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THERMAL AND PHOTOLYTIC DECOMPOSITION OF DIARYLMETHYLENETRIPHENYLPHOSPHAZINES AND DIARYLDIAZOMETHANES

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Abstract—Variously substituted diarylmethylenetriphenylphosphazines and diaryldiazomethanes have been subjected to thermal and photolytic decomposition conditions. The products obtained indicate the major pathway for fragmentation under both thermal and photolytic conditions to be one which serves to generate carbene, nitrogen and, in the case of the phosphazines, triphenylphosphine. The carbene produced from either diarylmethylenetriphenylphosphazine or diaryldiazomethane undergoes reactions which appear to be dependent upon the medium in which it is generated and its inherent stability.

INTRODUCTION

THE preparation of certain diarylmethylenetriphenylphosphoranes by the thermolytic decomposition of their corresponding triphenylphosphazines has been well documented.[1] The procedure is an inherently attractive one because of the stability and ease of preparation of phosphazines in general[2] and the utility of the product phosphoranes.[1d] However, the use of this method of phosphorane generation has been severely limited by factors which were not clearly delineated in previous work. Indeed, the mode of decomposition of the phosphazines themselves has been a subject of controversy.[3]

In hopes of resolving this controversy and generating specific phosphoranes needed for other work, an examination of the decomposition of some representative diarylmethylenetriphenylphosphazines was undertaken. Analysis of the products resulting from these decomposition reactions indicated that initial fragmentation of the phosphazine to triphenylphosphine and diaryldiazomethane might be involved and therefore the diaryldiazomethanes themselves were examined under the same reaction conditions.

RESULTS AND DISCUSSION

A. *Thermal decomposition.* Careful vacuum sublimation of the initial decomposition mixture resulting from the thermolysis of neat diphenylmethylenetriphenylphosphazine (I) leads to the isolation of diphenyldiazomethane. Examination of the thermolysis of either diphenyldiazomethane or the phosphazine (I) in decalin by electron spin resonance (ESR) techniques demonstrates the presence of the diphenylmethyl radical.[4] Thermolysis of the phosphazine is carried out at ca. 165°, at which temperature the spectrum characteristic of the radical species appears. No ESR signal is obtained from the phosphazine below this temperature. Thermolysis in the same solvent of diphenyldiazomethane generates the same spectrum at 140° and this signal persists at higher temperature.

When a solution of I in decalin was heated to 190°, decomposition occurred and the resultant products were separated by GLPC. The products were identified by selective isolation and comparison of behaviour with authentic samples on three (3) different columns (Experimental). These products included: benzophenone (~5%), triphenylphosphine (~25%), tetraphenylethylene (<2%), triphenylphosphine oxide (~20%), tetraphenylethane (~20%), diphenylmethyl azine (~30%), bisdiphenylmethyl ether (<2%) and benzhydrol (<3%).

If it is assumed that a zusammen or *cisoid* transition state configuration of the phosphazine (Fig. 1) is forbidden on steric grounds,[5]* there are, *a priori*, three reasonable pathways by which a substituted phosphazine might thermally decompose and yield the identified products and some phosphorane (Scheme 1).

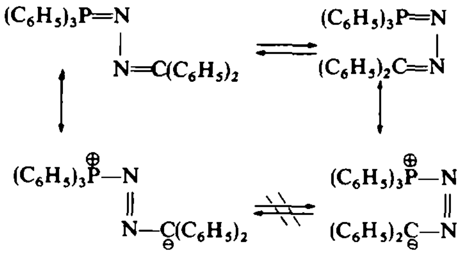
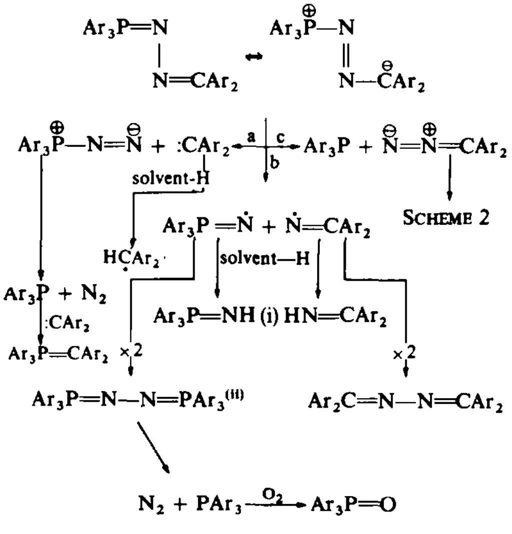


