Proton, Carbon-13, and Nitrogen-15 Nuclear Magnetic Resonance Studies of [^{15}N]Azoles: 1-Phenylpyrazole and the Tautomerically Mobile 3-Methyl-1-phenylpyrazolin-5-one

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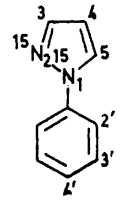
The ^{1}H, ^{13}C, and ^{15}N chemical shifts and ^{1}H–^{13}C, ^{1}H–^{15}N, ^{13}C–^{15}N, and ^{15}N–^{15}N coupling constants of 95% ^{15}N-enriched 1-phenylpyrazole and 1-phenyl-3-methylpyrazolin-5-one have been determined and assigned. In the case of 3-methyl-1-phenyl[$^{15}N_2$]pyrazolin-5-one only the ^{15}N n.m.r. spectrum [solvent $(CD_3)_2SO$] shows that slow exchange occurs between the NH and OH tautomers.

A RECENT survey of the literature concerning the tautomerism of heterocycles [1] shows that ^{1}H n.m.r. spectroscopy has proved a very useful technique. However ^{13}C n.m.r. spectroscopy is being more and more utilised to compete with and even to replace proton resonance. Although it is recognised [2,3] that ^{15}N n.m.r. spectroscopy may furnish structural information, the method is seldom used because ^{15}N-labelled compounds are necessary if ^{15}N–^{15}N or ^{13}C–^{15}N coupling constants are to be measured.

The availability of phenyl[$^{15}N_2$]hydrazine led us to synthesise two new labelled compounds: 1-phenyl[$^{15}N_2$]-pyrazole, as a reference molecule, and 3-methyl-1-phenyl[$^{15}N_2$]pyrazolin-5-one, the object of our interest; the tautomerism of this molecule has been studied previously [1] and it is thus appropriate for a study of the applicability of ^{15}N n.m.r. to tautomeric problems.

1-*Phenyl*[$^{15}N_2$]*pyrazole* (1).—The ^{13}C chemical shifts and ^{13}C–^{15}N couplings for 1-phenyl[$^{15}N_2$]pyrazole are summarised in Table 1. Assignments of the ^{13}C resonances are the same as quoted by Stothers [4] from the data of Rees and Green,[5] however the assignments of the couplings to N-1 or N-2 are not so certain. The observed coupling of C-3 (1.2 Hz) could be to either N-1 or N-2 since each of these couplings is expected to be small: $^{1}J_{CN}$ in pyridine [6] is 0.45 Hz, $^{1}J_{CN}$ in quinoline [7] is 0.6—2.4 Hz, and $^{2}J_{CN}$ in pyrrole [8] is 4 Hz. Similarly it is not possible to assign the two couplings at C-4 specifically to N-1 or N-2. The large coupling (12.1 Hz) at C-5 must be to N-1 by comparison with the values 12.8 Hz for $^{1}J_{CN}$ in pyrrole,[8] 12.0 Hz for the pyridinium ion,[6] and 13.8 and 15.9 Hz for the quinolinium ion [7] ($^{1}J_{CN}$ for a trigonal nitrogen atom has the smaller value noted above for pyridine and quinoline only when the nitrogen atom has a lone pair). For C-2′ the two couplings are equal, and the doublet splitting (2.0 Hz) of C-3′ is probably the three-bond coupling to N-1 (*cf.* $^{3}J_{CN}$ in aniline [9] is 1.2 Hz).



(1)

The ^{15}N chemical shifts, $^{1}J_{NN}$ values, and ^{1}H–^{15}N coupling constants for compound (1) are also given in Table 1. The N-1 signal is assigned as that to high field (by 82 p.p.m.) by analogy with the reported [10] ^{14}N assignments for *N*-methylpyrazole. The value for the one-bond ^{15}N–^{15}N coupling (12.8 Hz) is within the range noted by Bulusu *et al.*[3] (4.5—19 Hz). The ^{1}H–^{15}N coupling constants obtained from the proton spectrum of com-

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[8] J. M. Briggs, E. Rahkamaa, and E. W. Randall, *J. Magnetic Resonance*, 1973, **11**, 416.
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pound (1) are similar in magnitude to those for [^{15}N]-pyrrole,[11] 5-phenyl[^{15}N]isothiazole,[12] [^{15}N]pyrazole,[13] and [^{15}N]isoxazole.[14] In all these previous studies it was concluded that the ^{1}H–^{15}N coupling constants were negative, as must be the case here for compound (1).

