

pentane produces a purple-red solution that shows an IR band at 2008 cm⁻¹. Removing the pentane in vacuo yields a brown powder whose ¹H NMR spectrum shows it to be pure Mo(TIPT)₄ in quantitative yield (vs. an internal standard). Unfortunately, we have not yet been able to isolate what we believe to be Mo-(TIPT)₄(CO) due to its extreme solubility and sensitivity to moisture and air.

The addition of diphenyldiazomethane to Mo(TIPT)₄ yields a diamagnetic complex with the formula Mo(TIPT)₄(Ph₂CN₂).¹⁹ Its ¹³C NMR spectrum (C₆D₆) shows a resonance at 170.4 ppm. We suggest that the diazoalkane has added end-on to the metal to give what could be described as (TIPT)₄Mo=N=N=CPh₂. Related complexes have been prepared recently by similar methods.²⁰

The behavior of Mo(TIPT)₄ reported here contrasts strongly with that of Mo(SCMe)₃. We do not yet know if Mo(TIPT)₄ is reduced slowly in the presence of a large excess of a ligand such as CO. Also note that we have no evidence for or against formation of Mo(TIPT)₄(N₂) in solution, but since formation of Mo(TIPT)₄(CO) is reversible we would not expect a significant amount of Mo(TIPT)₄(N₂) to be present at ambient pressure.

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Registry No. 1, 97731-89-0; 2, 97731-90-3; Mo(TIPT)₄(EtC≡CEt), 97731-91-4; Mo(TIPT)₄(MeC≡CMe), 97731-92-5; Mo(EtC≡CEt)-Cl₄(thf), 97731-93-6; Mo(TIPT)₄(CH₃CN), 97731-94-7; Mo(TIPT)₄-(*t*-BuCN), 97731-95-8; Mo(TIPT)₄CO, 97731-96-9.

(18) Calcd for MoC₆₂H₉₅NS₄[Mo(TIPT)₄(CH₃CN)]: C, 69.02; H, 8.89; N, 1.30. Found: C, 68.56; H, 9.11; N, 1.07. Calcd for Mo(TIPT)₄(*tert*-BuCN): C, 69.65; H, 9.10; N, 1.25; Mo, 8.56; S, 11.44. Found: C, 69.58; H, 9.05; N, 1.39; Mo, 8.42; S, 11.56 (by difference).

(19) Calcd for MoC₇₃H₁₀₂N₂S₄: C, 71.17; H, 8.36; N, 2.27. Found: C, 71.15; H, 8.84; N, 2.14.

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Direct Observation of a 1,3-Biradical

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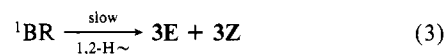
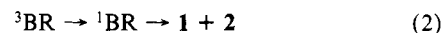
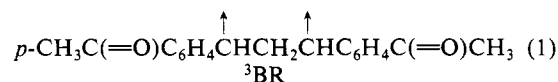
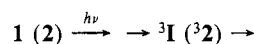
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Because of the predictions of Salem and Rowland¹ that the quantum-mechanical properties affecting intersystem crossing in 1,*n*-biradicals depend on the distance between the biradical termini and thus on *n*, there has been recent interest in experimental determination of the lifetimes of triplet biradicals as a function of *n*^{2,3} among other measures of distance.^{4,5} Although 1,4-bi-

radicals, particularly of the Norrish II type, are well studied,⁴⁻⁸ only a few direct observations of biradicals with *n* ≠ 4 have been reported. The acyl-alkyl series from Norrish I photolyses has so far yielded 1,5,⁹ 1,6,² and 1,8¹⁰ examples. Wagner and Scaiano have detected certain 1,5-biradicals generated by hydrogen abstraction.^{11,12} An elegant generation of a 1,5-biradical from Norrish I photocleavage of 2,2,6,6-tetraphenylcyclohexanone and subsequent decarbonylation has been described.³ While physical characterization is available for certain special cases,¹³ and trapping of others by dioxygen has given important experimental information about the effect of orbital orientation on lifetime,¹⁴ no direct information is available which allows comparison of 1,3-biradicals with the higher members of the series of unconstrained triplet 1,*n*-biradicals of general interest in room-temperature solution photochemistry.

We now report that photolysis of *trans*-1,2-bis(4-acetylphenyl)cyclopropane (**1**) allows the first direct observation of unconstrained 1,3-biradicals in fluid solution. Intermolecular sensitization of 1,2-diphenylcyclopropane geometric isomerization by aryl ketones is believed to proceed through an analogous intermediate.¹⁵ Intramolecular sensitization by the acetophenone chromophore avoids problems of intermolecular sensitization such as sensitizer absorption in the region of expected transient absorption and slow rates of excitation transfer.¹⁶

Irradiation of *trans*-1,2-bis(4-acetylphenyl)cyclopropane (**1**)¹⁷ rapidly ($\phi = 0.45 \pm 0.02$, benzene, 313 nm) affords the corresponding *cis* isomer **2** and slowly ($\phi \leq 0.005$) affords the *E/Z* isomers of 1,3-bis(4-acetylphenyl)propene (**3E/3Z**). The reaction was not affected by 0.5 M isoprene, 0.5 M ethyl vinyl ether, 0.5 M ethyl acrylate, or exposure to the atmosphere. The 1/2 photostationary ratio of 45/55 was stable under preparative conditions for up to 30–40 h, over which time period a 60–70% yield of **3E/3Z** built up. Excellent material balance was observed throughout, though small amounts of polymeric material were formed. The reaction sequence below is strongly indicated.



