of the Cycloadducts.—The aqueous acid hydrolysis, at 70 °C, of the cycloadducts (**3**) gave 5-(3-oxoprop-1-enyl)-furan-2,3-dicarboxylic acid (**5a**). Methanolysis afforded (**5b**) from (**3c**). Borohydride reduction of (**3c**) gave dimethyl 5-[3-(*N*-phenylamino)prop-1-enyl]furan-2,3-dicarboxylate (**6**).

N.m.r. and Mass Spectra.—The ^1H n.m.r. spectra of the furan cycloadducts (**3**) (Table 2) are characterized by a downfield doublet for 3-H at δ 8.09 ($J_{3,2}$ 8.82 Hz), irradiation of which simplified the pattern of 2-H at δ 7.08. Irradiation of 2-H

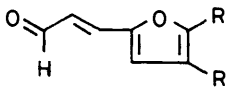
Table 1. Percentage yields of *O*,2-cycloadducts

Compd. (3)	a	b	c	d	e
Yield (%)	18	17	32	93	92

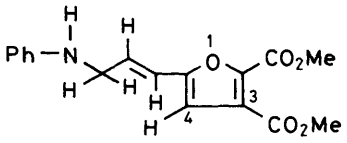
† For Part 55, see A. R. Katritzky and N. E. Grzeskowiak, *J. Chem. Res.*, 1981, (*S*), 208; (*M*), 2345.



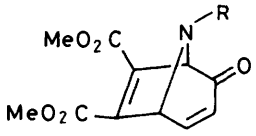
(4) a ; R = Ph
b ; R = 1,2-Di(*p*-nitrophenyl) vinyl



(5) a ; R = CO_2H
b ; R = CO_2Me



(6)



(7) a ; R = *trans* - 3 - (4 - Chlorophenyl) - 3 - oxoprop - 1 - enyl
b ; R = 5,6 - Diphenyl - 1,2,4 - triazin - 3 - yl

Table 2. N.m.r. data (δ/p.p.m.) of the cycloadducts (**3**). Coupling constants (*J*/Hz) in brackets

	a	**b**	**c**	**d**	**e**
		Common signals			
4-H	6.81s	6.96s	6.72s	6.72	
N=HC–CH=C*H*	7.1—7.4 (15.8)	6.75d (16.0)	6.91d (12.0)	6.66d	6.66d
N=HC–C*H*=CH					
N=*H*C–CH=CH	8.0dd				
CO_2Me	3.93s, 3.90s	3.92s, 3.90s	2.98s, 3.94s	3.88s, 3.76s	3.87s, 3.75s
		R-Group signals			
N–Me	3.5d				
$N–CH_2$		4.74s			
Ph		7.32			
Ar–C*H*=CArN				6.25s	
$Ar_2C=CH–N$					6.52s
p-$NO_2C_6H_4$				7.61d (3.5 Hz, 2-, 6-H)	7.61—8.32 (8.8 Hz, 2 × AA′BB′, 8 H)
				8.21d (3.5 Hz 3-, 5-H)	
m-$NO_2C_6H_4$				8.76s, 2-H 8.09d (8.0 Hz, 4-H) 7.50 (overlapped signal, 5-H) 7.97d (8.8 Hz, 6-H)	

allowed the identification of 1-H at δ 6.75 ($J_{1,2}$ 15.8 Hz). The large coupling constant is characteristic of the *trans*-substituted double bond, and is inconsistent with the presence of vicinal protons on a ring as for the azabicyclo[3.2.1] adducts (**4a**),[7] (**4b**), and (**7**)[8,9] for which the maximum coupling[10] would be (10 Hz). The resonance for 4-H of the furan cycloadducts (**3**) at δ 6.8 (singlet), is typical for substituted furans. The ^{13}C n.m.r. spectrum of compound (**4a**) shows a ketonic carbonyl peak at δ 192.6, while no such absorption is present in the ^{13}C n.m.r. spectrum of the furan cycloadduct (**3c**).

