

of the T_{-1} and S spin states. The T_{-1} -S degeneracy produces a local maximum in the CIDNP intensity and also in the total intersystem crossing rate, to which α is sensitive. Thus the biradical character (nonzero E_{ST}) imposed on a radical pair by a micellar environment has practical applications in the area of ^{13}C enrichment. The magnetic field dependence of CIDNP then becomes a useful predictive tool for this purpose.

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Registry No. **1a**, 102-04-5; **1b**, 6304-68-3; SOS, 142-31-4; SDeS, 142-87-0; SDS, 151-21-3.

"Spin-Charge Exchange" in a Stable Radical-Carbenium Ion

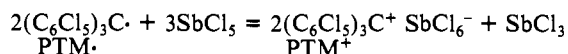
M. Ballester,* J. Castañer, J. Riera, and I. Pascual

*Instituto de Química Orgánica Aplicada (C.S.I.C.)
C. Jorge Girona Salgado, Barcelona 34, Spain*

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The *inert free radicals* are trivalent carbon species which not only do not dimerize and do not react with oxygen but are inert even toward aggressive chemicals, such as concentrated sulfuric acid, concentrated nitric acid, chlorine, bromine, etc.¹ Their half-life times in solution, in air, are of the order of 100 years. They also withstand temperatures up to 300 °C in air without significant decomposition. They possess therefore a general stability higher than that of an overwhelming majority of "normal", tetravalent carbon compounds and materials. In contrast, they are active in certain one-electron-transfer processes giving stable, isolable carbanion^{1a,2} and carbenium ion^{1c,3} salts.

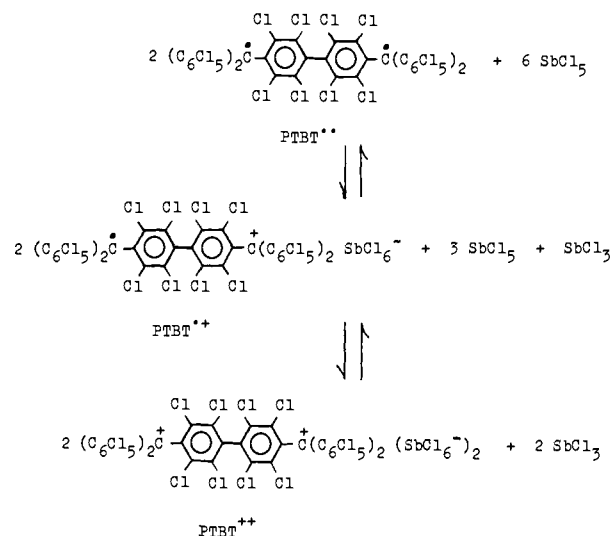
The oxidation of inert radical perchlorotriphenylmethyl (PTM•) with SbCl_5 ^{1c,3} takes place according to the equilibrium



The preparation of pure perchlorotriphenylcarbenium (PTM⁺) hexachloroantimonate can easily be performed by using a great excess of SbCl_5 in CH_2Cl_2 , with or without added chlorine, or in sulfuric chloride. Conversely, this salt reverts to PTM• with SbCl_3 . When the stoichiometric amount of SbCl_5 is employed a mixture of PTM• and PTM⁺ is obtained.

A remarkable inert carbon diradical is perchloro- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenylbi-*p*-tolyl- α,α' -diyl (PTBT:) ^{1a} and analogously it reacts with a stoichiometric proportion of SbCl_5 (in CH_2Cl_2 , at room temperature) affording two coupled, balanced equilibria, the components being PTBT:, perchloro- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenylbi-*p*-tolyl- α,α' -diylum (PTBT²⁺) ion, and perchloro- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenylbi-*p*-tolyl- α,α' -yl- α' -ylium (PTBT⁺) ion.

With use of a great excess of SbCl_5 , an excellent yield of salt PTBT²⁺ 2SbCl_6^- is obtained in form of green-blue crystals. This oxidation is followed by the ESR technique, and when the diradical PTBT: has disappeared, the spectrum of *pure* radical-cation

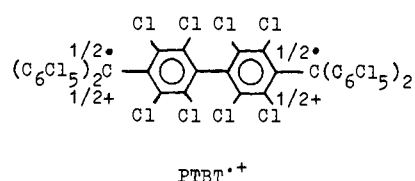


PTBT⁺ can be observed, although it decays because of conversion to PTBT²⁺.

