Table VI, are in reasonable agreement with those obtained from the esr widths, and thus appear to justify this potentially useful method.

We note that for the activation energies and preexponential factors (obtained from relative amplitudes) given Table VI, there is some solvent dependence noted for USQ. The preexponential factors of 1–2 $\times 10^{13}$ sec^{-1} for USQ lead to values of entropy of activation $\Delta S^{\ddagger} \sim 0$ at 25° (-0.6 and 0.9 cal deg^{-1} in ethanol and DME, respectively) as expected.

In vitamin K_1, although we cannot freeze out the internal rotation of the side chain, it is possible to obtain a value for the activation energy from the alternating line width effect. For the unbroadened line widths we made use of the lines shown with asterisks (lines with $M_{CH_3} = {}^3/_2$, $M_{CH_2} = +1$, $M_{H_{5-8}} = 0$ and $M_{CH_3} = {}^3/_2$, $M_{CH_2} = -1$, $M_{H_{5-8}} = 0$) in Figure 6, and for the broadened widths we used the lines indicated with the arrows ($M_{CH_3} = \pm {}^1/_2$, $M_{CH_2} = 0$, $M_{H_{5-8}} = 0$). Despite some problems of overlap, we do obtain a good straight-line fit for the data, and the activation energy is close to but somewhat smaller than that obtained for USQ in ethanol.

In comparing the above results with those on other methylene-containing systems such as vitamin E, we recall that (1) the asymmetry of the radical about the plane containing the methylene-carbon to ring-carbon bond and perpendicular to the benzene ring is the obvious reason for the static inequivalence of the two methylene protons, but (2) the *average* angle from this plane is 60°. Thus, in other cases, like vitamin E, where the asymmetry and average angle are similar, there most likely is a similar rapid dynamical averaging process.

Acknowledgment. The authors wish to thank Mr. S. B. Wagner for help in the computer simulation.

Chemistry of Radical Anions and Dianions of Diphenylacetylene

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Abstract: Diphenylacetylene (DPA) reacts instantly with sodium biphenylide ($\mathrm{B}\cdot^-,\mathrm{Na}^+$) in hexamethylphosphoramide (HMPA) and forms the radical ions $\mathrm{DPA}\cdot^-$. No further reduction takes place in HMPA even if $\mathrm{B}\cdot^-$ is in excess. The free $\mathrm{DPA}\cdot^-$ ions do not dimerize; their optical and esr spectra were recorded. Electron affinity of DPA was determined by two methods and found to be 0.27 V higher than that of biphenyl. At very low temperatures ($\leqslant -78°$) DPA in tetrahydrofuran (THF) reacts with metallic lithium giving first $\mathrm{DPA}\cdot^-,\mathrm{Li}^+$ and eventually insoluble $\mathrm{DPA}^{2-},2\mathrm{Li}^+$. Protonation of the latter at $-78°$ yields quantitatively *cis*-stilbene, indicating the *cis* structure of the dilithium salt. Above $-78°$ $\mathrm{DPA}^{2-},2\mathrm{Li}^+$ becomes protonated by THF giving $\mathrm{PhCH{:}CPh,Li}^+$ whose optical spectrum was recorded. Protonation of $\mathrm{PhCH{:}\bar{C}Ph,Li}^+$ with $\mathrm{CH_3OD}$ gives *trans*-PhCH:CDPh. Reduction of DPA in THF by metallic sodium at -78 or $-92°$ yields mixtures of $\mathrm{DPA}\cdot^-,\mathrm{Na}^+$ and the soluble $\mathrm{DPA}^{2-},2\mathrm{Na}^+$. The spectrum of the latter was determined. The disodium salt very slowly reacts with THF at $-60°$ and faster at higher temperatures giving again the salt of the $\mathrm{PhCH{:}\bar{C}Ph}$ carbanion. The protonation of $\mathrm{DPA}^{2-},2\mathrm{Na}^+$ or $\mathrm{DPA}\cdot^-,\mathrm{Na}^+$ by methanol at -78 or $-40°$ yields *trans*-stilbene, bibenzyl, and the parent hydrocarbon. It was shown that these results can be rationalized by assuming agglomeration of these salts and a rapid intra-aggregate electron transfer which competes with the protonation. At low temperatures $\mathrm{DPA}\cdot^-,\mathrm{Na}^+$ in THF reacts slowly with $\mathrm{B}\cdot^-,\mathrm{Na}^+$. It was proved that this process involves two steps: (I) rapid electron transfer yielding a minute equilibrium concentration of $\mathrm{DPA}^{2-},2\mathrm{Na}^+$ and (II) slow protonation of the latter by THF (k_p). The overall bimolecular rate constant is therefore $K_I k_p$ and not, as mistakenly concluded by Evans, a rate of a slow electron-transfer process.

