(*Z*)- and (*E*)-5-Arylmethylenehydantoins: Spectroscopic Properties and Configuration Assignment

Sau-Fun Tan, Kok-Peng Ang, and Yoke-Fan Fong
Department of Chemistry, National University of Singapore, Singapore

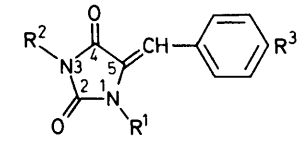
Both (*Z*)- and (*E*)-5-arylmethylene-1-methylhydantoins have been obtained directly in substantial proportions from condensations of 1-methylhydantoin with aromatic aldehydes. However, the products of similar condensations of hydantoin or 3-methylhydantoins consist almost entirely of the *Z*-isomers. The configurations of all the 5-arylmethylenehydantoins prepared can be unambiguously assigned by consideration of their ^{1}H and ^{13}C n.m.r., i.r., and u.v. spectra. The mass spectra of the isomers show similar fragmentation patterns.

5-Benzylidenehydantoin (**1**) was synthesized by Wheeler and Hoffmann[1] by condensation of hydantoin with benzaldehyde. Johnson and Bates[2] showed that, besides the predominant lower-melting form, a very small amount of a high-melting form could be obtained from large-scale preparations. Johnson and Hadley,[3] on the other hand, isolated both forms from the condensation of 1,3-diphenylhydantoin with benzaldehyde, but the higher-melting form was the major product. In each case, the lower-melting form was empirically assigned the *cis*- and the higher-melting form the *trans*-configuration. Subsequently, a number of other 1,3-disubstituted 5-benzylidenehydantoins were prepared;[4–9] the lower-melting isomers were the chief or (probably) the exclusive products, and some of them were transformed into the higher-melting isomers by treatment with hydrogen chloride. However, the configurations of these compounds were not determined. Several 5-arylmethylene-1-methylhydantoins were also prepared by hydrolysis of N^2-acetyl-5-arylmethylenecreatinines,[10,11] but only one isomer of each of these compounds was isolated.

It was suggested,[8,12] that the presence of substituents at both nitrogen atoms was necessary for the direct formation of two isomers. Isomerization *via* tautomerization involving the N-1 proton was postulated as the reason for the formation of only one form of 5-benzylidenehydantoin but two forms of 5-benzylidene-1,3-diphenylhydantoin. This appears to imply that the N-3 substituent is not a determining factor in geometric isomerism. Furthermore, the reasons for the preference of one form over the other were not clear and the assignments of configurations, in the two cases mentioned, were apparently based only on melting-point differences; in the other cases assignments seem not to have been attempted. These observations prompted us to prepare some 5-arylmethylenehydantoins (**1**)—(**4**) and the corresponding 3-methyl and 1-methyl derivatives (**5**)—(**8**) and (**9**)—(**12**), respectively, in order to study the effects of the N-1 and N-3 substituents on geometric isomerism and to assign configurations to the isomers from spectroscopic considerations.

Results and Discussion

Synthesis and Geometric Isomerism.—Only one isomer was isolated directly from each of the preparations of the *N*-unsubstituted and the 3-methyl compounds (**2**)—(**8**). On the other hand, each of the 1-methyl compounds (**9**)—(**12**) was obtained in two geometric isomeric forms, each in substantial proportions, demonstrating that substitution at both nitrogen atoms is not necessary for the ready formation of both isomers. On the basis of the melting points, one isomer of each of the compounds (**9**)—(**12**) corresponds closely to the only isomer of that compound previously synthesized.[10,11] Further, we confirm that a very small amount of the minor isomer of (**1**) could be isolated from a large-scale preparation. Although the minor isomers of the other compounds are not easily isolable, their existence is suggested in some cases by small absorptions in the ^{1}H n.m.r. or i.r. spectra of impure samples of the major isomers. The melting points and analytical data of all the compounds prepared are reported in Table 1 and their spectroscopic data in Tables 2 and 3.