FIG. 1

SCHEME 1



(i) see Ref. 19
(ii) see Ref 20

Ar=C_6H_5

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* Examination of space-filling models representative of the ground state triphenylphosphazines demonstrates unacceptable steric hinderance to a zusammen or *cisoid* configuration. We assume, in the absence of compelling evidence to the contrary, that the transition state geometry will possess the same unfavorable features for this conformation.

Of these, decomposition exclusively *via* path (a; Scheme 1) would seem to be excluded since although it predicts the observed radical, it also predicts the absence of azine. As has been previously noted,[1] and as we have found (*vide supra*), azine is a major product.

In addition, decomposition exclusively *via* path (b; Scheme 1) can be removed from consideration as a major decomposition route since (i) there is no evidence (ESR) that radicals other than the non-nitrogenous ones already reported[4] are present and (ii) utilization of a phosphorus sensitive detector (Experimental) for GLPC demonstrated the virtual absence of phosphorus containing compounds other than triphenylphosphine and triphenylphosphine oxide in this system. The intermediates and products, therefore, appear to dictate that decomposition follows path (c; Scheme 1) which has been intimated, in part, by previous investigators.[6]

Depending upon the extent of oxygen exclusion, variable amounts of benzophenone (II) and triphenylphosphine oxide were produced. Only extensive precautions permitted us to minimize (~5%) these products. The reaction of triplet carbene species with oxygen has been investigated and is in concert with our findings.[7] We presume that the carbene is reacting directly with oxygen and that the ketone arises *via* bisperoxide[7c] although we made no effort to demonstrate that this was indeed the pathway for its production.

Finally, several trapping experiments disclosed that only minor amounts of phosphorane (III) were being formed from I on thermolysis in decalin. The trapping technique was verified through the use of authentic phosphorane (Experimental) which was added to the reaction mixture. In this regard, it is important to note that Staudinger and Meyer[1] recognized that favorable yields of ylid (III) are obtained only on thermolysis of small amounts of phosphazine (I) neat and *in vacuo*, rather than in solution, which resulted in azine production.

When the thermolysis of 9-fluorenyltriphenylphosphazine in decalin was examined by ESR it was immediately noted that only a poorly resolved, short-lived ESR signal resulted. This is in contrast to 9-diazofluorene (IV) itself which readily provides long-lived neutral radical with a well resolved ESR signal.[4b] Therefore, in the case of the phosphazine, the carbene is abstracting hydrogen from solvent more slowly than it is reacting with other species; or, alternatively, the corresponding radical is reacting at an abnormally high rate to provide radical dimer or other species. Now, although it has been noted[8] that the thermolysis of IV results in significant amounts of carbene dimer $\Delta^{9,9'}$-bifluorene, we have found (Table 3) that less than 5% of the analogous tetraphenylethylene could be detected from thermolysis of diphenyldiazomethane (V), except when V was injected directly, without solvent, during GLPC analysis. In addition, radical dimer, 9,9'-bifluorene, in our studies, was found in ca. 10% yield while the analogous tetraphenylethane was detected in ca. 15% yield under identical thermolytic conditions. Thus, it appears that variation in carbene reactivity *vis-a-vis* solvent and/or other species present rather than subsequent radical behaviour is the determining factor in product distribution. This data also supports the contention that the tendency toward carbene dimerization is greater for fluorenylidene than for diphenylmethylene, as previously noted.[9]

In 1962, Wittig and Schlosser[6d] reported that equimolar amounts of triphenylphosphine and diazomethane or phenyldiazomethane in the presence of small amounts of Cu(I) salts gave the corresponding olefins (*via* phosphorane) in approxi-

$$[(C_6H_5)_2C{=}N{-}N{=}P(C_6H_5)_3 \leftrightarrow (C_6H_5)_2\bar{C}{-}N{=}N{-}\overset{+}{P}(C_6H_5)_3]$$