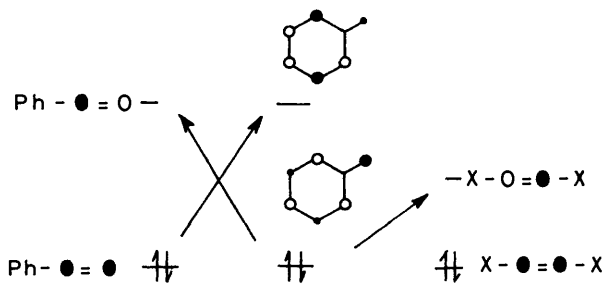
The ^1H n.m.r. spectra of compounds (**5a** and **b**) each display an aldehydic proton at δ 9.66 and, in addition, compound (**5a**) shows two acidic protons at δ 11.3.

The reduction product (**6**) shows a strong N–H stretch at 3 390 cm^{-1} and the ^1H n.m.r. spectrum shows the substituted furan ring (singlet) at δ 6.5. The large coupling constant ($J_{2,1}$ 16 Hz) between 2-H at δ 6.55 and 1-H at δ 6.42, indicates their *trans*-relationship.

The mass spectra of the cycloadducts (**3**) show in each case molecular ion peaks in high abundance, but not the molecular ions for the respective betaines or ionic products produced by retro reactions as have been observed for the azabicyclo[3.2.1]-octenone adducts.

Reactivity and Periselectivity.—The synthesis of dimethyl 5-[3-(*N*-substituted-imino)-1-enyl]furan-2,3-dicarboxylate (**3**) (Scheme 1) involves a thermally allowed cycloaddition in which a symmetrical disubstituted electron-deficient acetylene (DMAD) adds as a 2π addend across the O,2-positions of an *N*-substituted 3-oxidopyridinium betaine behaving as an 8π component ($\pi 8_s + \pi 2_s$). By contrast, the relatively less electron-deficient addend phenylacetylene adds across the 2,6-positions of the betaines (**2c**) and (**2e**) to give the azabicyclo[3.2.1]-octenone adducts (**4a**)[7] and (**4b**) ($\pi 4_s + \pi 2_s$).

These findings are explainable within the FMO context. Calculations[11,12,13] predict that the HOMO energies for acetylenes should be lower than, and the LUMO energies either higher than or equal to, those of the corresponding electron-deficient alkenes. In the TS for the cycloaddition of DMAD to the 3-oxidopyridinium betaine (Scheme 2), the betaine HOMO–DMAD LUMO interaction is the most important; the two interacting FMOs are so close in energy (Scheme 2). The betaine HOMO has its largest atomic orbital coefficient at the oxygen atom (−0.67) followed by that at C-2 (0.54).[14] Consequently, maximum bonding in the TS is attained when these two positions are involved.



Scheme 2. Schematic FMO interaction of 3-oxidopyridinium betaines with DMAD and phenylacetylene

The betaine HOMO has a pseudo-non-bonding character,[15] *i.e.* it has zero or very small coefficients at nitrogen and C-5. Thus, substitution at nitrogen by any substituent will have very little effect on the energy of the HOMO. Consequently, the same mode of cycloaddition is expected to be maintained throughout

the addition of DMAD to a series of betaines no matter how the nitrogen substituents varies.

In the TS for the cycloaddition of phenylacetylene, both the FMO interactions should be effective. As the betaine LUMO has a very small coefficient (almost zero) at the oxygen atom and large coefficients at C-2 and C-6,[14] maximum bonding in the TS is attained when the C-2 and C-6 positions are involved in cycloadditions of phenylacetylene.

Experimental

Melting points were determined using an Electrothermal melting point apparatus. I.r. and u.v. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer and a Pye-Unicam SP 800 spectrophotometer, respectively. ^1H N.m.r. and ^{13}C n.m.r. spectra were recorded in deuteriochloroform unless stated otherwise with $SiMe_4$ as an internal standard, at 60, 200, or 400 MHz (Bruker WH-400 spectrophotometer at the University of Guelph). Mass spectra were obtained using a Perkin-Elmer RMU spectrometer. Elemental analyses were performed by the Scandinavian Laboratories, Herlev, Denmark. Preparative t.l.c. and column chromatography were carried out using silica and Al_2O_3 (neutral).