(**1**) $R^1 = R^2 = R^3 = H$
(**2**) $R^1 = R^2 = H$, $R^3 = OMe$
(**3**) $R^1 = R^2 = H$, $R^3 = Me$
(**4**) $R^1 = R^2 = H$, $R^3 = Cl$
(**5**) $R^1 = R^3 = H$, $R^2 = Me$
(**6**) $R^1 = H$, $R^2 = Me$, $R^3 = OMe$
(**7**) $R^1 = H$, $R^2 = R^3 = Me$
(**8**) $R^1 = H$, $R^2 = Me$, $R^3 = Cl$
(**9**) $R^1 = Me$, $R^2 = R^3 = H$
(**10**) $R^1 = Me$, $R^2 = H$, $R^3 = OMe$
(**11**) $R^1 = R^3 = Me$, $R^2 = H$
(**12**) $R^1 = Me$, $R^2 = H$, $R^3 = Cl$

^{1}H *N.m.r. Spectra.*—The ^{1}H n.m.r. spectra of the two isomers of (**1**) confirm the configurations previously assigned by Johnson and Bates.[2] The most significant differences are found in the chemical shifts of the vinyl, N-1, and phenyl *ortho*-protons. The anisotropic effect of the 4-carbonyl group deshields the vinyl proton in the major *Z*-isomer (previously referred to as the *cis*-isomer) relative to that in the minor *E*-isomer (previously referred to as the *trans*-isomer). For the same reason, the phenyl *ortho*-protons (H_o) in the *E*-isomer are more deshielded than the corresponding ones in the *Z*-isomer. This effect on the more distant *meta*- (H_m) and *para*-protons is understandably much smaller, so that the two groups of multiplets representing these phenyl protons are more widely separated in the spectrum of the *E*- than in that of the *Z*-isomer. At the same time, the N-1 proton in the *Z*-isomer, owing to its proximity to the benzene ring, resonates at lower field than its counterpart in the *E*-isomer. Although the signals due to protons at N-1 and N-3 of this compound were previously reported to be indistinguishable,[13] separate peaks for them have now been clearly observed. The lowest field signal in each spectrum is assigned to the N-3 proton, under the influence of two adjacent carbonyl groups; its position is less affected by differences in configurations.

Comparison of the ^{1}H n.m.r. spectra of the only isolated isomers of compounds (**2**)—(**8**) with those of (*Z*)- and (*E*)-(**1**) clearly indicates that they all have the *Z*-configuration. The chemical shifts of their vinyl protons lie in the range δ 6.40—

Table 1. Melting points and analytical data

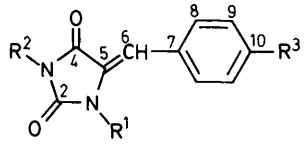
Compound	M.p. (°C)	Found (%)				Calc. (%)			
		C	H	N	Cl	C	H	N	Cl
(*Z*)-(**1**)	219—220	63.7	4.3	14.9		63.8	4.3	14.9	
(*E*)-(**1**)	277—279	62.9	4.3	14.6		63.8	4.3	14.9	
(*Z*)-(**2**)	244—244.5	60.3	4.3	12.8		60.6	4.6	12.8	
(*Z*)-(**3**)	276—277	65.3	4.9	13.6		65.4	5.0	13.9	
(*Z*)-(**4**)	295.5—296	53.7	3.2	12.9	16.2	53.9	3.2	12.6	16.0
(*Z*)-(**5**)	226—227	65.3	5.0	13.9		65.4	5.0	13.9	
(*Z*)-(**6**)	217—218	61.9	5.2	12.0		62.1	5.2	12.1	
(*Z*)-(**7**)	245—246	66.6	5.6	12.5		66.7	5.6	13.0	
(*Z*)-(**8**)	271—272	55.9	3.9	11.5	14.7	55.8	3.8	11.8	15.0
(*Z*)-(**9**)	135—136	65.3	4.9	13.7		65.4	5.0	13.9	
(*E*)-(**9**)	187—188	65.4	5.0	13.9		65.4	5.0	13.9	
(*Z*)-(**10**)	145—146	62.4	5.3	11.9		62.1	5.2	12.1	
(*E*)-(**10**)	245—246	62.4	5.2	12.2		62.1	5.2	12.1	
(*Z*)-(**11**)	181—182	65.9	5.9	12.6		66.7	5.6	13.0	
(*E*)-(**11**)	233—234	66.7	5.6	13.0		66.7	5.6	13.0	
(*Z*)-(**12**)	202—203	55.7	3.8	11.7	14.2	55.8	3.8	11.8	15.0
(*E*)-(**12**)	253—254	55.8	3.7	12.0	15.1	55.8	3.8	11.8	15.0

