The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/16409

Please be advised that this information was generated on 2019-04-12 and may be subject to change.
Table II Addition-elimination products 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>B.p. (°C/torr)</th>
<th>( \delta_{1H}^{20} ) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_5)≡C─CH─CH─CH(_3)(^a)</td>
<td>60</td>
<td>~23/19(^c)</td>
<td>1.4624</td>
</tr>
<tr>
<td>C(_2)H(_5)≡C─CH─(CH(_3))(_2)</td>
<td>74</td>
<td>34/15(^c)</td>
<td>1.4664</td>
</tr>
<tr>
<td>C(_2)H(_5)≡C─CH─(CH(_2))(_3)</td>
<td>72</td>
<td>46/0.2</td>
<td>1.5158</td>
</tr>
</tbody>
</table>

\(^a\) E/Z = 65/35. \(^b\) Varian EM-390 NMR spectrometer. \(^c\) Lit.11: 100–105\(^\circ\). \(^d\) See ref. 11. \(^e\) Lit.12: 38\(^\circ\)/15 torr. \(^f\) See ref. 12.

five washings with a saturated solution of ammonium chloride were carried out. After drying over anhydrous magnesium sulphate, the solvents were removed in vacuo. The product was distilled; b.p. 77\(^\circ\)/20 torr, \( n^\circ\)^20 1.4508, yield 1.5 g (20\(^\circ\)). \(^1\)H NMR (CCl\(_4\)): 0.91 (t, CH\(_3\)) 1.18 (s, 3 CH\(_3\)) 1.3–1.7 (m, CH\(_2\)) 1.88 (m, =C─CH\(_2\)) 5.47 (dt, =CH, 7 Hz, \( J_{2} \) 7 Hz) 6.28 (dt, OCH=, \( J_{1} \) 7 Hz, \( J_{2} \) 2 Hz).


\( n \) R─N=C \( \overset{\text{Ni}^{2+}}{\text{Ni}^{2+}} \) \( \rightarrow \) (R─N=C\(^{\prime}\))\(_n\)

Previous investigations of the structure have proved the polymers to be rigid rod compounds, with their main chain in a helical configuration\(^2\). Despite our considerable knowledge concerning the structure of the polymers, some important questions remain unanswered. One of the techniques which seems to offer the possibility of acquiring more information on the structure is \(^{13}\)C NMR. Unfortunately, \(^{13}\)C NMR of non-isotopically enriched polyisocyanides is troublesome and does not provide the required information. This is particularly true for the main-chain carbons, which are the carbon atoms of prime interest. In general, they have very long relaxation times, and thus require an extremely high number of Fourier transients to obtain a signal of useful intensity. Moreover, quadrupole coupling of the imino nitrogen considerably broadens the \(^{13}\)C signal of the main-chain carbons.

The aforementioned difficulties can be circumvented by investigating a polymer made by polymerization of an isocyanide properly labelled with \(^{13}\)C as well as with \(^{15}\)N in the isocyanato group. In order to meet the requirements imposed by the NMR technique, labelling with \(^{15}\)N should be as high as possible to prevent quadrupole coupling. The amount of \(^{13}\)C labelling should be approximately 20\(^\circ\), since higher \(^{13}\)C contents give rise to considerable coupling between the \(^{13}\)C nuclei in the polymer main chain. The need for an isocyanate labelled in this way prompted the study described below.

To our knowledge, no examples of isocyanates enriched in \(^{15}\)N, as well as in \(^{13}\)C in the isocyanate group, are described in the literature. \( \text{Godon and Bauer}^{3} \) have reported

some data concerning the rotational spectrum of methyl $^{13}$C-$^{15}$N-isocyanide, but the material used was only enriched in $^{15}$N (73.5%) and contained $^{13}$C in its natural abundance (1.1%).

Results and discussion

From a synthetic point of view, the well-known pathway, RNH$_2$ → RNHCHO → RN=C, is the most useful route for the preparation of large amounts of isocyanides in a pure form with fair to high yields. Thus, for the synthesis of $^{15}$N-labelled isocyanides, compounds having a $^{13}$N-labelled amino function are the most obvious starting materials. Unfortunately, only a limited number of representatives of this type of compounds are commercially available. Taking into account factors such as price, minimum number of reaction steps, yields, etc., ($\pm$)$^{13}$N-alanine (95% $^{15}$N) seemed to be a suitable starting material. The most straightforward conversion of this amino acid into a compound possessing a properly labelled isocyanido function is depicted in a general way in Scheme 1.