Under similar conditions, the same equilibrium mixture is obtained by an *one-electron-transfer process* between PTBT: and PTBT²⁺.

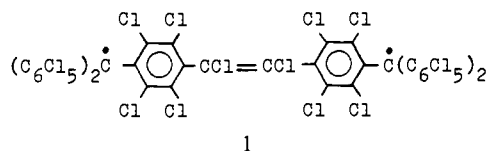


The ESR spectrum of radical-cation PTBT⁺ (Figure 1, curve a) indicates a fast "spin-charge exchange". Its existence, as inferred from the ^{13}C couplings, is straightforward and unequivocal on account of the absence of interfering nuclei and the simplicity of its hyperfine structure—as it occurs in other perchloro free radicals.¹ Table I reports the coupling constants with the α , bridgehead, and ortho ^{13}C s for both the radical-cation PTBT⁺ and monoradical PTM•. The data indicate that the *spin* densities at the nuclei in PTBT⁺ are half as high as in PTM• (Figure 1, curve b).



It is noteworthy that such an exchange takes place in spite of the severe steric inhibition of resonance due to the *quasi*-perpendicularity of two benzene rings in the biphenyl system as it occurs in PTBT:^{1a} and perchlorobiphenyl ($\sim 87^\circ$).⁴

It is pointed out that diradical PTBT: *does not* show a *spin-spin* exchange,^{1a} while vinylene diradical **1**, because of lower steric



inhibition,^{1c} does (half-normal ^{13}C couplings). The ultraviolet-visible spectrum of PTBT: is practically coincident with that of radical PTM• indicating that, within the relevant time scale, the former behaves also as two electronically independent moieties.^{1a}

The characterization, the yields, and the structural assignment of the salts here reported have been performed by hydrolytic conversion^{1c} into their fuchsonoid derivatives (perchloro- α' -(4-oxocyclohexadienylidene)- α,α' -triphenyl-bi-*p*-tolyl- α' -yl radical and perchloro- α,α' -bis(4-oxocyclohexadienylidene)- α,α' -di-

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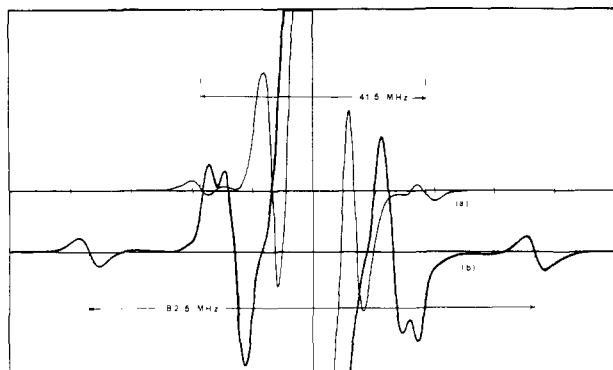


Figure 1. ESR hyperfine spectra of PTBT⁺• (a) and PTM• (b).

Table I. ESR Parameters

radical	¹³ C coupling constants, MHz			g value
	α	bridgehead	ortho	
PTBT ⁺ •	41.5	17.9	14.8	2.0026
PTM ⁺ • ^{1a,5}	82.5	35.5	30.0	2.0026

phenylbi-*p*-tolyl), elemental analyses, and IR and UV-vis spectra.

Registry No. PTBT⁺: 33135-34-1; PTBT²⁺, 89959-10-4; PTBT⁺•, 89959-12-6; PTBT²⁺•2SbCl₆⁻, 89959-11-5; PTBT⁺••SbCl₆⁻, 89959-13-7; perchloro-α'-(4-oxocyclohexadienylidene)-α,α,α'-triphenylbi-*p*-tolyl, 89959-14-8; perchloro-α,α'-bis(4-oxocyclohexadienylidene)-α,α'-di-phenylbi-*p*-tolyl, 89959-15-5.

Diels-Alder Reaction of Protonated Azo Compounds. Isolation of a Tetraalkyldiazonium Dication

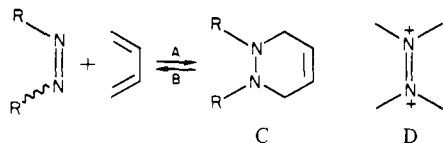
Stephen F. Nelsen,* Silas C. Blackstock, and Timothy B. Frigo

Department of Chemistry
S. M. McElvain Laboratories of Organic Chemistry
University of Wisconsin—Madison
Madison, Wisconsin 53706