Table 2. Chemical shifts (from Me_4Si); solvent $(CD_3)_2SO$

^1H Shifts

Compound	N–CH_3	vinyl H	H_o	H_m	N(1)–H	N(3)–H	Others
(*Z*)-(**1**)		6.45	7.64 (m)	7.40[a] (m)	10.57	11.15	
(*E*)-(**1**)		6.35	7.90 (m)	7.35[a] (m)	10.29	11.02	
(*Z*)-(**2**)		6.40	7.58 (d, *J* 9 Hz)	6.95 (d, *J* 9 Hz)	10.37	11.10	3.80 (OCH_3)
(*Z*)-(**3**)		6.41	7.52 (d, *J* 9 Hz)	7.22 (d, *J* 8 Hz)	10.42	11.17	2.34 ($ArCH_3$)
(*Z*)-(**4**)		6.40	7.65 (d, *J* 9 Hz)	7.42 (d, *J* 9 Hz)	10.56	11.25	
(*Z*)-(**5**)	2.99	6.53	7.64 (m)	7.48[a] (m)	10.72		
(*Z*)-(**6**)	2.97	6.50	7.58 (d, *J* 9 Hz)	6.95 (d, *J* 9 Hz)	10.57		3.80 (OCH_3)
(*Z*)-(**7**)	2.97	6.49	7.52 (d, *J* 8 Hz)	7.20 (d, *J* 8 Hz)	10.62		2.33 ($ArCH_3$)
(*Z*)-(**8**)	2.96	6.49	7.62 (d, *J* 9 Hz)	7.41 (d, *J* 9 Hz)	10.71		
(*Z*)-(**9**)	2.80	6.68	7.40 (s)			11.38	
(*E*)-(**9**)	3.10	6.37	7.93 (m)	7.35[a] (m)		11.30	
(*Z*)-(**10**)	2.88	6.60	7.34 (d *J* 9 Hz)	6.96 (d, *J* 9 Hz)		11.32	3.80 (OCH_3)
(*E*)-(**10**)	3.08	6.32	7.98 (d, *J* 9 Hz)	6.92 (d, *J* 9 Hz)		11.22	3.79 (OCH_3)
(*Z*)-(**11**)	2.83	6.62	7.24 (s)			11.30	2.33 ($ArCH_3$)
(*E*)-(**11**)	3.06	6.28	7.82 (d, *J* 8 Hz)	7.13 (d, *J* 8 Hz)		11.22	2.30 ($ArCH_3$)
(*Z*)-(**12**)	2.80	6.60	7.40 (s)			11.36	
(*E*)-(**12**)	3.08	6.33	7.93 (d, *J* 9 Hz)	7.36 (d, *J* 9 Hz)		11.30	

