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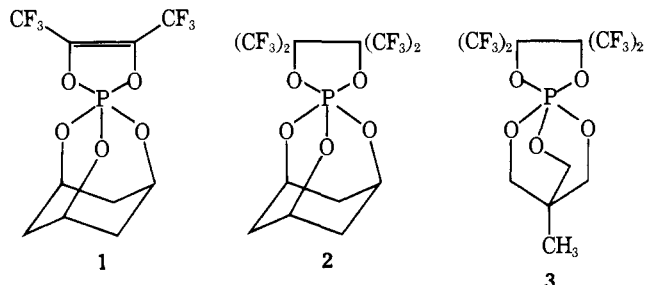
## Some Caged Polycyclic Phosphoranes<sup>1</sup>

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**Abstract:** A series of caged polycyclic thiooxyphosphoranes and oxyphosphoranes has been prepared by allowing the dithietene **6**, the dioxetane **14**, and hexafluorobiacyetyl to react with bicyclic phosphites. Those products which contain only six-membered rings in the bicyclic moiety have NMR spectra which show that, over the temperature range investigated, there is a rapid intramolecular motion which renders the nuclei under investigation equivalent. On the other hand, introduction of one or more five-membered rings into the bicyclic moiety leads to an inhibition of this intramolecular process, and activation energies of 12–19 kcal/mol are found for these substances. The increase in activation energy is probably associated with an increase in strain in the five-membered ring(s) during the intramolecular isomerization.

During the past several years Ramirez, Ugi, and their co-workers have prepared a number of caged polycyclic oxyphosphoranes by condensation of phosphites with hexafluoroacetone and hexafluorobiacyetyl.<sup>2</sup> Representative structures are **1–3**. These substances' structures have been studied by

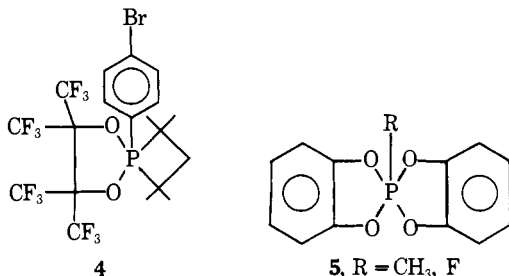


variable-temperature NMR measurements. The data show that the fluorines of the trifluoromethyl groups of **1** are equivalent over all the temperatures investigated. The same

is true for compounds **2** and **3**. Similarly, the hydrogens on the carbons bonded to oxygen of **1** are equivalent over the temperature range studied. Once again the same was found to be true for **2** and **3**. No structure, trigonal bipyramid or square pyramid, can account for the NMR data, and it has been concluded by Ramirez and Ugi that there is a low-energy intramolecular exchange pathway for interconversion of trigonal-bipyramidal structures which renders the various nuclei equivalent. An alternative ionization-recombination mechanism has been considered and rejected on the basis of the lack of change of the <sup>31</sup>P NMR chemical shifts with increasing polarity of solvent. It has been shown in the past that an ionization-recombination equilibrium does in general show changes in <sup>31</sup>P NMR chemical shifts with changes in solvent. More recently<sup>2</sup> it has been reported that FCCOP coupling has now been observed for compounds **1** and **2**. This observation removes any kind of dissociation-recombination mechanism as a means of accounting for the equivalent fluorines. Ramirez and Ugi have considered various intramolecular pathways by

which the nuclei are rendered equivalent, and they have stated, "Molecular models show that the adamantenoid phosphorane, **8** (compound **2** in this report), cannot undergo permutational isomerization by the BPR (Berry pseudorotation)<sup>3</sup> mechanism . . ."<sup>4</sup> Another mechanism was suggested for the isomerization, and this has been named the Turnstile Rotation mechanism. Further discussion of this mechanism and references can be found in ref 2.