Continuing our studies of the chemistry of radical ions and dianions, we have investigated now the electron-transfer processes involving diphenylacetylene, DPA. This hydrocarbon forms radical ions, $\mathrm{DPA}\cdot^-$, and dianions, DPA^{2-}. Their behavior is rather complex and influenced by the choice of cation and of solvent whose nature affects the state of aggregation of the reacting species. Not only free ions and ion pairs, but also some larger aggregates are present in the solutions of $\mathrm{DPA}\cdot^-$ and DPA^{2-} and such aggregates seem to be responsible for some peculiar reactions which have been observed in our studies.

Reactions in Hexamethylphosphoramide

HMPA is a powerful solvating agent of alkali ions and many alkali salts of carbanions and radical ions are fully dissociated in this medium.[1,2] Hence, the reactions observed in HMPA are of free ions and not ion pairs. The free radical anions, $\mathrm{DPA}\cdot^-$, may be formed in HMPA through electron transfer from

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(1) A. Cserhegyi, E. Franta, J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 7129 (1967).

(2) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969).

Table I. Esr Spectrum of DPA$\cdot^-$ Radical Ion

Solvent[a]	Temp, °C	Counterion	a_0	a_m, G	a_p	Ref
DME	−60	K^+	2.64	0.56	4.82	*b*
DME	~25	K^+	2.68 ± 0.05	0.62 ± 0.05	4.75 ± 0.05	*c*
DMF[e]	~25	$(n\text{-Bu})_4N^+$	2.80	0.60	5.08	*d*
HMPA	~25	Na^+ (free ion)	2.60 ± 0.05	0.53 ± 0.05	4.76 ± 0.05	This work

[a] DME = dimethoxyethane, DMF = dimethylformamide, HMPA = hexamethylphosphoramide. [b] C. S. Johnson and R. Chang, *J. Chem. Phys.*, **43**, 3183 (1965). [c] J. G. Broadhurst and E. Warhurst, *J. Chem. Soc.*, *A*, 351 (1966). [d] R. E. Sioda, D. O. Cowan, and W. S. Koski, *J. Amer. Chem. Soc.*, **89**, 230 (1967). [e] Formed electrolytically.

biphenylide ions, B$\cdot^-$, to DPA. The reaction

$$B\cdot^- + DPA \rightleftharpoons B + DPA\cdot^- \text{ (free ions)}$$

is quantitative and instantaneous at room temperature and no further reduction is observed, *i.e.*, the transfer

$$B\cdot^- + DPA\cdot^- \rightleftharpoons B + DPA^{2-}$$

does not take place in HMPA even if the excess of B$\cdot^-$ is large. This implies that the electron affinity of the *free* DPA$\cdot^-$ ion is rather low and the formation of DPA^{2-} becomes feasible only through its association with counterions.

The DPA$\cdot^-$ radical ions are identified by their optical and esr spectra. The former is shown in Figure 1: a sharp peak appears at λ_{max} 450 mμ (ϵ 5.4 × 10^4) with shoulders at 420 and 410 mμ, and a broad peak is seen at 860 mμ (ϵ 1.7 × 10^4). A similar spectrum was reported by Dadley and Evans[3] who examined DPA$\cdot^-$,Na$^+$ in THF at −60°. The extinction coefficients given in our paper were determined by converting a known amount of B$\cdot^-$ into DPA$\cdot^-$, a slight excess of DPA ensuring a quantitative conversion. These coefficients are substantially higher than those reported by Dadley and Evans.[3] The esr spectrum of DPA$\cdot^-$ in HMPA is identical with the spectra described by other investigators as shown by the results listed in Table I.