^{13}C Shifts

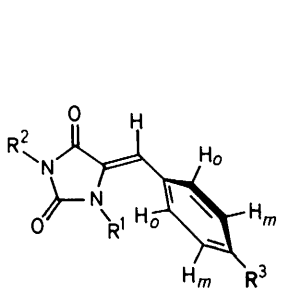


Compound	C-2	C-4	C-5	C-6	C-7	C-8	C-9	C-10	R^1	R^2	R^3
(*Z*)-(**1**)	155.7	165.6	128.1	108.3	133.0	129.4	128.8	128.4			
(*E*)-(**1**)	153.6	163.3	128.1	115.5	133.0	129.7	127.9	128.1			
(*Z*)-(**2**)	155.8	165.7	126.2	108.9	125.6	131.1	114.3	159.5			55.2
(*Z*)-(**3**)	155.5	165.5	127.2	108.5	130.1	129.3	129.3	138.0			20.9
(*Z*)-(**4**)	155.6	165.3	128.4	106.7	132.8	130.9	128.6	131.9			
(*Z*)-(**5**)	155.4	164.3	126.8	109.3	132.9	129.5	128.8	128.5		24.3	
(*Z*)-(**6**)	155.2	164.2	124.8	109.6	125.3	131.1	114.2	159.5		24.1	55.2
(*Z*)-(**7**)	155.1	164.2	125.9	109.5	129.9	129.4	129.4	138.2		24.1	20.9
(*Z*)-(**8**)	155.3	164.1	127.2	107.8	133.0	131.0	128.7	131.7		24.2	
(*Z*)-(**9**)	155.6	164.4	130.9	109.5	132.7	128.1	129.6	128.1	29.7		
(*E*)-(**9**)	153.4	162.9	130.5	115.5	133.1	130.2	128.0	128.3	25.9		
(*Z*)-(**10**)	155.7	164.4	129.9	109.9	124.7	131.2	113.7	159.2	29.8		55.2
(*E*)-(**10**)	153.3	163.0	128.7	116.1	125.7	132.0	113.5	159.5	25.9		55.2
(*Z*)-(**11**)	155.4	164.2	130.3	109.7	130.0	129.4	128.6	137.5	29.6		20.8
(*E*)-(**11**)	153.2	162.7	129.7	115.7	128.5	130.1	128.5	137.9	25.6		20.9
(*Z*)-(**12**)	155.5	164.1	130.8	108.0	132.6	131.3	128.0	131.5	29.7		
(*E*)-(**12**)	153.2	162.7	130.8	113.8	132.7	131.7	127.8	131.9	25.8		

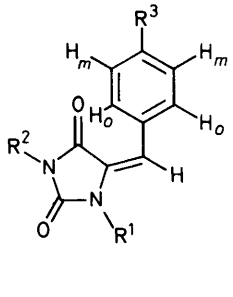
[a] Phenyl *meta*- and *para*-protons.

Table 3. I.r., u.v., and mass spectroscopic data

Compound	ν/cm^{-1} C=O	ν/cm^{-1} C=C	$\lambda_{max.}$(log ε)/nm	m/z $M^{+\cdot}$	m/z Ions from pathways (a)	(b)	(c)	(d)
(*Z*)-(**1**)	1 770, 1 720	1 665	315 (4.092)	188	117			90
(*E*)-(**1**)	1 750, 1 725	1 638	329 (4.193)	188	117			90
(*Z*)-(**2**)	1 770, 1 740	1 675	331 (3.877)	218	147		116	89
(*Z*)-(**3**)	1 765, 1 715	1 668	320 (3.314)	202	131		116	
(*Z*)-(**4**)	1 790, 1 770, 1 740	1 670	320 (4.351)	222	151		116	89
(*Z*)-(**5**)	1 780, 1 770, 1 720	1 660	316 (4.247)	202	117			90
(*Z*)-(**6**)	1 760, 1 715	1 660	332 (4.491)	232	147		116	
(*Z*)-(**7**)	1 780, 1 760, 1 712	1 660	320 (4.257)	216	131		116	
(*Z*)-(**8**)	1 790, 1 762, 1 720	1 665	320 (4.228)	236	151		116	89
(*Z*)-(**9**)	1 770, 1 725	1 660	308 (4.085)	202	131	116		90
(*E*)-(**9**)	1 760, 1 720	1 640	338 (4.097)	202	131	116		90
(*Z*)-(**10**)	1 765, 1 720, 1 715	1 664	323 (4.302)	232	161	146	115	89
(*E*)-(**10**)	1 755, 1 710, 1 700	1 640	348 (4.385)	232	161	146	115	89
(*Z*)-(**11**)	1 760, 1 710	1 660	312 (4.126)	216	145	130	115	89
(*E*)-(**11**)	1 750, 1 710	1 635	338 (4.025)	216	145	130	115	89
(*Z*)-(**12**)	1 782, 1 759, 1 735	1 660	312 (4.228)	236	165	150	115	89
(*E*)-(**12**)	1 758, 1 715	1 635	336 (4.304)	236	165	150	115	89