More recently, Trippett<sup>5</sup> and Schmutzler<sup>6</sup> have shown that compounds **4** and **5** exist in the crystalline state as square

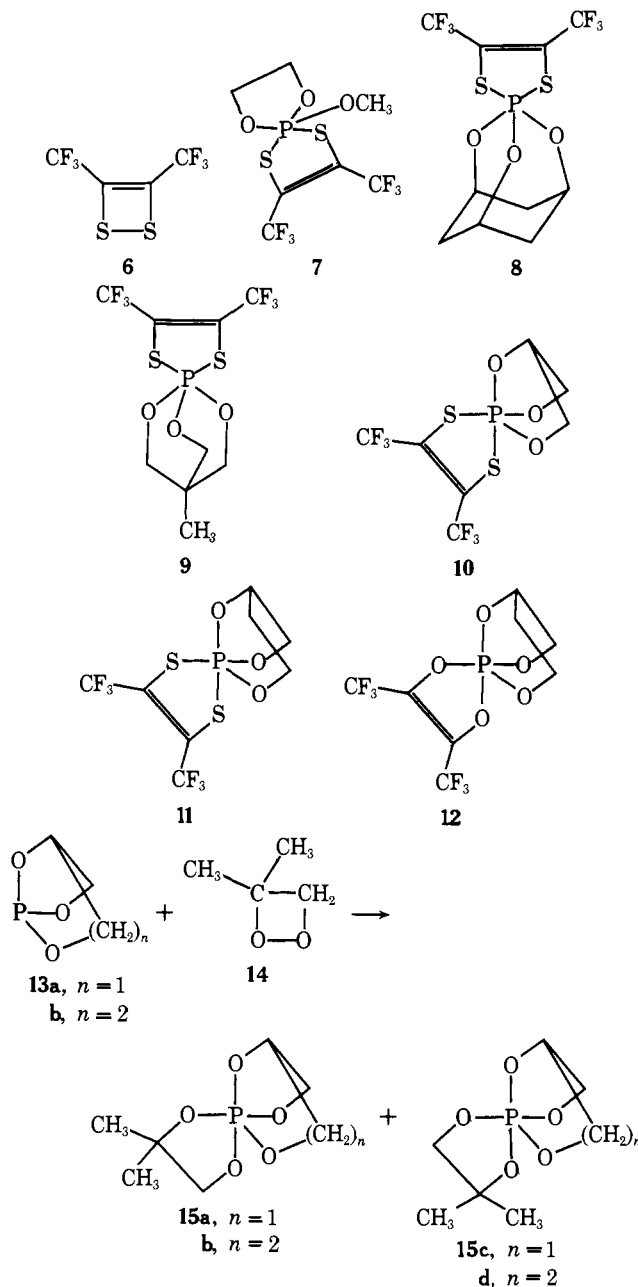


pyramids rather than trigonal bipyramids. These remarkable findings and others have led Holmes<sup>7</sup> to reconsider structures for pentacoordinate spirocyclic phosphorus compounds. He has reached the general conclusion that the interpretation of NMR data which has been used to assign trigonal-bipyramidal structures to molecules of this type is not unique and an alternative explanation is equally acceptable. In essence, this explanation postulates that the ground states of these molecules are more nearly square pyramids and that the isomerization process involves trigonal bipyramids as higher energy intermediates or transition states between interconverting square pyramids. Certainly the results<sup>5,6</sup> and discussion<sup>7</sup> serve to reopen and refocus many questions concerning the structures of pentacoordinate phosphorus compounds.

Recently it has been found that the dithietene **6** will react with a variety of trivalent phosphorus compounds to give phosphoranes.<sup>8</sup> These reactions occur under remarkably mild conditions, and they provide a route to novel sulfur-containing phosphoranes. It seemed of interest to prepare a variety of caged polycyclic phosphoranes from **6**. Similar materials were also prepared from dioxetanes and trivalent phosphorus compounds. This latter reaction was first discovered by Bartlett and his co-workers.<sup>9</sup> The compounds were prepared from a variety of bicyclic phosphites containing six- and five-membered rings.