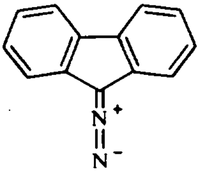
I

$$(C_6H_5)_2C{=}O$$

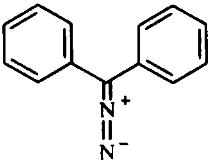
II

$$[(C_6H_5)_2C{=}P(C_6H_5)_3 \leftrightarrow (C_6H_5)_2\bar{C}{-}\overset{+}{P}(C_6H_5)_3]$$

III



IV



V

mately 25% yields and major amounts of azines. The use of preformed phosphazine increased the yield two-fold. From this data, kinetic studies,[10] and the initial observations by Staudinger and Meyer[1a] we conclude that more rapid generation of carbene in the presence of triphenylphosphine should result in formation of larger amounts of ylid.* We observe that thermolysis of preformed CuCl-phosphazine complex (Experimental) in decalin solvent provides a long-lived, stable radical species (ESR), but *no* significant enhancement of phosphorane yield. It would therefore appear that carbene is being generated and is reacting with solvent to form radical faster than it is reacting with triphenylphosphine in these systems.

Other triphenylphosphazines, e.g., those derived from benzaldehyde, benzil and 1,3-diphenylacetone, gave short lived, barely detectable ESR signals and a multitude of products when they were thermolyzed under conditions identical to those used for the diphenylmethyl and fluorenyl cases.[4b] This appears to indicate that highly reactive carbenes are being generated here and any resultant radicals, from reaction with the hydrogen donor solvent, were too short-lived to provide informative spectra.

Since it was evident that the diphenylmethylene and 9-fluorenylidenetriphenylphosphazines were decomposing to triphenylphosphine and the corresponding diazomethane, the thermolysis of the diaryldiazomethanes, in decalin (or bicyclohexyl) and in a non-H atom donor solvent (benzene) was examined. This provided the additional data indicated in Scheme II and Table 1 from which we conclude that the product distribution for phosphazine and diazo thermolysis appears to be determined by (a) the stability of the carbene and (b) the decomposition medium.

B. *Photolytic decomposition.* Compounds I and V were photolyzed (Experimental) in benzene and in decalin (or bicyclohexyl) solvents to provide the product distributions presented in Table 2. These photolyses were extremely sensitive to the presence of oxygen and contaminants capable of hydrogen donation. Large amounts of oxidative products were formed unless extensive precautions were taken to exclude oxygen. When oxygen was excluded the product distribution was strikingly solvent

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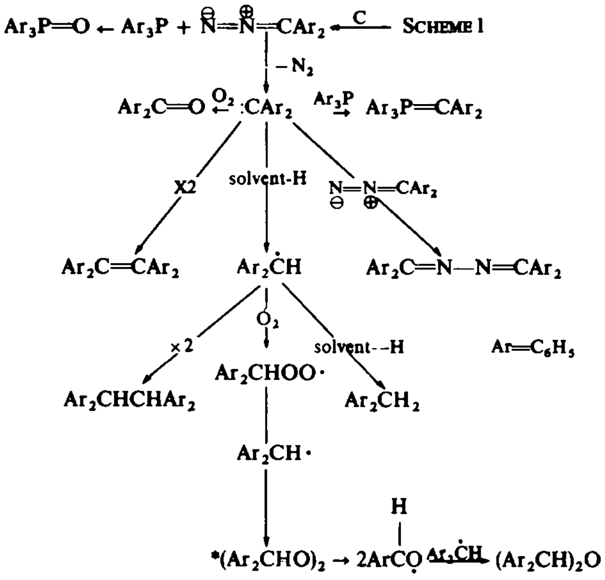
* It has also been established that Cu(I) salts catalyse the decomposition of diazo compounds to provide carbene species.[11]



SCHEME 2

dependent, i.e. major amounts of tetraphenylethane, radical dimer, were obtained only in the presence of hydrogen donating solvents (e.g. decalin).