Z-isomer



E-isomer

6.53, and those of H_o in the range δ 7.52—7.65; the N–H resonances are also similar to the corresponding signals in the spectrum of (*Z*)-(**1**).

The configurations of each pair of isomers of compounds (**9**)—(**12**) can be readily distinguished. The differences in the chemical shifts of their vinyl and phenyl *ortho*-protons follow the trend noted for the isomers of (**1**). On the other hand, while the N-1 proton of (*Z*)-(**1**) is more deshielded than that of (*E*)-(**1**), the 1-methyl protons in the *Z*-isomers of (**9**)—(**12**) are more shielded than their counterparts in the *E*-isomers. This can be explained by steric effects. While the N-1 proton in (*Z*)-(**1**) cannot prevent rotation of the benzene ring, particularly in solution, the bulkier 1-methyl group in (*Z*)-(**9**)—(**12**) could force the benzene ring to be twisted from coplanarity so that the methyl protons lie in its shielding region. This steric hindrance also results in striking differences in the phenyl signals. For the *Z*-isomers of (**9**), (**11**), and (**12**), this signal is practically a singlet at δ 7.24—7.40, confirming that the benzene ring is effectively not conjugated with the hydantoin ring and its protons therefore influenced by neither the 4-carbonyl nor the N-1 group. For (*Z*)-(**10**), the strongly electron-releasing methoxy-group shifts the H_m signal to higher field, leaving the H_o signal around the normal phenyl region. In the spectra of all the *E*-isomers of (**9**)—(**12**), the phenyl signal consists of two distinct doublets: the H_o peak being shifted considerably downfield by the anisotropic 4-carbonyl group. Furthermore, steric crowding between the 1-methyl and the phenyl groups in the *Z*-isomers may have forced the vinyl protons closer to the 4-carbonyl group, thus shifting their signals further downfield relative to that in (*Z*)-(**1**) while the corresponding protons in the *E*-isomers remain similar to those in (*E*)-(**1**).

^{13}C *N.m.r. Spectra.*—Differences in configuration are also reflected in the ^{13}C n.m.r. spectra of these compounds. This is particularly evident from comparison of the chemical shifts of the carbon atoms in the hydantoin ring and, to a smaller extent, of the exocyclic olefinic carbon atom.

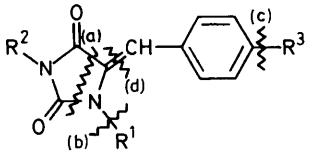
In comparison with 5-benzylhydantoin,[14] introduction of the side-chain double bond in 5-benzylidenehydantoin (*Z*)-(**1**) produces the expected upfield shift of 9.6 p.p.m. for the signal of C-4 and a smaller shift of 1.5 p.p.m. for that of C-2. The chemical shifts of these two carbon atoms show minimal changes in the ^{13}C spectra of compounds (**2**)—(**4**), confirming their similarity in configuration to (*Z*)-(**1**). The presence of the 3-methyl substituent in compounds (**5**)—(**8**) causes small additional shielding at both carbonyl carbon atoms. However, in the case of the 1-methyl compounds (**9**)—(**12**), while the C-2 and C-4 shifts of the *Z*-isomers are similar to those of the *N*-unsubstituted and 3-methyl compounds, the corresponding values for the *E*-isomers are significantly to higher field. The foregoing discussion of ^{1}H spectra has indicated that there is steric inhibition of resonance in these *Z*-isomers, but through-conjugation between the arylmethylene side chain and the hydantoin moiety in the *E*-isomers. Such conjugation should increase the shielding of the carbonyl carbon atoms but decrease that of the olefinic carbon atom. Accordingly, it is observed that, for the *E*-isomers, the C-2 and C-4 signals are consistently upfield and the C-6 signals downfield relative to the *Z*-isomers. The difference in chemical shifts (Δδ) between the isomers at C-2 is 2.2—2.4 p.p.m., unexpectedly greater than that (1.4—1.5 p.p.m.) at C-4. The Δδ value at C-6 is 5.8—6.2 p.p.m. The 1-methyl carbon atoms of the *E*-isomers resonate at δ 25.6—25.9, consistently to higher field than those of the *Z*-isomers (δ 29.6—29.8).