Masking of the carboxylic acid function is necessary because of the liability of isocyanides in the presence of acid. Esterification was performed according to a method described in the literature. Treatment of the starting compound with a solution of thionyl chloride in methanol afforded a quantitative yield of $^{15}$N]alanine methyl ester hydrochloride.

The $N$-formylation of the amino function is the crucial step in the synthesis, since at this stage the $^{13}$C label has to be introduced in the proper amount. In the literature, several reagents for the $N$-formylation of amino groups are described. However, these reagents are less suitable in this specific case, since they have to be used in large excess which is a drawback when dealing with expensive labelled compounds.

We used separately prepared acetic formic anhydride, enriched with $^{13}$C in the formyl moiety, as formylating reagent. This compound was prepared by a modification of the procedure described by Muramatsu et al. starting from acetyl chloride and an appropriate mixture of unlabelled and commercially available $^{13}$C-labelled (99% $^{13}$C) sodium formate.

By starting with sodium formate containing 18.5% of $^{13}$C, working under extreme exclusion of moisture, extending the reaction time to one night at room temperature, careful washing of the precipitated sodium chloride and removal of the solvent in vacuo at 0°C gave a reproducible 96% yield of undistilled product. According to the $^1$H NMR spectrum, this material was essentially pure acetic formic anhydride, the only contaminations being formic anhydride and acetic anhydride as indicated by small singlets at 8.78 ppm and 2.20 ppm, respectively. Presumably, these result from slow disproportionation of the mixed anhydride during its preparation. In view of the instability of the product, the 13C content was not checked using mass spectroscopy. However, from a determination of the isotopic enrichment of the isocyanide (vide infra), it could be unambiguously concluded that the $^{13}$C-enriched mixed anhydride contained 18.9 ± 0.5% 13C in its formyl moiety.

Since in formic acid an equilibrium is established which does not allow all of the 13C label originally present in the acetic formic anhydride to be incorporated into the $N$-formamide, the formylation procedure described by Muramatsu et al. is useless for our purpose.

However, we found that alanine methyl ester can be formylated in good yield using one equivalent of acetic formic anhydride in chloroform as solvent. The free amine was liberated from the hydrochloride salt, which was isolated from the esterification step (cf. Scheme 1), by treating a suspension of the salt in chloroform with dry ammonia gas. Contrary to published procedures, removal of the precipitated ammonium chloride by filtration, which gives rise to considerable loss of material, proved to be unnecessary. After removal of the excess of ammonia in vacuo at low temperature, the resulting mixture was treated with one equivalent of 13C-enriched acetic formic anhydride. According to its $^1$H NMR spectrum at 200 MHz, the material obtained after work up consisted of a mixture of the methyl esters of N-[13C]-formyl[15N]alanine (76% yield) and N-acetyl[13C]alanine (8% yield). Although in the spectrum most of the signals of the formamide and acetamide partly coincide, the molar ratio of the compounds could be determined from the integrals of the NH signals, which differ sufficiently in chemical shift. The acetamide presumably results from nucleophilic attack of the amine nitrogen on the acetyl moiety of the mixed anhydride and/or the acetic anhydride resulting from disproportionation (vide supra). Since the acetyl compound does not interfere in the preparation of the isocyanide and can be removed more easily in a later stage, the labelled formyl alanine methyl ester was not isolated in its pure form.

Treatment of the mixture of methyl esters with phosphorus oxychloride and triethylamine afforded methyl...
As a consequence of this rearrangement-fragmentation, the mass spectrum of the isotopically enriched isocyanide shows peaks at \( m/z \) 68, 69 and 70. From the relative intensities of these peaks the amounts of \( ^{15}N \) and \( ^{13}C \) labelling in the isocyanide moiety were calculated to be 96.4 \( \pm \) 0.5\% and 18.9 \( \pm \) 0.5\%, respectively, thus showing that all of the \( ^{13}C \) label originally used in the preparation of acetic formic anhydride had been incorporated into the isocyanide. From the peak intensities the relative amounts of \( R-^{14}N=^{13}C, R-^{15}N=^{12}C, R-^{14}N=^{13}C \) and \( R-^{15}N=^{12}C \) in the isotopically enriched compound were calculated to be 2.8\% 75.9\%, 0.9\% and 17.8\%, respectively. The remaining 2.6\% consists of molecules bearing \( ^{12}C \) and \( ^{13}C \) in the ratio of their natural abundance at positions other than in the isocyanide group.

