REACTION OF KETENIMINES WITH AZOIMIDE*

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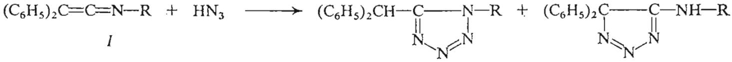
Diphenyl ketene N-aryl- or N-alkylimines react with NH$_3$ to give 1 : 1 adducts on the C=N bond of the cumulene system. Spectral properties of thus prepared 1-aryl- or 1- alkyl-5-diphenylmethyltetrazoles are discussed.

Ketenimines show a well documented[1] propensity to undergo ($4\pi + 2\pi$) cycloaddition reactions as 2π electron components utilising the cumulene C=C or C=N linkage. Surprisingly, the behaviour of these heterocumulenes towards inorganic azides was hitherto not studied. Triphenylketenimine reacts with organometallic azides to give an unstable monocycloadduct, resulting from addition to the C=C bond[2]. On the other hand, L'Abbé and coworkers[3] isolated a 1,2,3-oxathiazol-2-one derivative as an unexpected product of the reaction of dimethylketene N-arylimine with methanesulfonylazide.

In the present communication we described the reaction of ketenimines with azoimide and the spectral properties of the arising 1-aryl- or 1-alkyl-5-diphenylmethyltetrazoles.



I II III

Reaction of equimolar amounts of the compound *I* and azoimide in benzene at room temperature affords products of addition to the C=N bond in fair yields (Table I). The structure of the obtained tetrazoles *IIa*–*IIj* follows from their elemental analysis and spectral data. The other possible product *III*, containing an amino group,

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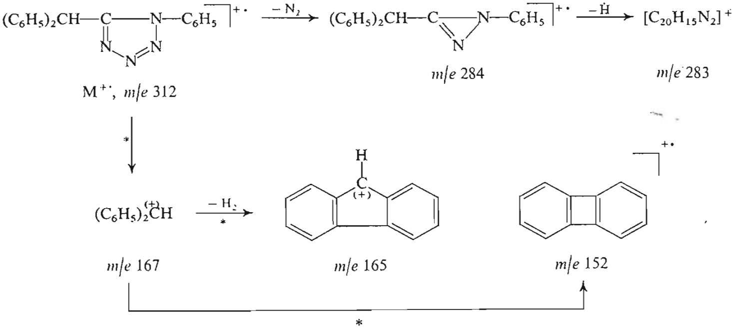
was not found in the reaction mixture. The IR spectra of the derivatives *IIa–IIj* (Table II) exhibit characteristic absorption bands at 1030, 1080 and 1110 cm^{-1}, due to breathing vibrations of the heterocyclic skeleton, and also a band, corresponding to vibration of the —N—N=N— system. We observed also an intense band at 1400 cm^{-1} which is due to the tetrazole stretching vibrations. The strong doublet at 1500 cm^{-1} and 1600 cm^{-1} was ascribed to $\nu(C{=}C)_{arom}$.

The ^{1}H-NMR spectra of the compounds *IIa–IIj* exhibit, in addition to signals due to the substituent R, a methine proton signal and a broad singlet due to 10 aromatic protons of the benzhydryl group (Table III). The chemical shift of the methine proton depends on the substitution of the aromatic nucleus and ranges over 14 Hz. Correlation with Hammett σ_p and σ_m constants afforded a linear dependence $\delta = 5{\cdot}71 + 0{\cdot}18\sigma$ (correlation coefficient $r = 0{\cdot}97$, significance level $P = 99{\cdot}0\%$). We measured mass spectra of the two 1,5-disubstituted tetrazoles *IIa* and *IIi*. The molecular ion of *IIa* produces the diphenylmethyl ion (base ion, *m/e* 167) which after elimination of hydrogen molecule and skeletal rearrangement of the aromatic rings forms the fluorenyl cation[4-6]. Another fragment, produced from the diphenylmethyl as well as fluorenyl cation[7], is represented by the ion-radical $(C_{12}H_8)^{+\cdot}$ (*m/e* 152) (Scheme 1).



SCHEME 1

The butyl group in the derivative *IIi* manifests itself by the radical $\dot{C}_4H_9$ which is splitted from the molecular ion under formation of species *m/e* 237. Other important processes, indicated by the spectra, are the loss of $\dot{H}$, $\dot{N}_2H$, and the elimination of the neutral molecule $C_4H_9N_3$ from $M^{+\cdot}$. The formation of other fragment ions of lower mass is analogous to the preceding case.

EXPERIMENTAL

The reaction course and purity of the compounds were checked by thin-layer chromatography on Silufol^R plates (detection with iodine vapours). The yields, melting points and analytical data of the synthesised derivatives are given in Table I. The IR spectra in the 700–3800 cm^{-1} region were taken on a UR-20 (Zeiss, Jena) spectrophotometer in saturated chloroform solutions (0·6 mm NaCl cells). The instrument was calibrated with a polystyrene foil; accuracy ± 1 cm^{-1} (Table II). ^{1}H-NMR spectra were measured in hexadeuterioacetone on a BS-487C (Tesla, Brno) 80 MHz instrument with tetramethylsilane as internal standard. The position of the signals (δ scale) was determined using a built-in frequency counter (Table III). The mass spectra were taken on an MS 902S (AEI Manchester) spectrometer; direct inlet, 70 eV, trap current 100 μA, temperature of the ionisation chamber 110°C. The regression parameters were calculated on a Hewlett-Packard 9810A calculator.