I.r. Spectra.—The foregoing configuration assignments are supported by the i.r. spectra. The *Z*-isomers of the arylmethylene derivatives of pyrazolone,[15] isoxazolone,[16] and 1,3-dihydroindol-2-one[17] have been shown to be planar by *X*-ray analysis. These are stereochemically related to the *E*-isomers of the present 5-arylmethylenehydantoins as far as the fragment

O=C–C=C–Ar is concerned. Although *X*-ray analysis has not been carried out here, one may reasonably speculate, by structural analogy, that these (*E*)-5-arylmethylenehydantoins are also planar. The resulting extended conjugation between the aryl and hydantoin groups should lead to lowering of both C=O and C=C stretching frequencies. By contrast, the *Z*-isomers, especially of the 1-methyl compounds, have been shown by the n.m.r. data to adopt twisted conformations where conjugation is disrupted. This is clearly seen in the differences in the C=O and C=C bands between the spectra of the *E*-isomers of (**1**) and (**9**)—(**12**) and those of all the *Z*-isomers of (**1**)—(**12**). Although there has been no complete agreement regarding assignment of the two carbonyl bands at 1 750—1 780 and 1 700—1 725 cm^{-1} to the 2- and 4-carbonyl groups in the hydantoin ring,[18–21] both bands occur at lower frequencies for the *E*- than for the *Z*-isomer of each of compounds (**1**) and (**9**)—(**12**). Better defined are the configuration and conjugation effects on the stretching frequency of the exocyclic C=C, at 1 635—1 640 cm^{-1} for the *E*-isomers, consistently lower than that (1 660—1 675 cm^{-1}) for all the *Z*-isomers.

U.v. Spectra.—The effectively more extended conjugation in the *E*- than in the *Z*-isomers is clearly manifested in the longer wavelength and more intense absorptions in the u.v. spectra of the former than of the latter of each pair of isomers of compounds (**1**) and (**9**)—(**12**).

Mass Spectra.—Unlike the other spectroscopic methods, mass spectrometry of these compounds has not proved useful for configuration determination. All the compounds studied show similar fragmentation patterns and the mass spectra of the *Z*- and *E*-isomers of any one compound closely resemble each other. In each case, the most intense peak in the spectrum is that of the molecular ion, which decomposes primarily by loss of OC–NR^2–CO [pathway (a)]. It is perhaps not surprising that fragmentation of either the *Z*- or the *E*-isomer of a compound by this pathway leads to the same daughter ion, which then undergoes further cleavages to give similar fragments. The other ions result from the loss of the N-1 methyl group, if any, [pathway (b)] and of the substituent R^3 [pathway (c)]. When R^3 = OMe, the losses of Me and O may take place in stages. Fission by pathway (d) gives the fragment $^+$CH–Ar. The relative intensities of these peaks in the spectrum vary among the compounds (**1**)—(**12**) but no definite trend has been detected.



