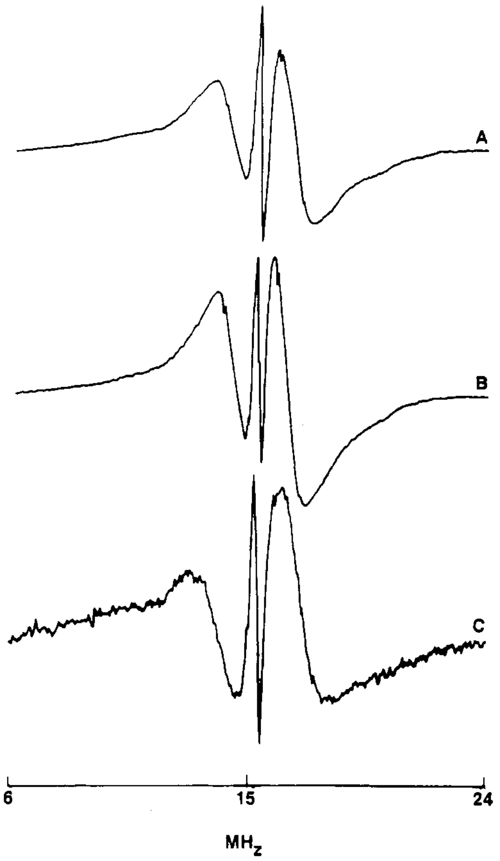

Figure 1. ENDOR spectra obtained for three low spin density *trans*-polyacetylene samples: (A) 95% trans isomer content, powder; (B) 95% trans isomer content, free-standing films; (C) thermally annealed low-spin free-standing film. Experimental conditions were microwave power incident on cavity, 10 mW; radio frequency power, 50 W (nominal); T = 140 K. Narrow spikes are decade markers arising from the radio frequency frequency source. Spectra are composed of two components: local hyperfine and distant ENDOR transitions. The variation in relative intensities between the two components is consistent with the difference in spin densities among the samples. Assignments of hyperfine tensors are the same as previously described.[7,8]

Figure 1B shows that identical results were obtained for low-spin *trans*-polyacetylene prepared as free standing films (also composed of 95% trans isomer).

Within the soliton framework, our results could be interpreted as evidence for fixed spins in these materials, solitons trapped within short trans isomer segments, just as the defects are thought to be trapped in *cis*-polyacetylene. We tested this interpretation by performing an identical thermal treatment on low-spin *trans*-polyacetylene. Any remaining cis isomer segments should be isomerized to the trans isomer, thus permitting the solitons to be freely mobile along the chain. The additional isomerization was confirmed by a slight increase in the trans isomer content as observed by IR and also by a factor of 3 increase in the spin density. Figure 1C shows the ENDOR spectrum for this material. Clearly there is no evidence for mobility of the defects, and the spectrum remains almost identical with that of *cis*-polyacetylene.

We envision two possible mechanisms to explain our results. The loss of local ENDOR structure in *trans*-polyacetylene samples prepared by the Shirakawa method can simply be a result of its high spin density; spin-spin exchange mechanisms represent the major contribution to the apparent dynamic narrowing of hyperfine interactions observed in ENDOR experiments.[9] The alternative explanation is that even after thermal isomerization, all solitons remain trapped in low-spin *trans*-polyacetylene. This would have to occur despite the fact that the polymer is identical structurally, chemically, and spectroscopically with the Shirakawa material. In addition, indistinguishable trapping mechanisms for the Shirakawa material at low temperatures, *cis*-polyacetylene, and low-spin *trans*-polyacetylene are suggested by the similarity of their ENDOR spectra. The absence of any corroborating evidence for additional trapping mechanisms suggests that spin exchange is the correct explanation, contrary to previous interpretations of the ENDOR data.

It is important to note that even though exchange dominates the magnetic properties of polyacetylene, EPR,[3] ESE,[14] NMR,[12] and DNP[18] experiments suggest an additional contribution from a thermally activated dynamic process. Whether slow 1-D motion might be responsible for the activated process is currently under investigation.