The infrared absorption spectrum of the enriched isocyanide showed two major peaks in the region of the isocyanide stretching frequency around 2100 cm\(^{-1}\). In accordance with the findings of Stephany\textsuperscript{14,15}, the position of these peaks proved to be solvent dependent. The positions of both peaks (\( \nu_{NC} \)) in the solvents deuteriochloroform and carbon tetrachloride are, together with their frequency differences (\( \Delta \nu_{NC} \)) and relative absorbances, presented in Table I. By relating the composition of the enriched isocyanide, as determined by mass spectroscopy, to the relative absorbances of the two peaks in the infrared spectrum, it can be concluded that the peak having the highest absorbance originates from \( R-^{14}N=^{12}C \), while the other peak originates from \( R-^{15}N=^{13}C \). This conclusion is supported by the observed frequency difference of approximately 37 cm\(^{-1}\), which is in fairly good agreement with the difference calculated by applying Hooke's law\textsuperscript{16}.

**Table I** Infrared data for methyl \( \alpha-(^{13}C,^{15}N) \)isocyanopropionate.

<table>
<thead>
<tr>
<th>Solvent\textsuperscript{a}</th>
<th>( \nu_{NC}/\text{cm}^{-1} )</th>
<th>( \Delta \nu_{NC}/\text{cm}^{-1} )</th>
<th>Relative absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC(_3)</td>
<td>2112.2</td>
<td>36.4</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>2073.8</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>2107.6</td>
<td>37.3</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>2070.3</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Concentration of isocyanide: 200 mg cm\(^{-3}\).

In order to relate these stretching frequencies to those of the non-enriched isocyanide, infrared absorption spectra of solutions of the latter compound in deuteriochloroform, carbon tetrachloride and \( n \)-pentane were recorded. Surprisingly, in all three solvents the absorption peak due to the isocyanide stretching vibration appeared to consist of two peaks spaced approximately 16 cm\(^{-1}\) apart. In addition to the anticipated solvent dependency of the peak positions, there is also a solvent dependency in the relative absorbances of the peaks. Table II summarises the characteristics of the isocyanide stretching vibrations of the unlabelled compound.

The precise origin of the doubling of the isocyanide absorption band for the unlabelled compound is still unclear. Although the infrared absorption spectra of many isocyanides have been studied\textsuperscript{14}, to our knowledge this phenomenon has not been observed earlier. Since the peaks of the enriched compounds do not display a doubling, the idea of a solvent-dependent conformational equilibrium, yielding two different isocyanides stretching absorptions, has to be abandoned. Presumably, the doubling is caused by Fermi interaction between the fundamental isocyanide stretching frequency and an overtone of another vibration in the molecule which is not observable in the spectrum.

**Table II** Infrared data for non-isotopically enriched methyl \( \alpha \)-isocyanopropionate.

<table>
<thead>
<tr>
<th>Solvent\textsuperscript{a}</th>
<th>( \nu_{NC}/\text{cm}^{-1} )</th>
<th>( \Delta \nu_{NC}/\text{cm}^{-1} )</th>
<th>Relative absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC(_3)</td>
<td>2158.3</td>
<td>14.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2143.8</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>2156.8</td>
<td>16.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2140.3</td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>( n )-C(_3)H(_2)</td>
<td>2154.4</td>
<td>17.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2136.9</td>
<td></td>
<td>3.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Concentration of isocyanide: 200 mg cm\(^{-3}\); in \( n \)-pentane a saturated solution of unknown concentration was used.

recorded between 4000 and 600 cm\(^{-1}\). Whether this assumption is correct will be investigated separately and we hope to return to this matter in a later publication.