3-Methyl-1-phenyl[$^{15}N_2$]*pyrazolin-5-one* (2).—This tautomeric compound has been studied previously in dimethyl sulphoxide solution by Feeney *et al.*[15] by ^{13}C n.m.r. (^{15}N at natural abundance). Our ^{13}C data for the di-^{15}N-labelled material in $CDCl_3$ are given in Table 2. In this solvent the compound exists predominantly as tautomer *a*, as evidenced by the high-field resonance for C-4 and by a triplet pattern in the ^{1}H-(continuous wave) decoupled ^{13}C spectrum, characteristic of the $-CH_2-$ group. The ^{13}C resonances of the phenyl ring were assigned by using the 1-phenylpyrazole assignments (Table 1) and off-resonance ^{1}H (continuous wave) decoupling experiments.

As with 1-phenylpyrazole, the assignment of the

TABLE 1

^{13}C and ^{15}N N.m.r. parameters for 1-phenyl[$^{15}N_2$]pyrazole [a]

Nucleus	δ [b]	Multiplicity	J(^{13}C–^{15}N)/Hz
C-3	141.1	d	1.2 ± 0.3
C-4	107.6	d, d	2.1 ± 0.3, 6.2 ± 0.3
C-5	126.8	d	12.1 ± 0.3 (N-1)
C-1′	140.5 [c]		
C-2′	119.4	t	1.6 ± 0.3
C-3′	129.5	d	2.0 ± 0.3 (N-1)
C-4′	126.5	s	
N-1	198.4	d	12.8 ± 1.2 [d]
N-2	280.4	d	12.8 ± 1.2 [d]

[a] 0.9M-Solution in $CDCl_3$. [b] ^{13}C Chemical shifts in p.p.m. downfield from internal Me_4Si; ^{15}N chemical shifts in p.p.m. downfield from ammonium ion reference (see Experimental section). [c] This resonance was not observed from the ^{15}N-enriched sample, presumably because of the multiplicity and a long spin-lattice relaxation time reducing the signal to noise ratio. The chemical shift was measured from a sample containing ^{15}N at the natural abundance level. [d] This value is ^{1}J(^{15}N–^{15}N). In addition the following parameters were measured from the 100 MHz proton spectrum: δ(H-3) 7.69, δ(H-4) 6.40, δ(H-5) 7.85; $^{2}J_{H(5)-N(1)}$ 4.4, $^{3}J_{H(3)-N(1)}$ 7.4, $^{3}J_{H(4)-N(1)}$ 6.0, $^{2}J_{H(3)-N(2)}$ 14.2, $^{3}J_{H(4)-N_2)}$ 1.0 Hz.

observed ^{13}C–^{15}N couplings to N-1 or N-2 is complicated. The assignments of the ^{13}C–^{15}N couplings at the phenyl ring carbon atoms follow those for compound (1). Lichter *et al.*[16] have studied ^{13}C–^{15}N couplings in some aliphatic amides in which they found $^{1}J_{CN}$ (to the carbonyl carbon atom) in the range 13.4—15.1 Hz and $^{2}J_{CN}$ (across the carbonyl group) in the range 6.9—10.3 Hz. Accordingly we assign the larger splittings at C-5 (11.0 Hz) and C-4 (13.3 Hz) to N-1. Thus the two-bond is larger than the one-bond coupling. As with 1-phenylpyrazole, the lack of available correlations precludes definite assignment of the 3.1 Hz splitting at C-3 to either N-1 or N-2. The large (9.8 Hz) splitting at the methyl carbon atom (C-6) is due to N-2. As the basis for this assignment we use the data of Lichter *et al.*,[17] who found $^{2}J_{CN}$ for *anti*-oxime types to be 2.4—11.6 Hz and for *syn*-oxime types to be 1—2 Hz.