Registry No. *trans*-Polyacetylene, 25768-71-2.

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Wagner-Meerwein Rearrangements of Radical Cations Generated by Triphenylpyrylium Tetrafluoroborate Photosensitized Electron Transfer of Azoalkanes

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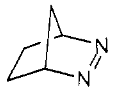
Received September 16, 1986

While there has been a surge of activity during the last decade on the chemistry of radical cations,[1] only little information exists on such reactive intermediates derived from azoalkanes. This is particularly surprising in view of the fact that azoalkanes display well-defined photoelectron spectra.[2] Recently, however, the first report[3a] of such species appeared, namely, the radical cation of 1,1′-azoadamantane, generated by chemical oxidation with the thianthrene radical cation. Furthermore, the photochemistry of the reluctant 2,3-diazabicyclo[2.2.2]octene in CCl$_4$ has been interpreted in terms of the corresponding azoalkane radical cation.[3b] Specifically, excited azoalkane served as donor, transferring an electron to ground-state CCl$_4$ as electron acceptor. Presently we report that the excited electron acceptor triphenylpyrylium tetrafluoroborate (TPT$^+$) acquires an electron from ground-state azoalkanes **1-4** as donors, resulting in the respective azoalkane radical cations. Loss of nitrogen from the latter affords rearranged photoproducts (eq 1) which we rationalize to be derived from the intermediary hydrocarbon radical cations.



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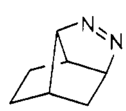

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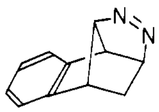

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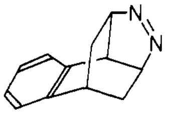

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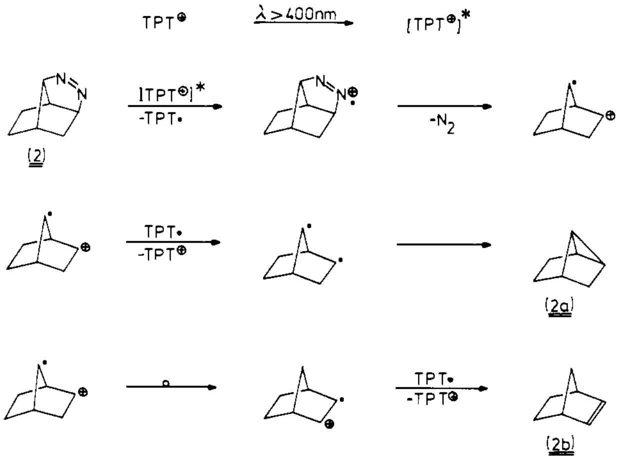
Table I. Product Distributions in the Direct, Triplet-Sensitized, and Electron-Transfer Photolyses of Azoalkanes **1–4**

		product distribution,[a] %		
azoalkane[b]	products[c]	direct[d]	triplet sensitized[e]	electron transfer[f]
1	**1a**	99.7	99.5	81
	1b	0.3	0.5	19
2	**2a**	100	100	6
	2b	0	0	94
3	**3a**	99.5	0[g]	89
	3b[h]	0.5	0	11
4	**4a**	80	96	0
	4b[h]	20	4	100

[a] Relative yields normalized to 100%. Determined by capillary GC on a 50-m OV-101 column, operated at column, injector, and detector temperatures of 17, 50, and 50 °C for **1**; 70, 120, and 120 °C for **2**; or 150, 200, and 200 °C for **3** and **4**; at a carrier gas (N_2) pressure of 0.5 kg/cm^2 for **1** and **2** or 0.8 kg/cm^2 for **3** and **4**. Error ca. ±0.5% of stated value. [b] Run in methylene chloride and/or *n*-pentane except in the triplet-sensitized photolysis for which acetone was used. Ca. 0.1 M solutions. [c] **1a–4a** are the cyclization products and **1b–4b** the Wagner–Meerwein rearrangement products (cf. eq 1); product balance was usually 80–90%, including other minor volatile products. [d] Rayonet photoreactor, equipped with 350-nm lamps. [e] Rayonet photoreactor, equipped with 300-nm lamps, with acetone as solvent and sensitizer. [f] Mercury high-pressure arc, eliminating all radiation below 400 nm by means of a UVW-55 filter, in the presence of stoichiometric amounts of triphenylpyrylium tetrafluoroborate (TPT). [g] 2,3-Diaza-7,8-benzotricyclo[4.3.0.0^{2,9}]nona-3,7-diene is formed exclusively (cf.: Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4133). [h] Benzonorbornadiene (**3b**); 6,7-benzobicyclo[3.2.1]octa-2,6-diene (**4b**).