## Results and Discussion

The compounds **7**–**11** have been prepared by allowing the appropriate phosphite to react with **6**. Compounds **7**–**9** exhibited equivalent fluorines in their <sup>19</sup>F NMR spectra for pairs of trifluoromethyl groups to the lowest temperature achievable in each case:  $-80^\circ\text{C}$  for **7**, ca.  $-100^\circ\text{C}$  for **8**, and  $-78^\circ\text{C}$  for **9**. These results are very similar to those found for compounds **1**–**3**. In the case of **7**–**9**, coupling between phosphorus and fluorine is observed over the temperature ranges, and thus a rapid, on the NMR time scale, ionization–recombination mechanism is eliminated as a means of making the fluorines equivalent. It seems very unlikely that the fluorines are accidentally equivalent. The proton NMR spectra of **7**–**9** were also recorded. That of **9** is particularly instructive. The three pairs of methylene hydrogens are all equivalent,  $\delta$  4.4 ( $J_{\text{POCH}} = 11$  Hz). This finding eliminates a static square-pyramidal structure for **9** at room temperature. Such a structure would have equivalent fluorines but nonequivalent hydrogens. Clearly no single structure can account for the data. Similarly, **8** shows equivalent O—C—H, hydrogen, and trifluoromethyl group fluorines. In the case of **7**, the data do not distinguish between a static square-pyramidal structure or a trigonal-bipyramidal



structure in which there is apical–equatorial switching of the two five-membered rings. The results obtained with **8** and **9** are in essence identical with those obtained by Ramirez and Ugi.<sup>2</sup> It is evident therefore that introducing sulfur into the five-membered ring has had no noticeable effect on the intramolecular permutational isomerization process.

The variable-temperature <sup>19</sup>F NMR spectrum of **10** is most interesting; at ambient temperature, the fluorines of the trifluoromethyl groups are equivalent. They are found as a doublet at  $\delta$  53.72 ( $J_{\text{FCCSP}} = 3.4$  Hz); on cooling, the signals coalesce at  $-26^\circ\text{C}$ , and at  $-80^\circ\text{C}$  there are two quartets, each line of which is split into a doublet. These are found at  $\delta$  52.15 and 53.88 ( $J_{\text{FCCCCF}} = 13$  Hz and  $J_{\text{FCCSP}} = 3.4$  Hz). These data lead to an activation energy for the process which renders the fluorines equivalent of ca. 12 kcal/mol.<sup>10</sup> It is interesting to note that introduction of the two five-membered rings in **10** vs. the two six-membered rings in **9** has significantly increased the activation energy required to achieve equivalent fluorines of the trifluoromethyl groups. Introduction of only one five-membered ring, compounds **11** and **12**, leads also to an increase in activation energies. Compound **11** shows equivalent fluorines

for its trifluoromethyl groups at 60 °C,  $\delta$  54.1 ( $J_{\text{FCCSP}} = 3.6$  Hz). Coalescence occurs at 25 °C, and at -100 °C two quartets are observed, each line of which is split into a doublet. These signals are found at  $\delta$  52.38 and 54.15 ( $J_{\text{FCCCF}} = 11$  Hz and  $J_{\text{FCCSP}} = 3.6$  Hz). The activation energy for the intramolecular exchange process is ca. 14 kcal/mol.

Substitution of oxygen for sulfur, **12** vs. **11**, leads to an increase in activation energy for the process which renders the fluorines equivalent. In this case, the coalescence temperature was found to be 124 °C, and the activation energy was found to be ca. 19 kcal/mol.

Reaction of **13a** and **13b** with **14** occurred smoothly at -78 °C. The reaction mixture from **13a** and **14** showed one major absorption at  $\delta$  20 relative to 85% phosphoric acid. The proton NMR spectrum revealed two absorptions for hydrogens of methyl groups. The areas of the absorption were in the ratio of 3:2. On warming, coalescence occurred at 74 °C, and one sharp singlet resulted. Decomposition of the phosphorane also began as the solution was heated; however, on cooling, the two absorptions for the different hydrogens of the methyl groups reappeared. These data are consistent with there being two phosphoranes present at room temperature. Each of these must have equivalent methyl groups, and the two compounds are not present in equal amount.

Reaction of **13b** with **14** also occurred readily to give a reaction mixture which had one major absorption at 30.5 in the  $^{31}\text{P}$  NMR spectrum. This absorption is in the region expected for oxyphosphoranes containing two five-membered rings. The proton NMR spectrum was complex; however, at 100 MHz and ambient temperatures three absorptions for hydrogens of methyl groups were found at  $\delta$  1.29, 1.27, and 1.23. On heating to 80 °C, these absorptions coalesced into one broad absorption. Cooling to ambient temperature resulted in a mixture which gave the original spectrum. A reasonable interpretation of these results is that there are two major components present in the reaction mixture and that both are oxyphosphoranes which interconvert rapidly on the NMR time scale on heating. Each of these materials has nonequivalent hydrogens of its methyl groups. It is believed that the fourth absorption for methyl group hydrogens, which was not observed, is obscured by either the 1.29 or 1.27 absorption. The relative ratio of these two oxyphosphoranes is ca. 2:1.