3-Hydroxypyridinium salts (**1a**, **b**),[16] (**1c**),[17] (**1d**),[18] and (**1e**) were generally prepared by the reactions of 3-hydroxypyridine with the appropriate organic halide. The betaines (**2a**),[19] (**2b**),[20] (**2c**),[10] (**2d**),[18] and (**2e**) were generated from the salts by successive reaction with methanolic sodium hydroxide, evaporation, and extraction into chloroform.

Dimethyl 5-[3-(N-*Methylimino*)*prop*-1-*enyl*]*furan*-2,3-*dicarboxylate* (**3a**).—DMAD (2.0 g, 0.021 mol) in MeCN (15 ml) was added dropwise to a stirred solution of the betaine (**2a**) (4.7 g, 0.043 mol) in dry MeCN (20 ml) at 0 °C under nitrogen. The reaction was stirred at 0 °C, for 1 h when the solvent was evaporated and the brown residue was subjected to preparative t.l.c. using light petroleum (b.p. 60—80 °C)–EtOAc (1:1) to yield the by-products *dimethyl* 5-(3-*oxoprop*-1-*enyl*)*furan*-2,3-*dicarboxylate* (**5b**) (0.2 g, 2%) as light yellow needles (from EtOH–heptane), m.p. and mixed m.p. (see below) 115—116 °C.

Purification of the crude residue by column chromatography using light petroleum (b.p. 40—60 °C)–Et_2O (1:1) gave the *cycloadduct* (**3a**) (2 g, 18%) as buff prisms [from light petroleum (b.p. 60—80 °C)–Et_2O], m.p. 104—107 °C (Found: C, 57.6; H, 5.1; N, 5.4. $C_{12}H_{13}NO_5$ requires C, 57.4; H, 5.2; N, 5.6%); $\nu_{max.}$(Nujol) 1 730 and 1 630 cm^{-1}; $\lambda_{max.}$(EtOH) 223 (log ε 3.96) and 310 nm (4.11); *m/z* 251 (12.5%).

Dimethyl 5-[3-(N-*Benzylimino*)*prop*-1-*enyl*]*furan*-2,3-*dicarboxylate* (**3b**).—DMAD (1.5 g, 0.011 mol) in MeCN (15 ml) was added dropwise to a stirred solution of the betaine (**2b**) (4.1 g, 0.022 mol) in dry MeCN (20 ml) at 0 °C under a stream of nitrogen. After 1 h, the solvent was evaporated, the brown residue was extracted with Et_2O, and the extracts were concentrated and purified by column chromatography, using light petroleum (b.p. 60—80 °C)–Et_2O (1:1) as the eluant, to give the *cycloadduct* (**3b**) (1.2 g, 17%) as needles [from Et_2O–light petroleum (60—80 °C)], m.p. 91—92 °C (Found: C, 66.0; H, 5.3; N, 4.2. $C_{18}H_{17}NO_5$ requires C, 66.0; H, 5.3; N, 4.2%); $\nu_{max.}$(Nujol) 1 740, 1 720 (ester C=O), 1 620, and 1 590 cm^{-1} (aromatic C=C); $\lambda_{max.}$(EtOH) 225 (log ε 3.94) and 314 nm (4.06); *m/z* 327 (6%).

Dimethyl 5-[3-(N-*Phenylimino*)*prop*-1-*enyl*]*furan*-2,3-*dicarboxylate* (**3c**).—DMAD (4.97 g, 0.05 mol) was added dropwise to a stirred solution of the betaine (**2c**) (6.0 g, 0.036 mol) in MeCN (25 ml) at 30 °C. The mixture was stirred for 2 h and the solvent was evaporated. The brown residue was extracted with Et_2O and the crude product was purified by column chromatography (Al_2O_3–Et_2O) to yield the *title compound* (**3c**) (3.5 g, 32%) as yellow flakes (from Et_2O), m.p. 112—113 °C (Found: C, 65.0; H, 4.8; N, 4.6. $C_{17}H_{15}NO_5$ requires C, 65.1; H, 4.8; N, 4.5%); $\nu_{max.}$(Nujol) 1 720 (ester C=O), 1 605, and 1 580 cm^{-1} (aromatic C=C); $\lambda_{max.}$(EtOH) 208 (log ε 4.15), 227 (4.31), and 353 nm (4.22); *m/z* 313 (100%).