The ^{15}N chemical shifts and $^{1}J_{NN}$ values for compound (2) are given in Table 2. As for 1-phenylpyrazole

TABLE 2

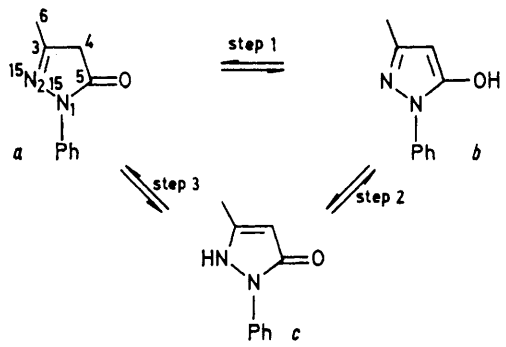
^{13}C and ^{15}N N.m.r. parameters for 3-methyl-1-phenyl-[$^{15}N_2$]pyrazolin-5-one (2) in $CDCl_3$ [a]

Nucleus	δ [b]	Multiplicity	J(^{13}C–^{15}N)/Hz
C-3	156.2	d	3.1 ± 0.6
C-4	43.0	d, d	13.3 ± 0.6 (N-1), 1.5 ± 0.6 (N-2)
C-5	170.6	d, d	11.0 ± 0.6 (N-1), <1.2 (N-2)
C-6	16.8	d	9.8 ± 2.4 (N-2)
C-1′	138.3	d	12.2 ± 1.2 (N-1)
C-2′	118.9	t	1.2 ± 0.3
C-3′	128.8	d	1.7 ± 0.3 (N-1)
C-4′	125.0	s	
N-1	172.2	d	12.0 ± 0.3 [c]
N-2	304.2	d	12.0 ± 0.3 [c]

[a] 0.7M-Solution. [b] See footnote *b* Table 1. [c] This value is ^{1}J(^{15}N–^{15}N). In addition $^{3}J_{H(6)-N(2)}$ (3.5 Hz) was measured from the 100 MHz proton spectrum.

(Table 1), the N-1 signal is assigned as that at higher field.

Proton n.m.r. studies [1] of the pyrazolone (unlabelled) in Me_2SO have indicated a major change in the position of the tautomeric equilibrium in comparison with solutions in chloroform. In Me_2SO solution 20% of



(2)

compound (2) exists in the form *a*, slowly interconverting with tautomers *b* and *c*. Tautomers *b* and *c* are in fast equilibrium; usually [1] it is believed that tautomer *b* predominates. Our ^{13}C n.m.r. data for the pyrazolone (2) in Me_2SO are summarised in Table 3. The assignments follow those of Feeney *et al.*[15] except that we have interchanged the C-3′ and -5′ assignment with that of C-4′ by considering the relative intensities of the resonances. It is noteworthy that the resonance from C-4 in $(CD_3)_2SO$ solution is substantially to lower field, as expected from *b* or *c*, than when observed from a solution in $CDCl_3$ (Table 2). The assignment of this peak to a –CH– group was confirmed by its doublet nature in the

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[13] J. P. Jacobsen, O. Snerling, E. J. Pedersen, J. T. Nielsen, and K. Shaumburg, *J. Magnetic Resonance*, 1973, **10**, 130.
[14] D. Crepaux and J. M. Lehn, *Org. Magnetic Resonance*, 1975, **7**, 524.
[15] J. Feeney, G. A. Newman, and P. J. S. Pauwels, *J. Chem. Soc.* (*C*), 1970, 1842.
[16] R. L. Lichter, C. G. Fehder, P. H. Patton, J. Combes, and D. E. Dorman, *J.C.S. Chem. Comm.*, 1974, 114.
[17] R. L. Lichter, D. E. Dorman, and R. Wasylishen, *J. Amer. Chem. Soc.*, 1974, **96**, 930.

off-resonance ^1H-(continuous wave) decoupled spectrum. Two small resonances observed at 118.1 and 124.5 p.p.m. were assigned to C-2′ and C-4′ of the minor tautomer *a*, in slow exchange with the major form *b* ⇌ *c*. The characteristic resonance from C-4 of *a* was obscured by the solvent resonance. The resolution obtained in the ^{13}C spectrum of compound (2) in $(CD_3)_2SO$ was poorer