The dimerization of DPA$\cdot^-$ ions is imperceptible in HMPA even at room temperature. The spectrum remains unchanged over many minutes, although a new species, absorbing at 620 mμ, is formed after several hours. The absorption at 620 mμ is *not* due to the formation of the dimeric dianions. The latter were prepared in THF (see a later part of this paper) and they absorb at λ_{max} 467 mμ (ϵ 1.1 × 10^4). However, the new species absorbing at 620 mμ is formed instantaneously on the addition of HMPA to their THF solution. A similar reaction is observed when the residue containing the dimeric dianions obtained by evaporating THF is dissolved in HMPA. These observations show that the stability of DPA$\cdot^-$ in HMPA is due to their slow dimerization and not to the unfavorable equilibrium. Indeed, even if the dimerization, 2DPA$\cdot^-$ $\rightleftarrows$ dimeric dianion, were thermodynamically unfavorable the irreversible and fast conversion of the dimeric dianions into the species absorbing at 620 mμ should shift the reaction to the right. Hence, the disappearance of DPA$\cdot^-$ would be rapid if the dimerization were fast.

The stability of DPA$\cdot^-$ in HMPA may be contrasted with the stability of quinoline radical ions, Q$\cdot^-$, in the same solvent. The former is governed by kinetic factors, whereas the latter is determined by the thermodynamics of the system.[4] The equilibrium

$$2Q\cdot^- \rightleftharpoons {}^-QQ^- \text{ (free ions)}$$

established in HMPA lies far to the left, whereas the analogous equilibrium

$$2Q\cdot^-,Na^+ \rightleftharpoons Na^+,{}^-QQ^-,Na^+$$

established in THF is far to the right.

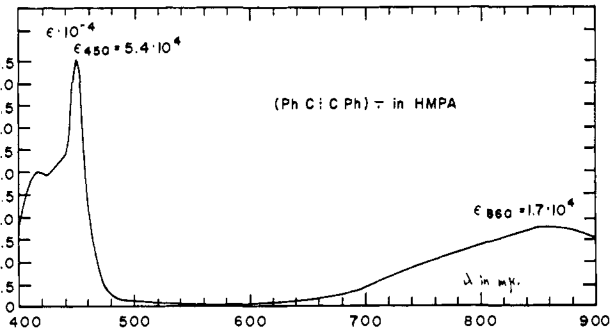
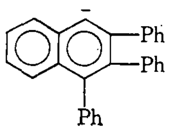


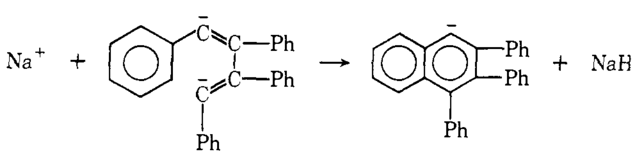
Figure 1. Spectrum of diphenylacetylene radical ion in HMPA at 25°.

The identity of the species absorbing at 620 mμ is not yet finally established. Tentatively it is identified as the anion I.



I

Apparently, the reaction



is facile in HMPA. Indeed, the protonation of the blue solution (λ_{max} 620 mμ) yields 2,3,4-triphenylnaphthalene and H_2 (or HD if D_2O is used as the protonating agent). The evolution of HD demonstrates that sodium hydride is formed in the aged solution.

Protonation with methanol of the freshly prepared DPA$\cdot^-$ solution in HMPA yields *trans*-stilbene and diphenylacetylene. For example, the addition of 5 ml

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[3] D. Dadley and A. G. Evans, *J. Chem. Soc.*, *B*, 418 (1967).

[4] J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 6421 (1968).