Treatment of the isotopically enriched isocyanide with a catalytic amount of nickel chloride afforded the corresponding polyiminomethylene, which was isolated as a light-brown solid. The polymer was soluble in chloroform, but insoluble in lower alcohols, water and hexane. In its infrared absorption spectrum the \(\geq\text{C} = \text{O}\) stretching vibration occurred at approximately 1745 cm\(^{-1}\). The spectrum revealed two \(-\text{N} = \text{C}\) stretching vibrations, at 1615 and 1660 cm\(^{-1}\), with relative absorbances of approximately 4 : 1. In view of the relative amounts of R\(-\text{N} = \text{C}\) and R\(-\text{N} = \text{C}(\text{13}^\text{C})\) in the monomer, these two absorptions have to be attributed to the \(-\text{N} = \text{C} (\text{13}^\text{C})\) and the \(-\text{N} = \text{C}(\text{13}^\text{C})\) stretching vibrations, respectively. In the infrared spectrum of the non-isotopically enriched polymer only one \(-\text{N} = \text{C}\) stretching vibration occurs at 1640 cm\(^{-1}\).

The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of the isolated polymer were in full accordance with the anticipated structure. As is usual for poly(iminomethylenes), the signals in the spectra appeared as broad bands. As a consequence no fine structure due to spin–spin couplings (\(\text{H}–\text{H}, \text{H}–\text{N}–\text{C} (\text{13}^\text{C})\)) was observable.

We have separated the polymer into fractions of narrow molecular weight, each of which will be investigated in detail using various NMR techniques. The results of these investigations will be presented in a forthcoming paper.

**Experimental**

**General.** Infrared (IR) spectra were recorded using a Perkin-Elmer 283 spectrophotometer. Accurate determinations of frequencies were performed under the following scanning conditions: spectral slit width: 3 cm\(^{-1}\); scanning speed: 0.67 cm\(^{-1}\) per min. The vapour spectrum of deuterium chloride was used as a calibration standard. Frequencies obtained in this way were accurate and reproducible within \(1\) cm\(^{-1}\) or less. \(^1\)H NMR spectra were obtained using Varian EM-390 (90 MHz) and Bruker WP-200 (200 MHz) spectrometers. \(^1\)H noise-decoupled \(^{13}\)C and \(^{15}\)N spectra were recorded by Pulse-FT NMR using a Bruker WP-200 spectrometer. \(^1\)H decoupled \(^{13}\)C NMR spectra were recorded for assignment control. \(^1\)H and \(^{13}\)C chemical shifts \(\delta\) are given in ppm downfield from internal tetramethylsilane. \(^{15}\)N chemical shifts are given in ppm upfield relative to the nitrate nitrogen of ammonium nitrate.

Abbreviations used are: \(s\) = singlet, \(d\) = doublet, \(q\) = quartet, \(br\) = broad. Mass spectra were recorded using a VG-Micromass Zab-2F instrument with an electron energy of 70 eV, an accelerating voltage of 8 kV, a resolving power of 1500 and an ionization current of 100 \(\mu\)A. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of W. J. Buis. \((\pm)-[\text{L}]-\text{Alanine methyl ester hydrochloride}\) (1). Starting from \((\pm)-[\text{L}]-\text{Alanine methyl ester hydrochloride}\), this compound was prepared in 100\% yield and \(1.5 \text{~g}\) for the labelled compound. \(^{13}\)C NMR (CDCl\(_3\)) \(\delta 1.63 (2 \times d, J(\text{H}, \text{H}) 7.08 \text{~Hz}, J(\text{H}, \text{H}) 2.93 \text{~Hz, 3, aliphatic CH}\_3), 3.85 (s, 3, ester CH\(\,\_3\)), 4.09 (methylene H, partly obscured by signal of solvent), 8.63 (br d, \(J(\text{H}, \text{H}) 66.04 \text{~Hz}, \text{NH}_\,\_2\)), \(^{13}\)C NMR (CDCl\(_3\)) \(\delta 15.4\) (aliphatic CH\(\,\_3\)), 48.5 (secondary carbon), 53.0 (ester CH\(\,\_3\)), 170.0 (carboxyl); \(^{15}\)N NMR (CDCl\(_3\)) \(\delta -159.26\) (amine nitrogen).

\[^{13}\text{C}\text{]}\text{formic anhydride}\) (2)\(^{10,17}\). This compound was prepared following the procedure described by Marumatsu et al.\(^9\), modified as described above. \(^1\)H NMR (CDCl\(_3\)) \(\delta 2.27\) (s, 3, CH\(\,\_3\)), \(9.10\) (s, 1, formyl).