TABLE 3

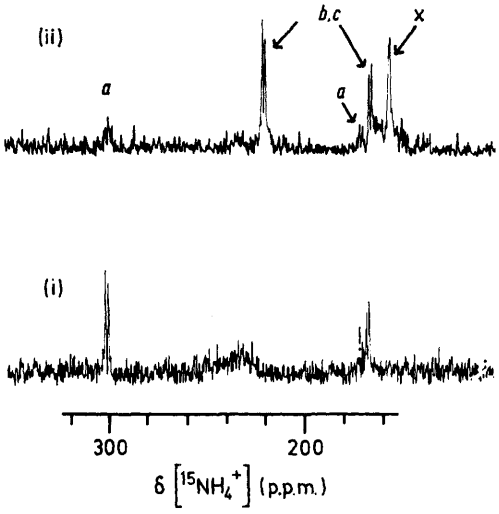
^{13}C N.m.r. parameters for 3-methyl-1-phenyl[$^{15}N_2$]-pyrazolin-5-one (2) in $(CD_3)_2SO$ [a]

Carbon	δ [b]	Multiplicity	$J(^{13}C-^{15}N)$/Hz	
C-3	148.4	s		Major form
C-4	89.0	d	9.8 ± 2.4 (N-1)	
C-5	154.6	d	15.9 ± 1.2 (N-1)	
C-6	13.9	d	7.3 ± 2.4 (N-2)	
C-1′	138.4	d	18.3 ± 2.4 (N-1)	
C-2′	120.4	s		
C-3′	128.8	s		
C-4′	124.9	s		
C-2′	118.1	s		Minor form
C-4′	124.5	s		

[a] 0.7M-Solution. [b] See footnote *b* Table 1.

than for the solution in $CDCl_3$, with the result that only the larger $^{13}C-^{15}N$ couplings (given in Table 3) were measurable. These couplings were assigned as for the solution in $CDCl_3$.

The ^{15}N n.m.r. spectrum of compound (2) in $(CD_3)_2SO$ has proved crucial for the discussion (see Figure). It



^1H Noise-decoupled ^{15}N spectra of 3-methyl-1-phenyl[$^{15}N_2$] pyrazolin-5-one (2) in $(CD_3)_2SO$; (i) at 30 °C; 14 000 pulses; (ii) at 85 °C; 8 192 pulses; X refers to a probable decomposition product. These are both ' magnitude ' spectra and so contain no information on the sign of the $^{15}N-\{^1H\}$ nuclear Overhauser enhancement

took a much longer accumulation time than did the spectrum of (2) in $CDCl_3$ (form *a*). Two well resolved doublets were observed at 299.9 and 167.8 p.p.m. and a weak absorption at 171.6 p.p.m. In addition there is a broad ($\Delta\nu_{\frac{1}{2}}$ *ca.* 125 Hz) resonance at about 234 p.p.m.

* The spectrum in $CDCl_3$ similarly showed the lower field of the two doublets to be substantially the more intense. This may be due to a combination of a differential $^{15}N-^1H$ nuclear Overhauser enhancement or different spin-lattice relaxation times for the two nitrogen nuclei.

The low-field doublet and the absorption at 171.6 p.p.m. are due to the minor component (*a*),* whereas the doublet at 167.8 p.p.m. and the broad resonance must be due to the combination of tautomers *b* and *c* interconverting at some intermediate rate. To further investigate this proposal, the ^{15}N spectrum of (2) in $(CD_3)_2SO$ was measured at 85 °C (see Figure). The broad resonance disappeared and two new absorptions were apparent, at 223.5 (doublet) and 158.2 p.p.m. Measurement of the spectrum again at 30 °C showed that the doublet at 223.5 p.p.m. reverted to the broad resonance, whereas the resonance at about 158 p.p.m. persisted. We therefore feel that this latter resonance is due to a decomposition product.

If tautomers *b* and *c* are interconverting at some intermediate rate (*R*) then the sharp nature of the higher field doublet (due to N-1) shows that it is in the fast exchange limit at 30 °C, whereas the broad nature of the N-2 resonance indicates that it is not, and that *R* is comparable to the frequency separation between the resonance positions for N-2 in *b* and *c*. In order to substantiate this proposition it is necessary to estimate the ^{15}N chemical shifts for tautomers *b* and *c*.