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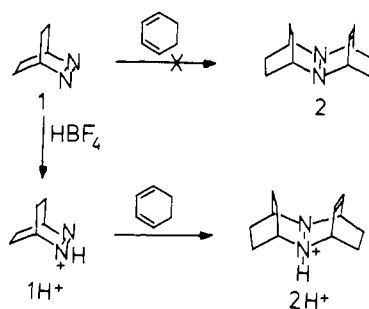
Although 1,2-diacylidimides such as triazolinedione derivatives are among the most potent of isolable dienophiles, the Diels-Alder addition of dialkyldiimides to dienes (reaction A) has not been



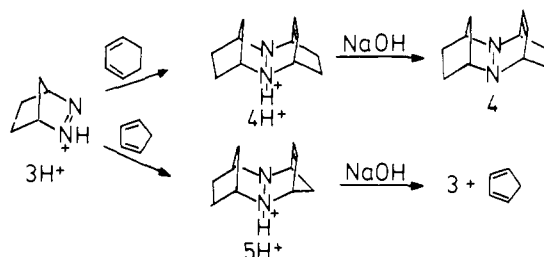
reported. The reverse reaction, retro Diels-Alder cleavage of 1,2,3,6-tetrahydropyridazines (C) is known to be an easy reaction.¹ We report here that protonation of bicyclic azo compounds makes equation A a high-yield reaction and use it to prepare the first example of an isolably stable tetraalkyldiazonium dication (D).

It was easily predictable that protonation at nitrogen would greatly increase the dienophilicity of the azo linkage. Protonated 1,1-dimethyldiazene was shown to be a dienophile by Urry and co-workers over 25 years ago.² Acids rapidly rearrange azo compounds with removable α-hydrogens to hydrazones, but bicyclic azo compounds such as **1** are protected against this rear-

Scheme I



Scheme II



angement (the hydrazone would have its C=N bond too twisted for appreciable double-bond character), and Heyman and Snyder³ showed that **1H**⁺ClO₄⁻ is isolable. Protonated **1** adds 1,3-cyclohexadiene in Diels-Alder fashion (Scheme I). The reaction proceeds slowly at room temperature, but we obtained a better conversion at 45 °C (97% **2H**⁺BF₄⁻ isolated by crystallization). A slight excess of diene is required for complete **1H**⁺ consumption because of polymerization, and it is necessary to avoid excess HBF₄, which polymerizes cyclohexadiene rapidly. Deprotonation of **2H**⁺ gives **2**, which undergoes retro Diels-Alder cleavage slowly at room temperature (half-life of about 7 h). Similarly, protonated 2,3-diazabicyclo[2.2.1]hept-2-ene **3H**⁺ adds to both cyclohexadiene and cyclopentadiene to give **4H**⁺ and **5H**⁺ (Scheme II). The major products have the stereochemistry shown, because there is a strong upfield shift of one of the protons on the CH₂ bridge (**4H**⁺, δ 1.38; **4**, δ 0.64; **5H**⁺, δ 1.26) as expected for the proton held in the shielding cone of the double bond. Although this is the geometry for endo addition of the dienophile, Allinger MM2 calculations⁴ on the related hydrocarbons (both N atoms replaced by CH) show that it is also the thermodynamic product. Deprotonation of **4H**⁺ gives **4**, which undergoes retro Diels-Alder cleavage more slowly than **2**, but deprotonation of **5H**⁺ at room temperature gives the cleaved products, cyclopentadiene and **3**, so the retro Diels-Alder cleavage clearly increases in rate in the order **4** < **2** < **5**.

The facile cleavage of Diels-Alder adducts **2**, **4**, and **5** demonstrates that the problem with Diels-Alder addition of cyclic dienes to **1** and **3** is not kinetic, but thermodynamic. Diels-Alder addition causes overall conversion of π(C=C) and π(N=N) bonds to two σ(C-N) bonds, which is certainly exothermic. Steric strain is obviously increased in the products compared to the starting materials, and the σ(NN) bond formed is certainly unusually weak because of large lone pair, lone pair interactions in the adducts, which have the lone pairs held at a nearly 0° dihedral angle. We have been unable to detect any **2** or **4** by NMR upon mixing neat cyclohexadiene with **1** or **3**, either at room temperature or upon mild heating. All three Diels-Alder reactions appear to be endothermic. The reason protonation makes the reaction proceed, then, is not kinetic, but thermodynamic. Azo compounds are exceedingly weak bases,⁵ but hydrazines are strongly basic, so the product is more stabilized by protonation than is the starting

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