The ketenimines were prepared by dehydration of the corresponding amides with triphenylphosphine dibromide[8]. The solution of azoimide in benzene was obtained according to ref.[9].

TABLE I

Physical Properties and Elemental Analyses of the Synthesized Substances

Compound	R	Formula (m.w.)	M.p., °C (yield, %)	Calculated/Found % C	Calculated/Found % H	Calculated/Found % N
IIa	4-CH_3O—C_6H_4	$C_{21}H_{18}N_4O$ (342·39)	133–134 (61)	73·66 73·57	5·29 5·19	16·36 16·39
IIb	4-CH_3—C_6H_4	$C_{21}H_{18}N_4$ (326·40)	135–135·5 (56)	77·27 77·15	5·58 5·70	17·16 17·28
IIc	C_6H_5	$C_{20}H_{16}N_4$ (312·37)	147–148 (54)	76·90 76·99	5·16 5·03	17·93 18·12
IId	4-Cl—C_6H_4	$C_{20}H_{15}ClN_4$ (346·81)	155–156 (42)	69·26 69·38	4·35 4·42	16·15 16·26
IIe	4-Br—C_6H_4	$C_{20}H_{15}BrN_4$ (391·27)	157–158 (48)	61·39 61·52	3·86 3·97	14·31 14·43
IIf	4-NO_2—C_6H_4	$C_{20}H_{15}N_5O_2$ (357·37)	211–212 (15)	67·21 67·32	4·23 4·12	19·59 19·70
IIg	3-Br—C_6H_4	$C_{20}H_{15}BrN_4$ (391·27)	86–87 (32)	61·39 61·49	3·86 3·69	14·31 14·12
IIh	2-CH_3—C_6H_4	$C_{21}H_{18}N_4$ (326·40)	96–98 (42)	77·27 77·21	5·58 5·69	17·16 17·20
IIi	i-C_4H_9	$C_{18}H_{20}N_4$ (292·38)	123–124 (18)	73·94 73·90	6·89 6·95	19·16 19·22
IIj	c-C_6H_{11}	$C_{20}H_{22}N_4$ (318·42)	162–163 (21)	75·44 75·31	6·96 6·87	17·59 17·63

Preparation of the Compounds *IIa–i*

A 1M solution of azoimide in benzene (10 ml; 10 mmol) was added to a solution of freshly prepared ketenimine (10 mmol) in dry benzene (10 ml). The mixture was set aside at room temperature for 7 days and the solvent removed on a rotatory evaporator. The remaining oil was cooled to a very low temperature and the separated solid was crystallised from methanol.

TABLE II

Infrared (cm^{-1}) Vibrations of the Substituted Tetrazoles

Compound	Tetrazole ring		ν(—N—N=N—)	$\nu(C{=}C)_{arom}$
	breathing	stretching		
IIa	1 032, 1 080, 1 109	1 461	1 273	1 497, 1 611
IIb	1 034, 1 085, 1 109	1 454	1 279	1 497, 1 602
IIc	1 031, 1 084, 1 111	1 456	1 275	1 506, 1 596
IId	1 033, — 1 099	1 456	1 284	1 506, 1 602
IIe	1 033, 1 075, 1 109	1 454	1 280	1 504, 1 603
IIf	1 030, 1 080, 1 110	1 455	1 285	1 506, 1 601
IIg	1 034, 1 080, 1 108	1 456	1 283	1 497, 1 594
IIh	1 034, 1 081, 1 109	1 463	1 275	1 503, 1 601
IIi	1 034, 1 079, 1 095	1 456	1 298	1 497, 1 602
IIj	1 033, 1 080, 1 100	1 455	1 280	1 495, 1 603

TABLE III

^{1}H-NMR Data of the Prepared Compounds (δ values in ppm)

Compound	CH^a	$(C_6H_5)_2C^b$	R	
IIa	5·65	7·25	7·03 (d, 2 H$_{arom}$) 3·83 (s, 3, CH$_3$)	7·27 (d, 2 H$_{arom}$)
IIb	5·69	7·27	7·25–7·33 (m, 4 H$_{arom}$)	2·40 (s, 3, CH$_3$)
IIc	5·69	7·26	7·22–7·59 (m, 5 H$_{arom}$)	
IId	5·76	7·26	7·40 (d, 2 H$_{arom}$)	7·58 (d, 2 H$_{arom}$)
IIe	5·76	7·27	7·36 (d, 2 H$_{arom}$)	7·73 (d, 2 H$_{arom}$)
IIf	5·83	7·24	7·71 (d, 2 H$_{arom}$)	8·34 (d, 2 H$_{arom}$)
IIg	5·80	7·27	7·18–7·83 (m, 4 H$_{arom}$)	
IIh	5·45	7·21^c	7·10–7·48 (m, 4 H$_{arom}$)	1·67 (s, 3, CH$_3$)
IIi	5·95	7·32^d	0·79 (d, 6, CH$_3$) 4·22 (d, 2, CH$_2$)	2·09 (m, 1, CH)
IIj	6·00	7·31	1·18–1·85 (m, 10, CH$_2$)	4·15 (m, 1, CH)

^{a} Singlet, ^{b} broad singlet, ^{c} doublet, ^{d} multiplet.

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