For tautomer *b* we use as a starting point the ^{15}N shifts for the pyrazole (1), and introduce corrections for the methyl and hydroxy-substituents. We have taken the nitrogen chemical shift substituent corrections from the data quoted by Witanowski *et al.* on the methyl-substituted pyrazoles [18] and hydroxy-substituted pyridines.[2] Thus for N-2 in *b* we take the value 280 p.p.m. from (1) and correct first by 5 p.p.m. (upfield) for the methyl group two bonds removed and then by 22 p.p.m. (upfield) for the hydroxy-group three bonds removed. This yields the prediction of 253 p.p.m. for N-2 in *b*. Similarly the shift of N-1 in *b* is predicted to be 140 p.p.m.

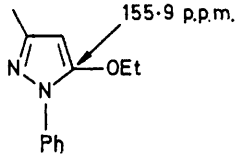
For tautomer *c* we note that N-1 is in a similar chemical environment to N-1 of *a* (observed at 171.6 p.p.m.). The difference in the chemical environment of N-2 between *b* and *c* may be compared with the difference for the two tautomers of 4-hydroxypyridine (which is believed to exist predominantly as the keto form). The calculated [2] nitrogen chemical shift for the hydroxy-form is 97 p.p.m. to lower field than the observed shift. If we take this as the difference for N-2 between *b* and *c*, then the N-2 resonance of *c* is predicted to occur at about 156 p.p.m. The observed and calculated ^{15}N shifts for tautomers *b* and *c* are summarised in Table 4.

Although the calculated ^{15}N shifts are not very precise, the arguments above are confirmed. First, the observed average ^{15}N shifts do lie between the extremes calculated for *b* and *c*. Secondly, the calculated ^{15}N chemical shift separation between *b* and *c* is greater for N-2 (97 p.p.m. = 885 Hz) than for N-1 (32 p.p.m. = 292 Hz).

That the ^{15}N spectrum of compound (2) in $(CD_3)_2SO$ displays broadening due to the exchange between *b* and *c*, whereas the ^{13}C spectrum does not, requires

[18] M. Witanowski, L. Stefaniak, H. Januszewski, and J. Elguero, *J. Chim. phys.*, 1973, **70**, 697.

comment. The ^{13}C resonance likely to show the greatest chemical shift difference between *b* and *c* is that due to C-5. Feeney *et al.*[15] have measured the ^{13}C chemical shifts for two model compounds, (3) and (4), closely related to tautomers *b* and *c*, respectively. The measured [15] ^{13}C chemical shifts (converted to the Me_4Si scale) are as indicated, and these must be corrected in the following manner. Stothers [19] concludes that the



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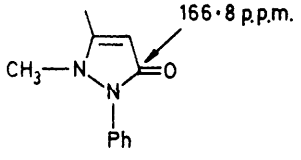

(4)

^{13}C chemical shift substituent effect due to a hydroxy-group upon an sp^2 carbon atom is essentially the same as upon an sp^3 carbon atom. If we assume the same holds true for the ethoxy-substituent [in (3)] then we can predict the ^{13}C shift of C-5 in *b*. Formal conversion of ethanol into diethyl ether shifts the α-^{13}C resonance [20] downfield by 10.1 p.p.m. Thus we predict the chemical shift of C-5 of *b* to occur at 145.8 p.p.m. Considering compound (4), we note that the carbonyl ^{13}C shifts [19] for 2- and 3-methylcyclopent-2-enone are within 0.4 p.p.m. of the shift for cyclopent-2-enone. Therefore the effect of the *N*-methyl substituent in (4) is small at C-5, and (4) is a good model for tautomer *c*: the C-5 signal is predicted to occur at about 166.8 p.p.m.

Thus the predicted ^{13}C shift difference for C-5 between *b* and *c* is 21 p.p.m. = 475 Hz. This value is substantially less than the 885 Hz shift difference for N-2 whereas that from N-1 (0.15) is notably different. The most likely source for the discrepancy is in the calculation of the shift for N-1 of tautomer *b* employing the large hydroxy-substituent effect (−57 p.p.m.).