Experimental

Hydantoin and 1-methylhydantoin were obtained commercially. 3-Methylhydantoin was prepared by methylation of hydantoin with dimethyl sulphate.[22] All the compounds (**1**)—(**12**) were obtained by condensations in piperidine[23] except for one large-scale preparation of (**1**) which was carried out by the acetate method[1] in order to obtain a small sample of (*E*)-(**1**). The *Z*- and *E*-isomers of (**1**) and (**9**)—(**12**) were separated by repeated recrystallization using 95% ethanol or methanol.

^{1}H and ^{13}C n.m.r. spectra were recorded for samples in $(CD_3)_2SO$ solution at 35 °C with a Perkin-Elmer R32 spectrometer at 90 MHz and with a JEOL FX90Q Fourier transform spectrometer, respectively. I.r. spectra were recorded with a Unicam SP1000 spectrophotometer for KBr discs. U.v. spectra (solvent ethanol) were obtained with a Shimadzu UV-260 spectrophotometer. Mass spectra were obtained with a V.G. Micromass 7035 instrument.

Acknowledgment

The award of a research scholarship to Yoke-Fan Fong and a research grant by the National University of Singapore are gratefully acknowledged.

References

1 H. L. Wheeler and C. Hoffmann, *Am. Chem. J.*, 1911, **45**, 368.
2 T. B. Johnson and J. S. Bates, *J. Am. Chem. Soc.*, 1915, **37**, 384.
3 T. B. Johnson and S. E. Hadley, *J. Am. Chem. Soc.*, 1915, **37**, 171.
4 D. A. Hahn and A. G. Renfrew, *J. Am. Chem. Soc.*, 1925, **47**, 147.
5 D. A. Hahn and E. Gilman, *J. Am. Chem. Soc.*, 1925, **47**, 2941.
6 D. A. Hahn and J. Evans, *J. Am. Chem. Soc.*, 1928, **50**, 806.
7 D. A. Hahn and E. Dyer, *J. Am. Chem. Soc.*, 1930, **52**, 2505.
8 D. A. Hahn and E. Gilman, *J. Am. Chem. Soc.*, 1925, **47**, 2953.
9 D. A. Hahn and M. K. Seikel, *J. Am. Chem. Soc.*, 1936, **58**, 647.
10 B. H. Nicolet and E. D. Campbell, *J. Am. Chem. Soc.*, 1928, **50**, 1155.
11 A. R. Frasca and E. B. Dennler, *Chem. Ind. (London)*, 1965, **38**, 1631.
12 Kirk-Othmer, 'Encyclopedia of Chemical Technology,' 3rd edn., 1980, vol. 12, p. 693.
13 R. A. Corral and O. O. Orazi, *Spectrochim. Acta*, 1965, **21**, 2119.
14 J. H. Poupaert, M. Claesen, J. Degelaen, P. Dumont, and S. Toppet, *Bull. Soc. Chim. Belg.*, 1977, **86**, 465.
15 B. Bovio and S. Locehi, *Cryst. Struct. Commun.*, 1972, **1**, 253.
16 J. Meunier-Piret, P. Piret, G. Germain, T. P. Putzeys, and M. Van Meerssche, *Acta Crystallogr., Sect. B*, 1972, **28**, 1308.
17 A. C. Coda, A. G. Invernizzi, P. P. Righetti, G. Tacconi, and G. Gatti, *J. Chem. Soc., Perkin Trans. 2*, 1984, 615.
18 H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, 'Infrared Determination of Organic Structures,' van Nostrand, New York, 1949, p. 14.
19 A. R. Katritzky, 'Physical Methods in Heterocyclic Chemistry,' vol. II, Academic Press, 1963, p. 228.
20 J. Derkosch, *Monatsh. Chem.*, 1961, **92**, 361.
21 W. A. Seth Paul and P. J. A. Demoen, *Bull. Soc. Chim. Belg.*, 1966, **75**, 524.
22 H. Blitz and K. Slotta, *J. Prakt. Chem.*, 1926, **113**, 240.
23 'Organic Synthesis,' ed. B. C. McKusick, Wiley, New York, 1973, vol. 43, p. 49.

Received 1*st April* 1986; *Paper* 6/636