Comparison of photolytic and thermolytic product distributions (Tables 1 and 2), as well as examination of corresponding decompositions of *ortho*, *meta* and *para*-methyldiphenyldiazomethanes, and IV permitted the following conclusions: (i) H atom availability during the photolytic decomposition is more significant *vis-a-vis* the ethane yield than in the thermolytic decomposition, i.e. about 2% ethane is obtained when photolyses are conducted in benzene solvent, compared to about 70% in decalin. Correspondingly, about 5% ethane is produced when the thermolyses are carried out in benzene, and only 30% in decalin. Therefore, the photolytic reaction is more effective in producing carbenic species able to H-atom abstract than is the thermolytic method. (ii) Sensitivity to oxygen is more marked in the photolytic series than in the thermolytic series for all compounds studied. The competitive reactions of carbene dimerization and hydrogen abstraction could not be detected when the relative concentrations of oxygen or ketone were high, i.e. when photolyses are conducted in benzene at low diazo concentrations (Table 3).

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* The peroxide intermediate (Scheme II) produced in the oxidative reaction is known to be thermally and photolytically labile[18] and hence, the stable diphenylmethyl ether is the observed product.

An anonymous referee has pointed out that benzhydrol, $(C_6H_5)_2CHOH$, might be expected as a product in this reaction i.e.

$$(C_6H_5)_2CHO\cdot + H - \text{solvent} \rightarrow (C_6H_5)_2CHOH + \text{solvent}.$$

Benzhydrol is stable under the conditions of isolation and its GLPC retention time, under the conditions used (Experimental), is similar to benzophenone. Nevertheless, the lack of significant OH absorption in the infrared spectrum of the crude reaction product and the shape of the curve obtained in GLPC analysis, in the absence and presence of added benzhydrol precludes the possibility of *more than* a 3% yield of this alcohol.

TABLE 1. THERMOLYSIS PRODUCTS[a]

	Solvent	$Ph_2C{=}CPh_2$	$Ph_2CHCHPh_2$	$Ph_2C{=}N{-}N{=}CPh_2$	$Ph_2CH{-}O{-}CHPh_2$[b]	Ph_2CO	Ph_3P	Ph_3PO
$Ph_3P{=}N{-}N{=}CPh_2$								
	Benzene	<2	10	30	<2	<5	25	20
	Decalin	<5	20	30	<2	<5	25	20
$Ph_2C{=}N{=}N$								
	Benzene	8	5	80	<2	<2	—	—
	Decalin	<5	30	50	<2	<5	—	—

[a] Representative amounts based on uncorrected area %. All thermolyses conducted at 190 ± 5°.

[b] See footnote, p. 3325.

TABLE 2. PHOTOLYTIC PRODUCTS[a]

	Solvent	$Ph_2C{=}CPh_2$	$Ph_2CHCHPh_2$	$Ph_2C{=}N{-}N{=}CPh_2$	$Ph_2CH{-}O{-}CHPh_2$[b]	Ph_2CO	Ph_3P	Ph_3PO
$Ph_3P{=}N{-}N{=}CPh_2$								
	Benzene	<2	<5	5	<2	<5	30	50
	Decalin	<5	25	<2	<2	<5	20	50
$Ph_2C{=}N{=}N$								
	Benzene	<2	<2	90	<5	<2	—	—
	Decalin	<2	70	20	<5	<2	—	—

[a] Representative amounts based on uncorrected area %.

[b] See footnote, p. 3325.

TABLE 3. $Ph_2C{=}N{=}N$ IN BENZENE CONCENTRATION DEPENDENCY—THERMOLYTIC AND PHOTOLYTIC PRODUCT ANALYSIS[a]

	$Ph_2C{=}CPh_2$	$Ph_2CH{-}CHPh_2$	$Ph_2C{=}N{-}N{=}CPh_2$	$Ph_2CH{-}O{-}CHPh_2$[b]	Ph_2CO
			Concentration 0·5 M $Ph_2C{=}N{=}N$ *in Benzene*		
Thermolysis-Sealed	8	5	80	<2	<2
Thermolysis-Open	5	<2	90	<2	<2
Photolysis-Sealed	<2	<2	95	<5	<2
			Concentration 10^{-1} *M* $Ph_2C{=}N{=}N$ in *Benzene*		
Thermolysis-Sealed	5	<2	95	<2	<2
Thermolysis-Open	8	<2	90	<2	<2
Photolysis-Sealed	5	<2	75	15	5
Photolysis-Open	<2	5	35	45	20
			Concentration 10^{-2} *M* $Ph_2C{=}N{=}N$ in *Benzene*		
Thermolysis-Sealed	<2	<2	90	<2	<2
Thermolysis-Open	<2	<2	90	<2	<2
Photolysis-Sealed	<2	<2	10	90	<2
			Direct Thermolysis of $Ph_2C{=}N{=}N$ *on GLPC (No Solvent)*		
	15	5	80	5	<2

[a] Representative amounts based on uncorrected area %. All thermolysis conducted at 190 ± 5°.

