(16) D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, 940 (1975); P. J. Thomas and C. J. M. Stirling, *ibid.*, 829 (1976).
(17) C. A. Grob, private communication.
(18) For a review of one aspect of this important subject, see J. A. Marshall, *Synthesis*, 229 (1971).

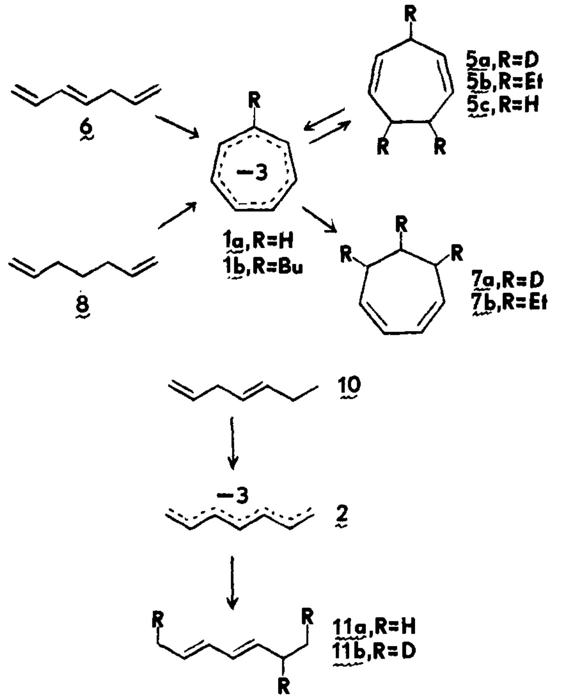
Barry M. Trost,* William J. Frazee
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 6, 1977

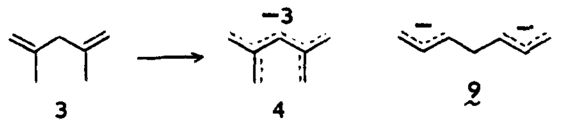
Cycloheptatrienyl and Heptatrienyl Trianions

Sir:

The third member in the series of 10π aromatic anions that begins with cyclononatetraenyl anion[1] and cyclooctatetraene dianion[2] is cycloheptatrienyl trianion (**1a**). Its heptaphenyl derivative was a possible reaction intermediate;[3] reduction of cycloheptatrienyl dianion radical with potassium and sodium gave "no unambiguous evidence" for trianion **1a** itself.[4] We wish to report metalation routes to the trilithium salts of **1a**, its *n*-butyl derivative **1b**, and its linearly conjugated analogue, i.e., heptatrienyl trianion (**2**).



As reported earlier,[5] allylic metalation of diene **3** gave, along with larger amounts of dianion, up to 18% yield of cross-conjugated trianion **4** (simple Hückel MO total π energy, $E_\pi = 10\alpha + 6.8\beta$), and this led us to try to similarly prepare cyclic trianion **1a** ($E_\pi = 10\alpha + 7.2\beta$). Either 1,4-cycloheptadiene



(**5c**) or 1,3,6-heptatriene (**6**)[6] on standing with 3 mol of *n*-BuLi (1.8 M in hexane) and 3 mol of tetramethylethylenediamine (TMEDA) at room temperature for 3–10 days gave a black precipitate which apparently contained the trilithium salt of **1a** solvated by TMEDA, in ~70% yield as indicated by the following evidence: (a) quenching with D_2O gave a 70% yield of a mixture of **5a** and **7a** with the latter predominating, the degree of deuterium incorporation being indicated by mass spectrometry and the location of the deuteriums by ^{1}H NMR; (b) quenching with diethyl sulfate[7] gave a 70% yield of triethylcycloheptadienes **5b** and **7b** (not separated, but mass spectrum and ^{1}H NMR consistent with these structures); (c) between 2 and 12 h after mixing the reactants, a singlet at δ 4.55 ± 0.15 is observed in the ^{1}H NMR (Figure 1) and a singlet at δ 66.0 in the ^{13}C NMR, after which time the tube was clogged with black precipitate (these values are close to those predicted for **1a** by extrapolation from the cyclononatetraenyl anion[1] and cyclooctatetraene dianion[2] values); (d) the appearance of the ESR signal expected for cycloheptatrienyl dianion radical dilithium ($a_H = 3.52$ and $a_{Li} = 0.83$ G[8]), highest concentration estimated at 10^{-5} M, accompanies the development of the black color (this species is most likely formed in this system by loss of an electron from trianion **1a**).[9]

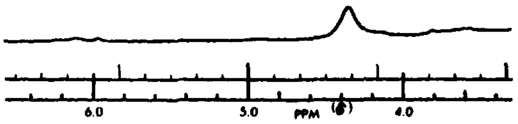


Figure 1. 60-MHz ^{1}H NMR spectrum of cycloheptatrienyl trianion (**1a**, peak at δ 4.4) in hexane–TMEDA; other peaks visible are due to cycloheptadienyl monoanion.