To show the feasibility of our methodology, 1,1′-azoadamantane and TPT$^+$ (stoichiometric amounts, 0.1 M solutions in acetonitrile) were irradiated (λ > 400 nm) at 25 °C, affording after aqueous workup *N*-acetyl-1-aminoadamantane (97%) and 1-acetyladamantane (3%), which were identical with authentic samples.



(1)

Clearly, the acetamide is the Ritter product derived from acetonitrile trapping of the 1-adamantyl cation, which is released from the intermediary azoadamantane radical cation, as initially observed[3a] in the chemical oxidation with the thianthrene radical cation. Control experiments showed that irradiation of the azoadamantane neither in the absence of TPT$^+$ nor with the latter in the dark led to the acetamide. Consequently, the electronically excited TPT$^+$ is a sufficiently strong oxidant (E_{ox} = 1.92 V)[5] to acquire an electron from the azoadamantane, leading to the radical cation of the latter. Its chemical fate has already been discussed.[3a]

Once it was demonstrated that electronically excited TPT$^+$ can oxidize azoadamantane to its radical cation, this photosensitized electron transfer was applied to the potentially more interesting azoalkanes **1–4**. The photochemical electron-transfer results are summarized in Table I, together with those of the direct and triplet-sensitized (acetone) photolysis. Before discussing these observations, it should be mentioned that, except for 2,3-diazabicyclo[2.2.1]heptene (**1**), the thianthrene radical cation tetrachloroaluminate in CH_2Cl_2[6] was not sufficiently strong as a chemical oxidant to afford the radical cations of the azoalkanes **2–4**, as evidenced by the lack of nitrogen loss of these substrates. Furthermore, attempts to trap the intermediary radical cations by carrying out the TPT$^+$-sensitized photolyses of the azoalkanes **1–4** in acetonitrile or methanol failed. The lifetimes of the hydrocarbon radical cations, which result on elimination of nitrogen from these azoalkane radical cations, are apparently too short. Finally, control experiments showed that the hydrocarbon products **1a,b–4a,b** were stable in the time lapse of the TPT$^+$-sensitized photolysis of the corresponding azoalkanes, indicating that the rearrangement products **1b–4b** were not derived from secondary photolyses of the cyclization products **1a–4a**.

From comparison of the three sets of data in Table I, it is evident that the results of the TPT$^+$ photosensitized electron transfer clearly stand out. While the direct photolysis, except for azoalkane **4**, and the triplet-sensitized photolysis (even more so) lead to very little rearranged hydrocarbon products **1b–3b**, such Wagner–Meerwein products are formed predominantly if not exclusively for the azoalkanes **2** and **4** or at least to an appreciable extent for the azoalkanes **1** and **3**.

These results are rationalized in the mechanistic scheme of eq 1, taking the azoalkane **2** as prototype. Electron transfer from the azoalkane **2** to the excited TPT$^+$ oxidant affords the azoalkane radical cation and the TPT radical. Loss of molecular nitrogen, either concertedly or stepwise, generates the radical cation formally derived from tricyclo[2.2.1.0^{2,7}]heptane (**2a**). A small fraction of the latter engages in electron back-transfer with the TPT$^\bullet$ radical to lead to the bicyclo[2.2.1]heptane-2,7-diyl, which collapses to the normal tricyclic hydrocarbon **2a**.[7] Most of the radical cation suffers Wagner–Meerwein rearrangement, yielding the norbornene radical cation, which on subsequent electron back-transfer produces norbornene (**2b**) as rearranged hydrocarbon. While Wagner–Meerwein rearrangements of norbornyl cations are well established,[8] only recently[4] have such processes been documented for strained radical cations. In this context it is most gratifying that the radical cation of bicyclo[2.1.0]pentane gives indeed the cyclopentene radical cation,[4a] although the mechanistic details of this type of rearrangement are yet unclear.