Dimethyl 5-{3-[2-(m-*Nitrophenyl*)-1-(p-*nitrophenyl*)*vinylimino*]*prop*-1-*enyl*}*furan*-2,3-*dicarboxylate* (**3d**).—The betaine (**2d**) (2.0 g, 0.0055 mol) and DMAD (1.18 g, 8.3 mmol) in MeCN (20 ml) were stirred together at 70 °C for 8 h after which time the solution was cooled and evaporated. The *title compound* (**3d**) (2.6 g, 93%) crystallized from MeCN as yellow flakes, m.p. 182—183 °C (Found: C, 59.3; H, 3.9; N, 8.3. $C_{25}H_{19}N_3O_9$ requires C, 59.4; H, 3.8; N, 8.3%); $\nu_{max.}$(Nujol) 1 740, 1 715 (ester C=O), 1 595 (phenyl ring), 1 515 (antisym. NO_2), and 1 345 cm^{-1} (sym. NO_2); $\lambda_{max.}$($CHCl_3$) 233 (log ε 4.4), 269 (4.46), and 338 nm (4.56); *m/z* 505 (65.8%).

Dimethyl 5-[3-(1,2-*Di*-p-*nitrophenylvinylimino*)*prop*-1-*enyl*]-*furan*-2,3-*dicarboxylate* (**3e**).—The betaine (**2e**) (3.0 g, 8.3 mmol), and DMAD (2.3 g, 16.2 mmol) in MeCN (30 ml) were stirred at 70 °C for 1 h. The cooled reaction mixture was filtered and the brown solid residue was washed with methanol to give the *cycloadduct* (**3e**) (3.9 g, 92%) as orange plates (from MeCN), m.p. 165 °C (Found: C, 59.5; H, 3.8; N, 8.4. $C_{25}H_{19}N_3O_9$ requires, C, 59.4; H, 3.8; N, 8.3%); $\nu_{max.}$(Nujol) 1 740, 1 720 (ester C=O), 1 595 and 1 515 (aromatic C=C), 1 530 (antisym. NO_2), and 1 345 cm^{-1} (sym. NO_2); $\lambda_{max.}$($CHCl_3$) 241 (log ε 4.23), 333 (4.35), and 384 nm (4.37); *m/z* 505 (66.4%).

8-(1,2-*Di*-p-*nitrophenylvinyl*)-6-*phenyl*-8-*azabicyclo*[3.2.1]-*octa*-3,6-*dien*-2-*one* (**4b**).—The betaine (**2e**) (2.59 g, 7.1 mmol) and phenylacetylene (1.7 g, 16.7 mmol) were stirred in dimethylformamide (15 ml) at 130 °C for 6 h. The solvent was evaporated from the cooled reaction mixture and the residue was washed with light petroleum (b.p. 60—80 °C), and extracted with CH_2Cl_2. Evaporation and purification by preparative t.l.c. using light petroleum (b.p. 60—80 °C)–EtOAc (2:1) gave *compound* (**4b**) (0.8 g, 24%) as deep orange needles (from MeCN), m.p. 234—235 °C (Found: C, 69.4; H, 4.0; N, 7.9. $C_{27}H_{19}N_3O_5$ requires C, 69.6; H, 4.1; N, 9.0%); $\nu_{max.}$(Nujol) 1 685 (α,β-unsaturated C=O), 1 610, 1 585 (aromatic C=C), and 1 530 cm^{-1} (antisym. NO_2); $\lambda_{max.}$(EtOH) 208 (log ε 4.49), 272 (4.54), and 388 nm (4.0); *m/z* 465 (32%); δ_H(Me_2SO) 8.25 (2 H, dd, AA, BB system, *J* 8.8 Hz, ArH), 7.2—8.0 (13 H, m, ArH), 7.72 (1 H, q, 4-H), 5.91 (1 H, d, $J_{3,4}$ 9.9 Hz, 3-H), 5.86 (2 H, s, 7-H and vinylic H), 5.19 (1 H, d, $J_{5,4}$ 5 Hz, 5-H), and 4.81 (1 H, d, $J_{1,7}$ 1.5 Hz, 1-H).