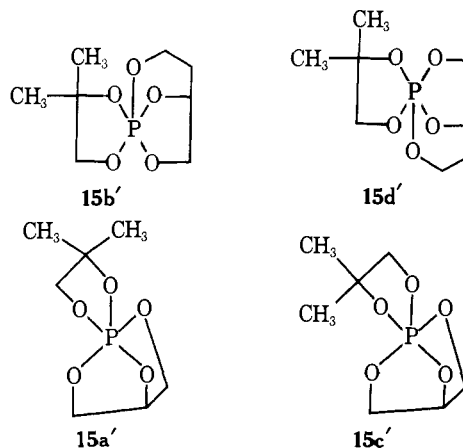
The results of this investigation show quite conclusively that introduction of one or more five-membered rings into the bicyclic moiety of oxy or mixed thiooxybispirobicyclic phosphoranes leads to significant increases in activation energies required to render  $\text{CF}_3$  or  $\text{CH}_3$  groups equivalent in the various molecules. Westheimer<sup>11</sup> in his pioneering research has shown that five-membered ring containing oxyphosphoranes have restrictions on structure due to a combination of strain and electronic effects; thus it is generally accepted that a diequatorial five-membered ring with two oxygens bonded to phosphorus is a high-energy species. Similarly, one predicts that in a square pyramid a dioxy five-membered ring spanning a basal-apical position, ideal bond angle 105°, should be a higher energy structure than the same ring spanning two basal positions, ideal bond angle 88°.

In the cases of compounds **10–12**, **15a,c**, and **15b,d**, the higher activation energies required to interconvert structures over the compounds with six-membered rings are probably associated with an intramolecular exchange process which requires that the five-membered ring expand the O–P–O bond angle during the interconversion. Just how the interconversions occur is not answered by the data.

In fact, the NMR data do not even define the ground-state structure of these molecules, i.e., whether they are trigonal-bipyramidal, square-pyramidal, or of intermediate structure. Two examples should suffice to illustrate this point. Compounds **15b** and **15d** are represented as trigonal bipyramids.

Each has nonequivalent methyl groups which could become equivalent by interconversion between the two structures. Structures **15b'** and **15d'**, which are square pyramids, equally well account for the ambient temperature NMR data. Both pairs of structures seem relatively strain free, there being no structure in which strain is introduced into a five-membered ring.

In the case of **15a** and **15c**, all of the five-membered rings span apical-equatorial positions of the trigonal-bipyramidal structure. The alternate square-pyramidal structures, **15a'** and **15c'**, have one ring which spans apical-basal positions with an



ideal bond angle of 105°. This might represent a more strained situation than is found in **15a** and **15c**; however, it does not seem reasonable to eliminate these two structures on this basis alone.

## Experimental Section

Proton NMR spectra were recorded with Varian T-60 and HA-100 NMR spectrometers. The  $^{31}\text{P}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded with a Varian HA-100 NMR spectra. The  $^{13}\text{C}$  NMR spectra were recorded with a Varian CFT-20 spectrometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-7 mass spectrometer. The dithietene **6** was prepared according to the procedure reported in the literature,<sup>12</sup> as was hexafluorobiacyl.<sup>13</sup>

**Preparation of Compounds 7–10.** These substances were prepared by adding a solution of **6**, 1 mmol/ml of methylene chloride, to a solution of 1 mmol of the trivalent phosphorus compound/2 ml of methylene chloride at -78 °C and under an argon atmosphere. The solutions were allowed to warm slowly to room temperature and processed in the following manners. In the case of compound **7**, evaporation of the solvent yielded a yellow liquid which was distilled, bp 97–98 °C (1.0 mm). The material was analyzed.

Anal. Calcd for  $\text{C}_7\text{H}_7\text{F}_6\text{O}_3\text{PS}_2$ : C, 24.14; H, 2.01. Found: C, 24.15; H, 2.42.

The mass spectrum revealed a molecular ion at  $m/e$  348, calcd 348.