TABLE 4

Estimated values for $K = [b]/[c]$ from ^{13}C and ^{15}N chemical shifts of compound (2) in $(CD_3)_2SO$

	Chemical shift			
Nucleus	Observed average *b*,*c*	Calculated *b*	Calculated *c*	$K = [b]/[c]$
C-5	154.6	145.8	166.8	1.39
N-1	167.8	140	172	0.15
N-2	223.5	253	156	2.29

and explains why the ^{13}C spectrum does not display any resonance broadening due to the chemical exchange.

We believe the ^{13}C chemical shifts predicted above are more reliable than the predicted ^{15}N shifts. The equilibrium constant, $K = [b]/[c]$, calculated from the various predicted and observed chemical shifts is given in Table 4. The values of *K* derived * from C-5 and N-2 data are in reasonable agreement (1.39 and 2.29) whereas that from N-1 (0.15) is notably different. The most likely source for the discrepancy is in the calculation of the shift for N-1 of tautomer *b* employing the large hydroxy-substituent effect (−57 p.p.m.).

Conclusion.—The observation of temperature-dependent ^{15}N spectra of the pyrazolone (2) in $(CD_3)_2SO$ leads us to conclude that all three tautomers (*a*—*c*) are present. The reason why this is apparent from ^{15}N spectra rather than from ^{13}C spectra is because the ^{15}N chemical shift difference (in Hz) for the N-2 site (the site of protonation) is much greater than for any of the ^{13}C sites (which are all at least one bond removed from the site of protonation). The appearance of the ^{15}N spectrum at 30 °C leads to the conclusion that the equilibrium between the tautomers is best represented as:

$$a \underset{\text{Step 1 or 3}}{\rightleftharpoons} [b \underset{\text{Step 2}}{\rightleftharpoons} c]$$

where the activation parameter for step 2 is lower than for step 1 or 3.

Previous proton n.m.r. data [1] showing 20% of (2) in the form *a*, coupled with the deduction here from ^{13}C chemical shift data that $[b]/[c]$ is *ca.* 1.4, give the following overall contributions to the structure of (2) at *ca.* 30 °C in Me_2SO solution: *a*, 20%; *b*, 47%; *c*, 33%.

EXPERIMENTAL

N.m.r. Spectra.—^{13}C (22.63 MHz) and ^{15}N (9.12 MHz) spectra were obtained with a Bruker HFX-13 instrument operating in the pulse-Fourier transform mode. The instrument was equipped with a B-SV-2 ^1H broad band decoupler unit and free induction decays were accumulated in a Fabritek 1074 CAT (4 K store) and transformed with a PDP-8/I computer. The digitisation in the resulting frequency domain spectra was 2.44 Hz per channel (5 kHz spectral width) or 0.244 Hz per channel (500 Hz spectral width). Pulse flip angles of about 30° were employed for both ^{13}C and ^{15}N spectra, without a 'pulse delay.' ^{13}C Spectra were referenced to Me_4Si and ^{15}N spectra to the $^{15}NH_4^+$ resonance from external $^{15}NH_4{}^{+15}NO_3^-$ (5M in 2N-HNO_3). The samples were contained in 10 mm o.d. tubes and deuterium in the solvent provided the field-frequency stabilisation signal.

^1H Spectra were obtained with a Varian HA-100 instrument operating in the frequency sweep mode.

Materials.—Phenyl[$^{15}N_2$]hydrazine (95% enrichment) was obtained from Isokommerz. 1-Phenyl[$^{15}N_2$]pyrazole was prepared by the method of Finar and Hurlock [22] (65% yield) and 3-methyl-1-phenyl[$^{15}N_2$]pyrazolin-5-one was prepared according to Knorr [23] but by heating for 1 h at 100—110 °C instead of 15 min (60% yield).

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* In the solid state 3-methyl-1-phenylpyrazolin-5-one has been shown [21] to exist as a 50 : 50 mixture of tautomers *b* and *c*.

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[20] Ch. 5 of ref. 4.
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[22] I. L. Finar and R. J. Hurlock, *J. Chem. Soc.*, 1957, 3024.
[23] L. Knorr, *Ber.*, 1883, **16**, 2597.