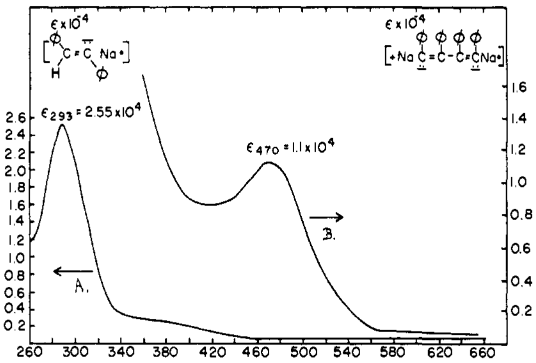


Figure 2. Curve A, spectrum of the PhCH:C̄Ph carbanion in THF; curve B, spectrum of Na^+, $^-CPh{:}CPh{\cdot}CPh{:}CPh^-$, Na^+ in THF.

of methanol to 40 ml of 3.5×10^{-3} M solution of DPA·⁻ in HMPA produced about 50% of DPA and 45% of *trans*-stilbene. If the protonation of DPA·⁻ is relatively slow then the resulting radicals, PhCH:ĊPh, could be reduced by the nonprotonated DPA·⁻ yielding the respective ions. Their subsequent protonation would produce stilbene, and thus stilbene and diphenylacetylene in 1:1 proportion are the products of the reaction. Alternatively, these products could result from the disproportionation of the radicals formed by the fast protonation.

Electron Affinity of DPA in HMPA

Two techniques were utilized in determining the electron affinity of DPA in HMPA. The potentiometric titration[2,5] led to the value of 0.27 V in a scale in which the electron affinity of biphenyl is taken as the reference zero. Studies of the equilibrium

$$\text{chrysene}\cdot^- + \text{DPA} \rightleftarrows \text{chrysene} + \text{DPA}\cdot^- \qquad K_{\text{C,DPA}}$$

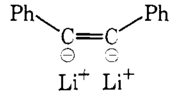
led to $K_{\text{C,DPA}} = 0.2$ at 25°. The relative electron affinity of chrysene in respect to biphenyl was determined by potentiometric titration in HMPA[6] to be 0.30 V; hence, on the basis of the equilibrium results the electron affinity of DPA is 0.26 V in agreement with the value obtained by the direct titration.

Low-Temperature Reduction of DPA by Metallic Lithium in THF

The reduction of DPA ($10^{-2}M$) by metallic lithium in THF at −77° yields initially DPA·⁻,Li⁺. Its formation is manifested by the spectrum of the solution which, at the early stages of the reaction, is identical with that recorded in HMPA. Prolonged contact with lithium reduces the radical ion further and eventually some insoluble compound precipitates as a red slurry. Its insolubility prevented us from studying its spectrum; moreover, this compound decomposes when the temperature of the slurry is raised above −77°. It is imperative, therefore, to maintain a very low temperature of the suspension if we wish to preserve its identity.

Separation of the red slurry from the chunks of the residual lithium was accomplished at −77°. Its hydrolysis and subsequent titration of the resulting alkali shows that the ratio DPA:Li = 1:2 (within 5%). Addition of an excess of DPA to the slurry (still maintained at −77°) converts it quantitatively to 2DPA·⁻, Li⁺. The latter is soluble in THF and the solution is stable at −77°. Thus, one concludes that the red slurry is the dilithium salt of DPA^{2-}. Study of its protonation by methanol, performed at −77°, provides further support for this conclusion. The protonation yields *cis*-stilbene as the *only* product of the reaction. The isomer was identified by its nmr spectrum[7] showing two sharp peaks at 393.5 cps (1) and 428 cps (5), by its uv spectrum having a characteristic single peak at $\lambda_{\max}$ 280 mμ, and by vpc analysis (the *cis* and *trans* isomers are readily separated on a silicone column; however, such a column does not separate *cis*-stilbene from bibenzyl). Pure *cis*-PhCD:CDPh is obtained when deuterated methanol is used; only the 428-cps peak, but not the one at 393.5 cps, appears in its nmr spectrum.

The formation of *cis*-stilbene through protonation of DPA^{2-},2Li⁺ indicates a definite geometry of the salt, *viz.*



It is probable that the Li⁺ cations are located one above and the other below the nodal plane of the dianion because then each Li⁺ may interact with *both* lone electron pairs as well as with the π-electron cloud. The above tentative structure may reflect the known tendency of the organolithium compounds to form dimers or higher agglomerates. It will be shown later that a similar reduction of DPA by metallic sodium, even if carried out at −78 or −90°, produces a mixture of the sodium salts of the respective mono- and dianions and these yield *trans*-stilbene, together with some other hydrocarbons, when protonated at −78°. No *cis*-stilbene was detected in the products of their protonation.