Surprisingly, attempts to prepare acyclic trianion **2** ($E_\pi = 10\alpha + 6.5\beta$) by metalating 1,6-heptadiene (**8**) gave instead cyclic trianion **1a**, as indicated by its D_2O quench products **5a** and **7a**. This requires an oxidation, which apparently occurs by the expulsion of lithium hydride[10] by an anionic intermediate which is most likely dianion **9**; the resulting heptatrienyl anion then proceeds to **1a** as above.[11] On the other hand, metalation of 1,4-heptadiene (**10**) with a large excess of *n*-BuLi-TMEDA followed by quenching with water gave an essentially quantitative yield of a heptadiene mixture consisting (GC and ^{1}H NMR comparison with an authentic sample) almost entirely of 2,4-heptadienes (**11a**); when the quench was with D_2O, this product was 35% monodeuterated, 45% dideuterated, and 20% trideuterated, indicating the formation of some of the trilithium salt of linearly conjugated trianion **2**.[12]

Monoalkyl derivatives of **1a**, e.g., **1b**, can be prepared in one step by mixing cycloheptatriene with 3 mol of the appropriate alkyllithium and 3 mol of TMEDA; the initial addition[6] is followed by two metalations.

Thus, of the three trianions **1a**, **2**, and **4**, the former, cyclic and aromatic, is as expected the most easily prepared. Like other aromatic anions, it may prove to be an interesting ligand.

Acknowledgment. Financial support from the National Science Foundation (GP-38070X) is gratefully acknowledged.

References and Notes

(1) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964).
(2) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).
(3) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **87**, 2200 (1965).
(4) N. L. Bauld and M. S. Brown, *J. Am. Chem. Soc.*, **89**, 5417 (1967).
(5) R. B. Bates, W. A. Beavers, M. G. Greene, and J. H. Klein, *J. Am. Chem. Soc.*, **96**, 5640 (1974).
(6) This triene is known to metalate readily to heptatrienyl anion, which cyclizes above −30 °C to cycloheptatrienyl anion (R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Am. Chem. Soc.*, **91**, 4608 (1969)).
(7) When methyl and ethyl bromides and iodides were used, up to 25% yield of 7-methyl- or 7-ethylcycloheptatrienes were formed along with trialkylcycloheptadienes 5 and 7. These products probably result from a sequence which starts with attack of the trianion 1a on the halogen of the alkyl halide, and is almost completely avoided with diethyl sulfate (W. Priester, R. West, and T. L. Chwang, *J. Am. Chem. Soc.*, **98**, 8413 (1976)).
(8) This dilithium salt has not been described before, but the disodium salt was found to have $a_H = 3.52$ and $a_{Na} = 1.76$ G.[4]
(9) ESR signals were not found during the preparations of acyclic trianions 2 and 4.
(10) Evidence for the formation of lithium hydride was vigorous reaction with

D_2O to give HD (mass spectrum).

(11) 1-Methyl-3-butylcyclohexane (12%) was also formed in this reaction, no doubt analogously to the 1-methyl-3-butylcyclopentane formed from 1,5-hexadiene (J. J. Bahl, R. B. Bates, W. A. Beavers, and N. S. Mills, *J. Org. Chem.*, **41**, 1620 (1976)).

(12) ^1H NMR showed the deuteriums to be in the methylene and methyl groups as expected for **11b**.

Joseph J. Bahl, Robert B. Bates*
William A. Beavers, Curtis R. Launer
Department of Chemistry, University of Arizona
Tucson, Arizona, 85721

Received March 31, 1977

Amendment of the CIDNP Phase Rules. Radical Pairs Leading to Triplet States[1]

Sir:

One of the assumptions in the radical-pair theory of chemically induced dynamic nuclear polarization (CIDNP)[2,3] is that the probability of annihilation of the radical pair is proportional to the singlet character of the pair. This assumption is certainly valid when the radical pair is destroyed by a pair combination or disproportionation reaction. In these cases the triplet state of the product is generally antibonding or at least energetically inaccessible. In this communication we want to discuss and demonstrate an important ambiguity in the interpretation of CIDNP spectra which may arise in cases where the radical pair is of higher energy than the triplet state of the reaction product.

Inclusion of this possibility leads to four reaction sequences

$$S_r \rightarrow RP \rightarrow S_{pr} \quad (1)$$

$$T_r \rightarrow RP \rightarrow S_{pr} \quad (2)$$

$$S_r \rightarrow RP \rightarrow T_{pr} \rightarrow S_{pr} \quad (3)$$

$$T_r \rightarrow RP \rightarrow T_{pr} \rightarrow S_{pr} \quad (4)$$

Sequences 1 and 2 describe the conventional CIDNP experiments where S_r and S_{pr} are the singlet states of reactant and product, respectively, and T_r is the triplet reactant and RP is the radical pair. If the radical-pair state lies above the triplet state of the product, two other pathways (3 and 4) become available where T_{pr} is the triplet state of the product. Since sequences 1 and 4 involve no intersystem crossing in the radical pair, they give the same CIDNP spectra. Similarly, sequences 2 and 3 give indistinguishable spectra because each involves intersystem crossing in the pair state. For a given experimental spectrum the precursor multiplicity cannot be assigned unless the multiplicity of the exit channel is also defined. It is therefore necessary to amend the qualitative polarization phase rules formulated by Kaptein[4] by an "exit channel" factor, γ, which is positive for the singlet exit channel and negative for triplet. All other parameters remain the same.