Analogous schemes (eq 1) apply to the other azoalkane substrates studied here. At the present time it is difficult to understand the relative proportions of cyclization vs. rearrangement products in terms of structural variations of the azoalkanes **1–4** (Table I), since little is known as yet on the chemical details of the azoalkane as well as hydrocarbon radical cations proposed as reactive intermediates in eq 1. It should, therefore, be productive to apply the present methodology of TPT$^+$-sensitized photolysis of tailor-made azoalkanes to gain mechanistic insight into the elusive radical cations and explore their chemical fate.

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Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for generous financial support of this work. M. Dörr is grateful to the Fonds der Chemischen Industrie for a doctoral fellowship (1984–1986). Appreciation for spectral services is expressed to Dr. G. Lange (MS) and Dr. D. Scheutzow (NMR).

Total Synthesis of Zincophorin

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Received October 3, 1986

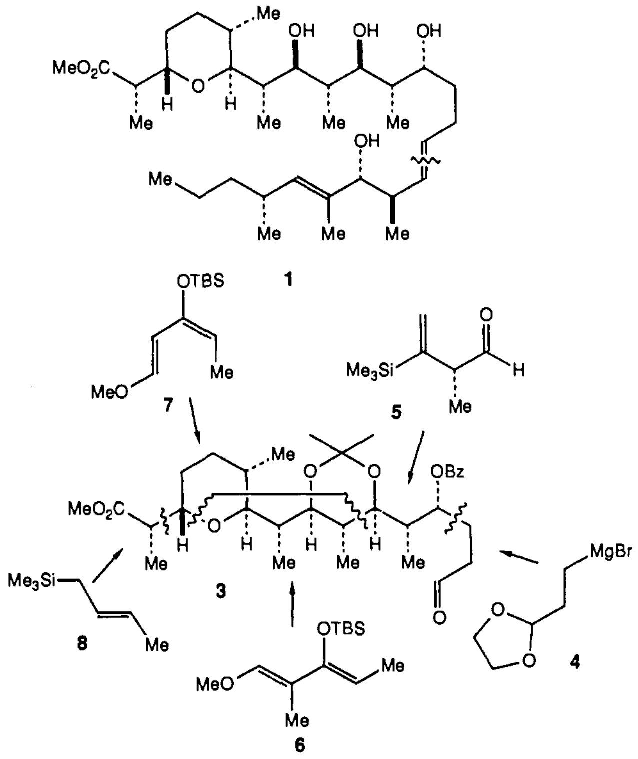
During a search for new ruminant growth-promoting factors, the ionophore zincophorin (**1**) was isolated from a strain of *Streptomyces griseus*.[1] As its name implies, zincophorin has a very high affinity for zinc(II) cations. The affinity also extends to magnesium (II) and in fact a combined zinc–magnesium salt complex has been obtained. The gross structure and stereochemistry of zincophorin are known from crystallographic measurements. Several novel structural features of zincophorin, as well as its strong antibacterial properties, render this ionophore a worthy target for synthetic exploration. Our plan called for the coupling of two enantiomerically homogeneous subunits, sulfone **2** and the aldehyde **3** (see disconnection line in structure **1**).

Elsewhere[2] we have described a degradation which starts with zincophorin and leads to differentially protected aldehyde enantiomer **3** and to sulfone enantiomer **2**. A stereoselective synthesis of enantiomerically pure **2** was also achieved. In this paper we describe the synthesis of aldehyde **3** and its coupling with sulfone **2**. The *first total synthesis of zincophorin has thus been achieved.* In so doing we were obliged to deal with several stereochemical patterns which had not previously been addressed in our program. The solutions are described in Scheme I.