**Methyl ester of N\(^{-}\text{D}\,[\text{L}]-\text{N}-\text{alanine}\) (3).** A stream of sodium-dried ammonia gas was led into a vigorously stirred suspension of 3.02 g (22 mmol) of 1 in 25 ml of chloroform. The temperature of the mixture was kept below \(-10^\circ\text{C}\). After 15 minutes, the excess ammonia was removed by mild suction (minimum pressure: 100 mm), keeping the temperature of the mixture below \(-10^\circ\text{C}\). Subsequently, a solution of 2.14 g (24 mmol) of CDCl\(_2\) in 4 ml of chloroform was added dropwise at \(-10^\circ\text{C}\), whereafter the mixture was stirred overnight at room temperature. The mixture was filtered by suction and the precipitate of ammonium chloride washed thoroughly with chloroform. Methanol (20 ml) was added to the combined filtrate and washings. After 1 h stirring at room temperature the solution was concentrated in vacuo. The oily residue was codistilled with toluene in vacuo (14 mm) several times in order to remove acetic acid. After removing the last traces of volatile compounds at 0.01 mm, 2.5 g of a 9 : 1 mixture of 3 and N-acetylc\(^{13}\text{N}\)-alanine methyl ester (4) was obtained. \(^1\)H NMR of 3 (CDCl\(_3\)) \(\delta 1.45 (2 \times d, J(\text{H}, \text{H}) 7.08 \text{~Hz}, J(\text{H}, \text{H}) 1.15 (2 \times q, J(\text{H}, \text{H}) 6.56 (4 \times d, J(\text{H}, \text{H}) 7.57 \text{~Hz}, J(\text{H}, \text{H}) 1.47 \text{~Hz, 2, aliphatic CH}\_3), 2.04 (d, \(J(\text{H}, \text{H}) 11.91 \text{~Hz, 2, formyl carbon})}, 52.69 (s, ester CH\(\,\_3\)), 160.69 (d, \(J(\text{C}, \text{C}) 13.40 \text{~Hz, formyl carbonyl})\), 173.19 (s, ester carbonyl). \(^1\)H NMR (CDCl\(_3\)) \(\delta 1.51\) (amide CH\(\,\_3\)), 3.75 (ester CH\(\,\_3\)), \(\approx 4.65\) (methylene H), \(6.33 (2 \times d, J(\text{H}, \text{H}) 7.32 \text{~Hz, J(\text{H}, \text{H}) 15.91 \text{~Hz, NH})\). Methyl \(\text{-a}([\text{L}]-\text{N}-\text{isocyano})\text{propionate}\) (5). In an atmosphere of dry nitrogen a solution of 2.4 g of the mixture of 3 and 4, obtained in the previous experiment, was heated at 68 °C and decanted. The light-brown solid was washed several times with methanol.

[Methyl \(\text{-a}([\text{L}]-\text{N}-\text{isocyano})\text{propionate}\) (5)](15)\(^{-}\text{N}\)-alanine\(\_2\)](15)\(^{-}\text{N}\)-alanine in 20 ml of methylene chloride was cooled to \(-5^\circ\text{C}\). At this temperature a solution of 1.75 ml (19.1 mmol) of phosphorus oxychloride in 2 ml of methylene chloride was added dropwise over a period of 45 minutes with vigorous stirring. After an additional stirring period of 1 h at \(-5^\circ\text{C}\), the mixture was allowed to come to room temperature. While keeping the temperature lower than \(25^\circ\text{C}\) a solution of 3.7 g of sodium carbonate in 25 ml of water was added. Subsequently the solution was cooled to \(-5^\circ\text{C}\) and decanted. The light-brown solid was collected by centrifugation and decantation. The yellow-brown solid was washed several times with methanol, followed by centrifugation and decantation. After drying in vacuo over phosphorus pentoxide, 1.15 g (70%) of polymer was obtained. \(^1\)H NMR (CDCl\(_3\)) \(\delta 1.14\) (Av\(\,\_3\) 76 Hz, 3, aliphatic CH\(\,\_3\)), 3.6 (Av\(\,\_3\) 42 Hz, 3, ester CH\(\,\_3\), 1.15 g (70%) of polymer was obtained. \(^1\)H NMR (CDCl\(_3\)) \(\delta 1.14\) (Av\(\,\_3\) 76 Hz, 3, aliphatic CH\(\,\_3\)), 3.6 (Av\(\,\_3\) 42 Hz, 3, ester CH\(\,\_3\), 1.15 g (70%).
4.4 (Δν = 84 Hz, 1, methine proton). 13C NMR (CDCl3) δ 19 (Δν = 200 Hz, aliphatic CH3), 52 (Δν = 40 Hz, ester CH3), 62 (Δν = 150 Hz, secondary carbon), 164 (Δν = 90 Hz, polymer main chain carbon), 172 (Δν = 100 Hz, C=O). 13N NMR (CDCl3) δ −150 (Δν = 175 Hz, C=N). IR (KBr) 1745 (C=O), 1660 and 1615 cm⁻¹ (N=C). Anal. Calcd for C, 52.28; H, 6.33; N, 12.63; O, 28.76.