It has been recognized for some time[5] that the fluorescence quenching of photoexcited aromatic hydrocarbons by electron donors proceeds by charge transfer and may lead to the triplet hydrocarbon faster than can be rationalized by either intersystem crossing in unquenched singlet hydrocarbon or diffusional recombination of hydrocarbon radical anions with donor radical cations in the bulk solution. A well-studied system exhibiting this behavior is pyrene as acceptor with aniline derivatives as donors.[5-7] We have chosen this system to investigate the CIDNP effect as a case where the predominant exit channel of the radical pair has been clearly established to be the triplet state of pyrene.

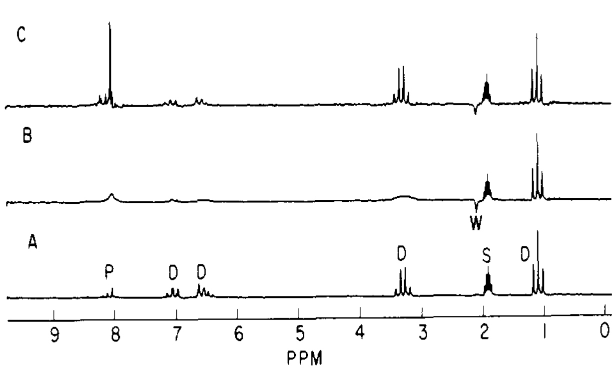


Figure 1. 90-MHz ^1H FT NMR spectra of 10^{-2} M pyrene and 10^{-1} M *N,N*-diethylaniline in CD_3CN (P = pyrene, D = diethylaniline, W = water[9] and S = solvent): (A) initial dark; (B) during irradiation; and (C) 0.5 s after termination of irradiation as explained in text.

When a 10^{-2} M solution of pyrene containing 10^{-1} M *N,N*-diethylaniline in acetonitrile-d_3 is irradiated in the probe of an FT NMR spectrometer, the pyrene transitions broaden[8] and appear in enhanced absorption (Figure 1). The aromatic and methylene protons of diethylaniline are also broadened while the methyl protons remain sharp. The broadening of the pyrene signals is caused by electron exchange between pyrene radical anion and ground-state pyrene[10] resulting in a reduction of the T_2 of the pyrene protons. Similarly, exchange between the diethylanilinium radical ion and diethylaniline causes broadening of the diethylaniline signals. Because CIDNP is related to T_1 it is possible[11] to eliminate the broadening but retain the polarization by sampling the magnetization after the light has been shut off. Thereby, the radicals decay within milliseconds while the CIDNP effect remains observable for seconds (T_1). The result is shown in Figure 1. Besides the strong enhanced absorption of the pyrene signals, a weak enhanced absorption of the diethylaniline methylene protons (~30%) is noticeable as well as a reduction in the aromatic proton intensities.[12]

If one were to interpret the results using the conventional rules,[4] one would deduce from the *g*-factor difference and signs of the hyperfine interaction[13] that triplet pyrene was undergoing charge-transfer quenching with diethylaniline via pathway 2. This is unacceptable for two reasons. First, electrochemical potentials for the reduction[14] of pyrene and oxidation[15] of diethylaniline put the radical-ion pair 0.7 V above triplet pyrene[16] making charge transfer to the triplet state several orders of magnitude slower than its decay rate. Second, fluorescence studies carried out in our laboratory and elsewhere[17] show that under the conditions of the NMR experiments >95% of the singlet pyrene is quenched. Consequently, in line with the conclusions of previous investigators,[5-7] the reaction sequence occurs via pathway 3, where the radical-ion pair is formed from the singlet state of pyrene and is predominantly annihilated via the triplet state. Interestingly, although the energetics allow the ion pair to exit to either the singlet or triplet state of the product, the latter is preferred.[18] Other donors such as 3,5-dimethoxy-*N,N*-dimethylaniline[7] behave the same way. We obtained similar results in the photochemical charge transfer between naphthalene and 1,4-diazabicyclo[2.2.2]octane (Dabco).

In conclusion, it appears necessary to supplement CIDNP results with information such as quenching kinetics, redox potentials, and excited-state energies before conclusions on the electronic multiplicity of the intercepted state in charge-transfer reactions can be reached.[19]

References and Notes

(1) Supported by the National Science Foundation Grant No. NSF CHE 76-01795.

(2) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Polarization," Wiley, New York, N.Y., 1973.

(3) G. L. Closs, *Adv. Magn. Reson.*, **7**, 157 (1974).