[b] See footnote, p. 3325.

The relative insensitivity to the mode of treatment (thermal or photolytic), as reflected in product distribution, was noted at high (ca. 0·5 molar) concentration where azine (80–90%) was the major product with small (5–8%), but significant, amounts of tetraphenylethylene being detected under both sets of conditions. At lower concentrations (ca. 10^{-1} molar), competitive reactions of oxygen (and/or ketone) contaminant were indicated by a higher (ca. 15%) amount of diphenylmethyl ether in the photolytic series and in the absence of high levels of hydrogen donors. The product distribution at this concentration in the thermolytic series remained essentially unaffected.

The importance of direct oxygen trapping during the photolysis was demonstrated (Table 3) by carrying out photolysis without an inert atmosphere. Typical of the results was the increase in the quantity of benzophenone produced (He atmosphere, 5%, air, 20%).

Finally, at a concentration of 10^{-2} molar, the difference between thermolysis and photolysis is appreciable. Here the competitive reactions giving rise to diphenylmethyl ether dominate the photolysis series (Table 3), while thermolysis continues to provide azine as the major product. Therefore, at this concentration, for thermolysis, the rate of azine production and/or the overall production of singlet carbene must be more significant than in photolysis, if it is assumed that azine production is best represented by the reaction of singlet carbene with unreacted V.[12]

It thus appears, from this series, that at high concentrations, neither photolysis nor thermolysis is able to provide conditions which permit discrimination between the carbene intermediate species and only azine results from either singlet or triplet carbene reaction (whichever may be produced *in situ*). As expected, the oxidatively derived contaminants are essentially eliminated and it is only at the lower concentrations that the reactions noted in Scheme II can be realized and insight into their relative significance adduced.

Therefore, we conclude that in general, at high concentrations, reaction of carbene with unreacted diazo compounds predominates over carbene dimerization, hydrogen abstraction and oxygen trapping while at low concentration, carbene reactions with oxygen and/or ketone dominate over carbene dimerization or diazo reaction.

Experiments are in progress which are designed to shed light on the multiplicity of the carbenic intermediate at low and high concentrations.

CONCLUSION

Diarylmethylenetriphenylphosphazine decompositions, both thermal and photolytic, appear to proceed in a similar step-wise fashion; first, to the diazo compound and triphenylphosphine and then to the carbene *via* diazo decomposition. The product distributions from phosphazine or diazo parent can be accounted for on the basis of carbene stability, concentration, hydrogen atom availability and oxygen availability. Product analysis is indicative, in general, of a more radical-like behaviour of the carbene produced in the photolytic series; hence, more triplet carbene production and/or availability might be inferred. However, a conclusion regarding the initial spin state of the carbene is not possible from this study.

EXPERIMENTAL

First derivative ESR spectra were obtained as previously reported.[4b] Temps are considered accurate to

±5°. PMR spectra were obtained on a Varian A-60A spectrometer; IR spectra on a Beckman IR5-A spectrophotometer,[*] and UV spectra on a Perkin–Elmer 237 Spectrophotometer. Mps were determined with a Fisher–Johns block and are uncorrected. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del. The GLPC chromatographic analysis, utilizing a phosphorus-sensitive detector was performed by Greenwood Laboratories, Chadds Ford, Pa. All other GLPC analyses were conducted with an Aerograph A90-P3 chromatograph using a thermal conductivity detector and a 5′ × ¼″ Cu columns of (1) 5% SE-30 on acid washed DMCS Chromosorb G (60–80 mesh), (2) 3% OV-17 on Gas Chrom Q (60–80 mesh) and/or (3) 5% polyphenyl ether (6 rings) on Diaport S (60–80 mesh). He was used as a carried gas throughout. Representative settings were: injection port, 290°, detector 340° and He flow, 80 ml/min.