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Transient spectroscopy (mode-locked Nd-YAG laser, fourth harmonic, 266 nm, fwhm 1.75 ns including broadening by detection electronics, unfocused, ca. 20 mJ/pulse) afforded strong signals identical in lifetime, λ_{max} , and OD from either 1 or a 1-2 mixture containing >90% 2 in which 2 absorbs >92% of the 266-nm excitation. Were the signal only derived from 1, its intensity in the irradiation of the mixture would have been ca. tenfold less. With 1 M isoprene, the lifetime of the signal from 1 in heptane was unaffected; its OD was attenuated almost precisely by the amount expected based on the relative extinction coefficients of 1 and isoprene at 266 nm. Lifetimes from 1 (or the 1-2 mixture) were as follows: heptane, 14.7 ± 1 ns; methanol, 13.4 ± 1 ns (13.0 ± 1.5 ns). Absorption maxima were 320 nm in heptane and 327 nm in methanol (± 5 nm).

Similar results were obtained for *trans*-1-(4-acetylphenyl)-2-phenylcyclopropane (4),¹⁷ $\tau = 15.0 \pm 1$ ns in heptane (λ_{max} 311 nm), unaffected by isoprene except by competitive absorption of 266-nm excitation. However, *trans*-1,2-dianisylcyclopropane (5)¹⁷ afforded only a modest fluorescence and no observable absorption signal.

We assign triplet multiplicity to the absorbing transients in view of the very fast ISC expected for substituted acetophenones.¹⁸ The absence of isoprene quenching rules out the spectroscopic states ³1, ³2, or ³4. The identical nature of the transient from 1 and from the 1-2 mixture demonstrates that it is a stereorandomized species. The transient is not the diarylpropene triplet ³3, since irradiation of 3 in CH₃OH affords a transient, λ_{max} 310 nm, with a different lifetime, $\tau = 29 \pm 1$ ns. This value agrees well with previously reported lifetimes²⁰ for 1,3-diarylpropene triplets in methanol. The results are best consistent with assignment of the transient from 1 or 2 as ³BR, particularly since the absorbance maxima are in excellent accord with expectation for benzylic biradical termini.²¹

That isoprene fails to quench ³1, ³2, and ³4 is presumably due to their extremely short lifetimes. Allowing 10% error in OD measurement and assuming diffusion-controlled quenching suggests a maximum lifetime ≈ 20 ps for any quenchable precursor of the observed transients. The extreme reactivity of the spectroscopic triplets toward central C-C bond scission can be expected from the extreme exothermicity (ca. 40 kcal/mol²²) of the ³1 \rightarrow ³BR reaction.

That mono- and diacetyl 1,3-diphenylpropane-1,3-diyls have identical lifetimes is presaged by the lack of a polar substituent effect on olefin triplet lifetimes²³ and the small effect on Norrish II biradicals.⁷ An expectation based on the work of Salem and Rowland,¹ that polar contribution to the singlet biradical should increase the ISC rate, is not followed. It would predict that the asymmetric 4-derived biradical would have the shorter lifetime.

Lifetimes for 1,3-diarylpropane-1,3-diyls at ~ 15 ns are shorter than diarylalkene triplets at ca. 60 ns,²⁴ triplet 1,1,4,4-tetraphenyl-1,4-butanediyl (500 ± 100 ns),³ and triplet 1,1,5,5-tetraphenyl-1,5-pentanediiyl (900 ± 200 ns).³ We believe this is a useful series for examination since the number of aryl groups at biradical termini has only a small effect on the lifetime.^{2,8} The effect of interterminal distance on ISC rate (i.e., triplet biradical lifetime) is a blend of two factors. As the chain length between the termini increases, the lifetime will be shortened by a decreasing ΔE_{ST}

resulting from a diminishing exchange integral but lengthened by diminishing spin-orbit coupling.¹ Perhaps not surprisingly, the results show that 1,3 and the longer biradicals follow expectation based on diminution of spin-orbit coupling with distance.

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Cyclization Dynamics of Polymers. 18. Capture Radius Effects in the End-to-End Cyclization Rate of Polymers, Excimers vs. Exciplexes

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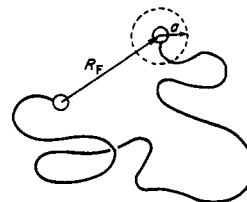
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The theory of diffusion-controlled cyclization of polymers makes an unusual prediction.¹⁻³ It suggests that the size of the capture radius a affects the cyclization rate constant, k_{cy} , when polymers chains are short but that this dependence disappears for longer chains. The important parameter is the ratio a/R_F , where R_F is the root-mean-squared end-to-end distance of the chain. R_F increases, of course, as the chain gets longer.



These predictions are based upon the Rouse-Zimm (bead and spring) model for polymers.⁴ Here the polymer is envisioned as a series of beads connected by harmonic springs. The beads contain the mass of the polymer and serve as friction centers for interaction with solvent. This model, in spite of its simplicity, is remarkably successful in describing such properties of polymers as translational and rotational diffusion and intrinsic viscosity.⁴

This peculiar sensitivity of k_{cy} to the distance between the end groups at which cyclization is detected has attracted considerable attention among various theoretical research groups.^{2,5} An excellent review has appeared.^{3b} Nonetheless one knows that the concept of a capture radius is an artifice of convenience: real chemical reactions have distance-dependent rate constants. The distance dependence of chemical reaction rates can vary signif-

(18) A referee has suggested that more physical evidence regarding the multiplicity of the biradical is necessary to turn a "good argument" into proof. We cannot disagree with the general desirability of having as much data as possible in support of transient assignments, and do plan further physical characterization, but we find the present data convincing. To our knowledge there are no known singlet photoreactions of *p*-alkylacetophenones nor is there any cogent evidence given recent thermochemical work¹⁹ that simple singlet 1,3-biradicals are barrier protected, as would be necessary if the 15-ns lifetime does not reflect spin protection.

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