Acknowledgements

The authors are indebted to Dr. W. Heerma and Miss M. Sarneel for the mass spectral determination of isotopic enrichment. This research was financially supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Coalescence phenomena in the NMR spectra of some cycloheptatrienes

A. W. Zwaard, H. J. E. Smits and H. Kloosterziel

Department of Organic Chemistry, Gorlaeus Laboratories, P.O. Box 9502, The University, 2300 RA Leiden, The Netherlands

(Received January 4th, 1982)

Abstract. Coalescence phenomena have been observed in the NMR spectra of a variety of 7-substituted 1,3,5-cycloheptatrienes upon varying temperature and/or solvent. Using two different methods, the energy of activation of the process responsible for coalescence has been determined. Within a group of structurally similar para-substituted phenyl sulphides a linear relation has been found between the energy of activation and the acidity constant of the corresponding benzenethiol, suggesting the occurrence of ion pairs. The relatively low energy of activation for the phenyl sulphides, when compared with the values of the phenyl sulphones, may result from the structure of the intermediate ion pairs. In addition to the above, a different exchange process between cycloheptatrienyl sulphones and tropylium salt via sulphonium ions has been observed.

Introduction

In the course of our work on cycloheptatrienyl* anions we have synthesized a variety of substituted 1,3,5-cycloheptatrienes, among which are several 7-substituted sulphides (1) and their corresponding sulphones (2). The NMR spectra of these compounds show interesting properties. A gradual broadening of the 1H or 13C NMR signals due to the seven-membered ring, with final coalescence to one signal, is observed on increasing either the polarity of the solvent or the temperature.

\[
\begin{array}{cccc}
1 \ n = 0 & a \ R = \text{t-Bu} & h \ R = \text{C}_6\text{H}_4\text{F-p} \\
2 \ n = 2 & b \ R = \text{CH}_2\text{Ph} & i \ R = \text{C}_6\text{H}_4\text{Cl-p} \\
& c \ R = \text{CH}_2\text{C}_6\text{H}_5\text{Cl-p} & j \ R = \text{C}_6\text{H}_4\text{Br-p} \\
& d \ R = \text{Bu} & k \ R = \text{C}_6\text{H}_4\text{CO}_2\text{Me-p} \\
& e \ R = \text{C}_6\text{H}_4\text{OMe-p} & l \ R = \text{C}_6\text{H}_4\text{NO}_2-p \\
& f \ R = \text{C}_6\text{H}_4\text{Me-p} & m \ R = \text{C}_6\text{F}_5 \\
& g \ R = \text{Ph} \\
\end{array}
\]

Several reactions, reported by Pietra et al., might also be of interest, e.g. the formation of 1,7-difunctionalized cycloheptatrienes instead of 7,7-dithioacetals (the expected products) when tropone is treated with the appropriate dithiol.

For the four compounds, studied by Kessler et al., a polar mechanism via contact ion-pairs seems to be responsible for the observed phenomena, although in the azide the migration is non-random and the mechanism is intermediate between sigmatropic and ionic. On the other hand, the migration observed for the tin compound is a (1,5)-sigmatropic shift. Pietra et al. suggest several mechanisms for their rearrangements, among which is a rapid 1,7-sigmatropic shift of the sulphur substituent.

Results

The 13C and 1H NMR spectra of 7-(pentafluorophenylthio)-1,3,5-cycloheptatriene (1m) are strongly solvent-