Thermolysis experiments were conducted in Pyrex ampules, sealed under He, and placed in an oil bath maintained at 190 ± 5° for a period of 0·5 hr. GLPC analysis over a period of time showed that the products were stable at room temp even when open to the air. Stability to GLPC conditions was ascertained by reproducible repetitive injections, collection of representative component fractions, and re-injection onto the column. Peak identification was through relative retention times and complete analysis of the isolated components. Composite IR spectra of known mixtures of identified components were prepared and compared to the spectra of reaction mixtures. Good agreement, following the results of GLPC could routinely be found.

Photolytic experiments were conducted with a Hanovia medium pressure 450 watt, type L, No. 679A-36 immersion lamp using a Pyrex filter, No. 516. This filter conducts less than 20% of the radiation under 2900Å and over 50% of the 3100 Å and longer wavelengths. Sample tubes were 12″ by 2 mm o.d. quartz. The tubes containing the sample to be photolyzed were placed along the outer surface of the immersion well which, in turn, was within a water bath maintained at room temperature. Alternatively, the immersion well was filled with the solution to be photolyzed and maintained under an atmosphere of He. Despite all precautions, the presence of oxidative products in the photolyses was never completely eliminated. This problem has been encountered previously.[12b]

Benzophenone, tetraphenylethylene, and 9,9′-bifluorene were purchased from Aldrich Chemical Co., Milwaukee, Wisc. and used as received. Decalin, (98%, min.) and hydrazine hydrate (95%) were obtained from Eastman Organic Chemicals, Distillation Products Industries, Rochester, N.Y.; mercuric oxide (yellow powder) from General Chemical Division, Allied Chemical and Dye Corp., N.Y. Triphenylphosphine was obtained through the courtesy of the Carlisle Chemical Works, Inc., Reading, Ohio. *ortho*, *meta*, and *para*-Methylbenzophenones were purchased from K and K Laboratories, Inc., Planeview, N.Y. and were used as received. Diphenylmethyltriphenylphosphonium bromide, (m.p. 250–252°), was prepared from triphenylphosphine and diphenylbromomethane and reacted with PhLi (22·6% by wt), Alpha Inorganics, Beverly, Mass., according to Coffman and Marvel[13] to yield triphenylphosphinediphenylmethylene, m.p. 170° (lit.[14] 172–174°). Benzophenone azine, m.p. 161° (lit.[14] 164°) was prepared from its corresponding ketone and hydrazone. Phosphazines were prepared by a minimum of two independent routes.[2a–d] Diphenylmethylenetriphenylphosphazine, m.p. 170° (dec), (lit.[2c] 165° dec); 9-fluorenylidenetriphenylphosphazine, m.p. 21° (dec) (lit.[2c] 205° dec); benzylidenetriphenylphosphazine, m.p. 135° (lit.[2c] 129–130°); 1,1-diphenyl-2-methylethelidenetriphenylphosphazine, m.p. 123°. (Found: C, 81·42; H, 6·10; Calc. for $C_{33}H_{29}N_2$: C, 81·72; H, 6·0%). CuCl diphenylmethylenetriphenylphosphazine, m.p. 185–186°, (Found: C, 67·23; H, 4·67; N, 5·34; P, 5·59. Calc. for $CuCl \cdot C_{33}H_{29}N_2$: C, 67·10; H, 4·55; N, 5·04; P, 5·40%). 1,1,2,2-Tetraphenylethane, m.p. 209° (lit.[15] 208–209°) was prepared from azo-*bis*-diphenylmethane, m.p. 110° (dec) (lit.[15] 114°, dec). Diazo compounds were prepared from their corresponding hydrazones according to published procedures.[16a,b] The preparation of crystalline diphenyldiazomethane was accomplished according to the procedure of Miller[17] yielding a solid, m.p. 29° (lit.[17] 30–32°). Diphenylmethyl ether was prepared by reaction of benzhydrol and conc H_2SO_4 and isolated as a yellow oil which crystallized slowly on standing, m.p. 103–105° (lit[18] 108°). The PMR spectrum ($CDCl_3$, TMS = 0) showed a singlet (1 H) at $\delta = 5{\cdot}4$ ppm and a singlet (5 H) at $\delta = 7{\cdot}4$ ppm.

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[*] The spectrophotometer was purchased from funds provided by a grant (CA 08841) from the National Cancer Institute, National Institutes of Health. We gratefully acknowledge this financial aid.

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