The  $^{31}\text{P}$  NMR spectrum showed one absorption at  $\delta$  -17 relative to 85% phosphoric acid. The  $^{19}\text{F}$  NMR spectrum at 30 °C consisted of a doublet at  $\delta$  54.2 relative to trichlorofluoromethane ( $J_{\text{PSCCF}} = 5.2$  Hz). At -80 °C the doublet was found at  $\delta$  52.7. The  $^1\text{H}$  NMR spectrum had a doublet at  $\delta$  3.68 ( $J_{\text{POCH}} = 17$  Hz), 3 H which is assigned to the hydrogens of the methyl group and a complex absorption  $\delta$  3.92–4.37, 4 H, which is assigned to the hydrogens of the ring. The  $^1\text{H}$  NMR spectrum was unchanged on heating to 130 °C.

Compound **8** was isolated as a solid and recrystallized from methylene chloride. It had mp 125–129 °C (sealed tube). The mass spectrum gave a molecular ion  $m/e$  386, calcd 386. Analysis gave a satisfactory value for hydrogen; however, the carbon value was low by 0.40%.

The  $^{31}\text{P}$  NMR spectrum had one absorption at  $\delta$  -7.8. The  $^{19}\text{F}$  NMR spectrum had one doublet at  $\delta$  53 ( $J_{\text{PSCCF}} = 3.7$  Hz). At -100 °C the doublet was found at  $\delta$  52.3. The  $^1\text{H}$  NMR spectrum showed three absorptions for 2 H each at  $\delta$  2.0, 7.3, and 5.0. The latter is assigned to the hydrogens on carbons bonded to oxygen, and the absorption was a fairly clean doublet ( $J_{\text{POCH}} = 25$  Hz).

Compound **9** was prepared as above. The reaction mixture was

clean, and it showed one absorption in the  $^{31}\text{P}$  NMR spectrum at  $\delta$  -9, a doublet was found in the  $^{19}\text{F}$  NMR spectrum at  $\delta$  55.8 ( $J_{\text{PSCCF}} = 3.7$  Hz). On cooling to  $-78$  °C the doublet shifted to  $\delta$  52.75. The  $^1\text{H}$  NMR spectrum showed a singlet at  $\delta$  0.73 (3 H), which is assigned to the methyl group hydrogens, and a doublet at  $\delta$  4.40 ( $J_{\text{POCH}} = 11$  Hz, 6 H), which is assigned to the hydrogens of the methylene groups.

Compound **10** is fairly unstable, and attempts to work with it led to decomposition. A freshly prepared solution of **10** was evaporated, and the residue was subjected to mass spectral investigation. A molecular ion was found at  $m/e$  346, calcd 346. The  $^1\text{H}$  NMR spectrum was complex. The  $^{31}\text{P}$  NMR spectrum showed one major absorption at  $\delta$  17.5. The  $^{19}\text{F}$  NMR at 30 °C had a doublet at  $\delta$  53.72 ( $J_{\text{PSCCF}} = 3.4$  Hz). Coalescence occurred at  $-26$  °C, and at  $-80$  °C there were two quartets, each line of which was split into a doublet at  $\delta$  52.15 and 53.88 ( $J_{\text{PSCCF}} = 3.4$  Hz and  $J_{\text{FCCCCF}} = 13$  Hz).

Compound **11** was obtained as a liquid, bp 123–125 °C (0.3 mm). On standing, the distillate solidified to give a material mp 65–67 °C.

Anal. Calcd for  $\text{C}_9\text{H}_9\text{F}_6\text{O}_3\text{P}_3\text{S}_2$ : C, 26.66; H, 1.94. Found: C, 26.56; H, 2.09.

The mass spectrum revealed a molecular ion at  $m/e$  360, calcd 360.

The  $^1\text{H}$  NMR spectrum was complex. The  $^{31}\text{P}$  NMR spectrum showed one absorption at  $\delta$  -12.5. The  $^{19}\text{F}$  NMR spectrum at 60 °C had a doublet at  $\delta$  54.1 ( $J_{\text{PSCCF}} = 3.6$  Hz). Coalescence occurred at 25 °C, and at  $-100$  °C there was found two quartets, each line of which was split into a doublet at  $\delta$  52.38 and 54.15 ( $J_{\text{FCCCCF}} = 11.0$  Hz and  $J_{\text{PSCCF}} = 3.6$  Hz).