Grignard reagent **4**[3a] reacts with the known *S* aldehyde **5**[3b] (THF, −78 °C) in a diastereofacially specific reaction to afford (90%) carbinol **9**.[4] Treatment with sodium hydride–HMPA occasions C → O silicon migration. Aqueous workup provides alcohol **10**. Protection of the hydroxyl group of **10** was accomplished (91%) with benzyloxymethyl chloride and Hunig's base. Compound **11**, upon ozonolysis, gave rise (80%) to aldehyde **12**, which was to serve as the heterodienophile in a cycloaddition with the known diene **6**.[5]

The reaction, mediated by anhydrous magnesium bromide (CH_2Cl_2, −50 °C), occurs with exo topography under apparent chelation control.[5] Compound **13a** was obtained in 80% yield.[6] Clean reduction ($NaBH_4$–$CeCl_3$)[7a] to **13b** set the stage for a Ferrier displacement[7b] using 3,4-dimethoxybenzyl alcohol as the nucleophile (*p*-TsOH, benzene). Compound **14**, thus available from **13a** in 78% yield, was subjected to hydroboration (BH_3–THF)–oxidation (H_2O_2–NaOH), thereby producing alcohol **15** in 68% yield. Swern oxidation followed by reduction (L-Selectride), and deprotection with DDQ,[8] led successively to compounds **16**, **17**, and hemiacetal **18** (55% overall yield) (Scheme II).

Scheme I



The scheme now called for disconnection of the properly configured pyran ring followed by elaboration of a new aldehyde from the anomeric carbon. Compound **19**, obtained via the reduction ($LiBH_4$) of **18**, was protected at its primary alcohol as a mono-*tert*-butyldiphenylsilyl ether.[9] The two secondary alcohols were engaged as a cyclic acetonide (dimethoxypropane, PPTS). After deprotection (*n*-Bu_4NF) followed by Swern oxidation, aldehyde **20** was in hand (70% from **19**), setting the stage for the all crucial second cyclocondensation reaction.

To reach the required **21**, a trans topography and a Cram–Felkin diastereofacial sense has to be attained.[5] It will be recalled[10] that the 4*Z* version of diene **7**, upon cyclocondensation (mediated by $BF_3 \cdot Et_2O$) with simple aldehydes, leads to cis pyrones. *However, reaction of the 4E diene 7 with aldehyde 20 leads selectively to the required trans pyrone 21.*[11] After reduction of the ketone, and acetylation, the acetate **22** was in hand. Upon treatment with (*E*)-crotylsilane **8**, in an extension of our recently developed carbon Ferrier displacement methodology,[12] compound **22** gave **23** as the major product.[12b]

The side chain was adjusted (i, OsO_4–$NaIO_4$; ii, Jones oxidation; iii, CH_2N_2) to produce **24** (45% overall). Finally, a three-step sequence (i, H_2-Pd/C; ii, BzCl, Py; iii, *p*-TsOH, acetone) led to the isolation (43%) of fully synthetic **3**. The infrared and NMR spectra of the material thus obtained, as well as its chromatographic mobility and optical rotation,[13] were identical with those

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(11) (a) The initial products of the reaction were identified as threo and erythro aldol products (cf. ref 10), as well as the *trans*-pyrone **21** in a ratio of 4:1:0.5 after chromatographic separation (68% combined yield). The threo isomer was then cyclized (PPTS, benzene) to the *trans*-pyrone **21** in 75% yield. The total combined yield of **21** was 46% overall from **20**. (b) See ref 10 for a discusion of the reactivity differences between (4*E*)-**7** and (4*Z*)-**7**.

(12) (a) Danishefsky, S. J.; Lartey, P.; DeNinno, S. *J. Am. Chem. Soc.*, in press. (b) With $BF_3 \cdot Et_2O$ as the catalyst (propionitrile, −78 °C), compound **23** is obtained as the major product (3.5:1) relative to its C-2 (zincophorin numbering) epimer in 60%. With $ZnBr_2$ in nitromethane, yields up to 77% have been realized, but the epimer ratio is less favorable (2.8:1).

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