Hydrolysis of Cycloadducts (**3d**) *and* (**3c**).—A suspension of the adduct (**3d**) (2.33 g, 4.6 mmol) in MeOH (25 ml), conc. HCl (2 ml), and water (20 ml) was stirred at 70 °C. After 2 h, the reaction mixture was filtered and the residue was washed with distilled water to give 4-*nitro*-2-(m-*nitrophenyl*)*acetophenone* (1.3 g, 98%) as pale yellow plates (from EtOH), m.p. 135—136 °C (Found: C, 85.8; H, 6.1. $C_{14}H_{12}O$ requires, C, 85.7; H, 6.1%); $\nu_{max.}$(Nujol) 1 690, 1 600, 1 520, and 1 355 cm^{-1}.

Evaporation of the filtrate gave a pale yellow solid (0.8 g) which partially dissolved in THF (20 ml). Ammonium chloride was filtered off, and the filtrate was evaporated to yield (**5a**) (0.6 g, 67%) as cream prisms (from EtOH), m.p. 270 °C (decomp.) (Found: C, 51.4; H, 3.2. $C_9H_9O_6$ requires C, 51.4; H, 2.9%); $\nu_{max.}$(KBr) 3 100 (aryl C–H stretching), 3 000—2 500 (O–H stretching, carboxylic acid), 1 710, 1 670 (aldehyde C=O), 1 620, 1 570, 1 515, 1 320, 830, and 745 cm^{-1}; $\lambda_{max.}$(EtOH) 22 (log ε 4.00) and 311 nm (4.21); δ_H(Me_2SO) 11.3 (2 H, br, 2 × CO_2H), 9.66

(1 H, d, *J* 7.6 Hz, CHO), 7.63 (1 H, d, *J* 15.9 Hz, OHCCH=C*H*), 7.41 (1 H, s, 4-H), and 6.62 (1 H, dd, *J* 15.9, 7.6 Hz, OHCC*H*=CH); *m/z* 210 (14.4%).

The cycloadduct (**3c**) (0.13 g, 0.39 mmol), MeOH (10 ml), and trichloroacetic acid (0.07 g, 0.39 mmol) were refluxed together for 30 min. The evaporated reaction mixture was purified by preparative t.l.c. using EtOAc–light petroleum (b.p. 60—80 °C) (1:2) to give the aldehyde diester (**5b**) (60 mg, 64%) as yellow plates (from EtOH), m.p. 115—117 °C (Found: C, 55.3; H, 4.5. $C_{11}H_{10}O_6$ requires C, 55.5; H, 4.2%); $\nu_{max.}$(KBr) 3 110 (aryl CH), 2 820—2 730 (aldehyde CH), 1 740 (ester C=O), and 1 715 and 1 680 cm^{-1} (α,β-unsaturated C=O); $\lambda_{max.}$(EtOH) 223 (log ε 4.11) and 310 nm (4.32); δ_H 99.4 (1 H, d, *J* 8 Hz, CHO), 7.3 (1 H, d, *J* 16 Hz, OHCCH=C*H*), 7.10 (1 H, s, 4-H), 6.76 (1 H, dd, *J* 16, 8 Hz, OHCC*H*=CH), and 3.89 and 3.95 (6 H, 2 × s, 2 × MeO_2C); *m/z* 238 (13%).