**Preparation of Compound 12.** A solution of 2.33 g (0.012 mol) of hexafluorobiacyl in 5 ml of methylene chloride was added dropwise with stirring over 20 min to an ice-cold solution of **13b**, 1.35 g (0.01 mol) in 5 ml of methylene chloride. The reaction mixture was allowed to warm to room temperature. After 30 min, the solvent was removed under vacuum to give yellow crystals which were dissolved in 10 ml of methylene chloride, which was then evaporated under vacuum. This process was repeated twice more. The purpose of the treatment was to remove excess hexafluorobiacyl. Ultimately, 3.20 g (97%) of the compound **12** was obtained. The material had mp 63–67 °C, and it was found to be unstable at room temperature in the crystalline form. The mass spectrum had a molecular ion at  $m/e$  328, calcd 328.

The  $^1\text{H}$  NMR spectrum showed complex absorption. The  $^{31}\text{P}$  NMR spectrum had one absorption at  $\delta$  28. The  $^{19}\text{F}$  NMR spectrum had two quartets at  $\delta$  62 and 63.5 ( $J_{\text{FCCCCF}} = 10$  Hz). A solution of **12** in toluene was heated; coalescence of the two  $^{19}\text{F}$  absorptions occurred at 124 °C.

**Preparation of Compounds 15a and 15c.** The general procedure for the preparation of these substances involved addition of an excess of the dioxetane<sup>14</sup> (**14**) in methylene chloride to a solution of the phosphite, **13a**, in methylene chloride at  $-78$  °C. On warming to room temperature, the excess dioxetane decomposed. Solvent removal in vacuo removed the products of the decomposition and left relatively pure phosphorane. The  $^{31}\text{P}$  NMR spectrum generally showed one absorption at  $\delta$  20, ca. 80%, and another at  $\delta$  -19, ca. 20%. This latter absorption was probably due to five-membered ring containing phosphate(s). On occasion, a sample was obtained which was essentially pure phosphorane.

The  $^1\text{H}$  NMR spectrum in methylene chloride had singlet absorptions at  $\delta$  1.39 and 1.32 in the area ratio of 3:2. These were assigned to hydrogens of methyl groups. Two doublets were observed at  $\delta$  3.63 ( $J = 15$  Hz) and  $\delta$  3.70 ( $J = 15$  Hz). These two absorptions were assigned to methylene hydrogens of the two monocyclic rings. Absorptions for hydrogens of the bicyclic system were found from  $\delta$  3.82 to 4.28.

A sample was dissolved in 1,2-dichloroethane and its variable-temperature  $^1\text{H}$  NMR spectrum was investigated. At room temperature the two absorptions for the hydrogens of the methyl groups were found at  $\delta$  1.28 and 1.21. These two absorptions coalesced into a sharp singlet at 74 °C. Decomposition of the phosphorane also occurred on heating; however, when the sample was cooled, the singlet collapsed into the two original absorptions.

The  $^{13}\text{C}$  NMR spectrum of a methylene chloride solution was recorded at  $-20$  °C; it showed two methyl group carbon doublets at  $\delta$  26.60 ( $J_{\text{POCC}} = 5.5$  Hz) and  $\delta$  26.12 ( $J_{\text{POCC}} = 5.8$  Hz) in the ca. ratio of 2:3. The rest of the spectrum was exceedingly complex.

**Preparation of Compounds 15b and 15d.** These compounds were prepared by adding a slight excess of the dioxetane (**14**) in methylene chloride to a solution of **13b** in methylene chloride at  $-78$  °C. Evaporation of the solvent and attempted sublimation resulted in decomposition of the products.

The  $^{31}\text{P}$  NMR spectrum had a broad absorption at  $\delta$  30.5. Small absorptions were found at  $\delta$  -11.5 and 5.5. These are most likely due to phosphates. The  $^1\text{H}$  NMR spectrum of the products in 1,2-dichloroethane had absorptions at  $\delta$  1.29, 1.27, and 1.23; at 80 °C these absorptions coalesced into one broad absorption. On cooling to room temperature the original absorptions reappeared.

## References and Notes

- (1) This research has been supported by the National Science Foundation and by the Public Health Service Research Grant No. CA-10737 from the National Cancer Institute. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of  $^{13}\text{C}$  NMR equipment.
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