Sodium Borohydride Reduction of the Cycloadduct (**3c**).—To a stirred solution of the cycloadduct (**3c**) (0.7 g, 2.24 mmol) in MeOH (20 ml) at 25 °C, was added sodium borohydride (0.9 g, 24 mmol). The colour immediately faded. Stirring was continued for 10 min. The solvent was evaporated and the residue was extracted with Et_2O. The combined extracts were concentrated and purified by preparative t.l.c. [light petroleum (b.p. 60—80 °C)–EtOAc (2:1)] to give *compound* (**6**) (0.29 g, 40%) as prisms [from Et_2O–light petroleum (b.p. 60—80 °C)], m.p. 63—64 °C (Found: C, 64.7; H, 5.6. $C_{17}H_{17}NO_5$ requires C, 64.7; H, 5.6%); $\nu_{max.}$(Nujol) 3 390sh (NH), 1 745, 1 720, 1 660, 1 605, 1 500, 1 250, 1 080, 970, 850, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 213 (log ε 4.26), 248 (4.27), and 301 nm (4.19); δ_H 7.16 (1 H, s, NH), 7.1—7.2 (2 H, m, ArH), 6.4—6.78 (3 H, m, ArH), 6.55 (1 H, dt, *J* 4.87, 16 Hz, CH=C*H*CH_2), 6.51 (1 H, s, 4-H), 6.42 (1 H, m, *J* 16, 1.4 Hz, C*H*=C*H*CH_2), 3.94 (2 H, dd, *J* 4.87, 1.4 Hz, CH=CHCH_2), and 3.90 and 3.86 (6 H, 2 × s, 2 × CO_2Me); *m/z* 315 (100%).

References

1 A. R. Katritzky and Y. Takeuchi, *J. Am. Chem. Soc.*, 1970, **92**, 4134.
2 N. Dennis, B. Ibrahim, and A. R. Katritzky, *J. Chem. Soc., Chem. Commun.*, 1975, 425.
3 N. Dennis, B. Ibrahim, and A. R. Katritzky, *J. Chem. Soc., Chem. Commun.*, 1974, 500.
4 N. Dennis, A. R. Katritzky, and H. Wilde, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2338.
5 A. R. Katritzky, A. T. Cutler, N. Dennis, G. J. Sabongi, S. Rahimi-Rastigoo, G. W. Fischer, and I. J. Fletcher, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1176.
6 G. Ferguson, K. J. Fisher, B. Ibrahim, Christina Y. Ishag, G. M. Iskander, A. R. Katritzky, and Masood Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 1216.
7 N. Dennis, A. R. Katritzky, S. K. Parton, Y. Nomura, Y. Takahashi, and Y. Takeuchi, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2289.
8 A. R. Katritzky, S. Rahimi-Rastgoo, G. J. Sabongi, and G. W. Fischer, *J. Chem. Soc., Perkin Trans. 1*, 1980, 362.
9 A. R. Katritzky, A. Boonyarakvanich, and N. Dennis, *J. Chem. Soc., Perkin Trans. 1*, 1980, 343.
10 N. Dennis, A. R. Katritzky, T. Matsuo, S. K. Parton, and Y. Takeuchi, *J. Chem. Soc., Perkin Trans. 1*, 1974, 746.
11 K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, 1973, **95**, 7287.
12 W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1966, **88**, 2384.
13 H. O. House, L. E. Huber, and M. J. Umen, *J. Am. Chem. Soc.*, 1972, **94**, 8471.
14 A. R. Katritzky, N. Dennis, M. Chaillet, C. Larrieu, and M. El Mouhtadi, *J. Chem. Soc., Perkin Trans. 1*, 1979, 408.
15 N. Dennis, B. Ibrahim, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2296.
16 S. L. Shapiro, K. Weinberg, and L. Freedman, *J. Am. Chem. Soc.*, 1959, **81**, 5140.
17 C. F. Koelsch and J. J. Carney, *J. Am. Chem. Soc.*, 1950, **72**, 2285.
18 A. R. Katritzky, B. A. Boyce, and N. Dennis, *Pol. J. Chem.*, 1981, **55**, 1351.
19 A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc. C*, 1971, 874.
20 J. Banerji, N. Dennis, J. Frank, A. R. Katritzky, and T. Matsus, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2334.

Received 28*th January* 1987; *Paper* 7/144