As the temperature of the red slurry is raised the insoluble precipitate gradually dissolves and eventually a clear, brown-reddish solution is formed at room temperature. This solution is relatively stable although further reactions, which change its color into a dark bluish green, take place after a day. The spectrum of the freshly prepared reddish brown solution shows a strong absorption band at 293 mμ with a shoulder at about 380 mμ which extends far into the visible region (to about 600 mμ), as seen in Figure 2. Its protonation with CH_3OD yields *trans*-stilbene as the only product. However, nmr and mass spectroscopic analysis shows that only one of its olefinic hydrogens is then deuterated. Obviously, the first protonation of the dianion occurred before the methanol was added.

Protonation of the DPA^{2-},2Li⁺ salt which takes place in THF solution at temperatures ranging from −60 to +25° could be caused by some protonating impurities present in THF, or by the ether itself, or it may result from an intramolecular proton transfer, *viz.*

$$C_6H_5\bar{C}{:}\bar{C}C_6H_5 \longrightarrow C_6\bar{H}_4CH{:}\bar{C}C_6H_5$$

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[5] J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

[6] J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **71**, 3063 (1967).

[7] The nmr spectrum of *trans*-stilbene shows seven peaks in the range 430–447 cps and a peak at 421 cps.

The presence of some protonating impurity is improbable. Its concentration should exceed 2×10^{-2} M to account for the results, and the vpc analysis of the ether did not show any foreign peaks. The hypothesis of the intramolecular proton transfer was ruled out by the mass spectrographic analysis. Had this been the case the mass spectrum of the stilbene produced by the ultimate protonation with CH_3OD should give a large parent peak at mass 182 with a smaller one (due to C^{13}) at mass 183, while actually a large peak at mass 181 with a small one at mass 182 was observed. The mass spectrum of the ordinary *trans*-stilbene shows a large peak at mass 180 with a small one at mass 181. All these observations indicate that the initial protonation of $DPA^{2-},2Li^+$, prior to the addition of methanol, should be attributed to reaction with THF, this process being tentatively represented by the equation

$$DPA^{2-},2Li^+ + THF \longrightarrow PhCH{:}\bar{C}Ph,Li^+ + CH_2{:}CH{\cdot}CH_2CH_2O^-,Li^+$$

or

$$PhCH{:}\bar{C}Ph,Li^+ + CH_2{:}CH_2 + CH_2CH\bar{O}$$

Experiments performed in fully deuterated THF followed by the addition of CH_3OD support this conclusion. The resulting stilbene contained *two* D atoms as proved by its nmr and mass spectroscopic analyses. It is interesting also to note that the decomposition of the dilithium salt is slower in deuterated THF than in the ordinary solvent. Apparently the isotope effect (lowering of zero-point energy) makes the deuterated THF a weaker acid than the ordinary ether.

The above results show that THF may act as a weak acid. However, they do not identify the acidic proton. The gain of the C=C bond and the possible formation of the alcoholate ion suggest that the β proton should react more easily than the α one. Indeed, $CH_2{:}CHCH_2CH_2OH$ was isolated and identified by glpc from the products of the reaction. However, its yield is only 20% of the expected amount. Apparently, the α proton is after all more acetic and the reaction yields then ethylene and acetaldehyde. Some observations reported in the literature[8] show that other dianions are also slowly protonated in THF; a slow protonation of anthracene dianions by THF was noted in our laboratory.

Protonation of $DPA^{2-},2Li^+$ with methanol at −77° yields *cis*-stilbene, while the stepwise protonation, first by THF and then by methanol at 25°, yields *trans*-stilbene. In the presence of methanol, which was added to the red slurry at −77°, the carbanion, $Ph{\cdot}CH{:}\bar{C}Ph$, formed by the first step of the protonation is rapidly protonated further by the excess of methanol. Hence, the lifetime of $PhCH{:}\bar{C}Ph,Li^+$ is short and, because it is kept at −77°, its isomerization is probably slow and apparently negligible during its short lifetime prior to its protonation. On the other hand, only DPA^{2-} is protonated by THF when the temperature of the slurry is raised, while the resulting $PhCH{:}\bar{C}Ph$ carbanion remains intact. The ions are left for a relatively long time in the solution which eventually attains room temperature, and therefore they have ample time to isomerize.

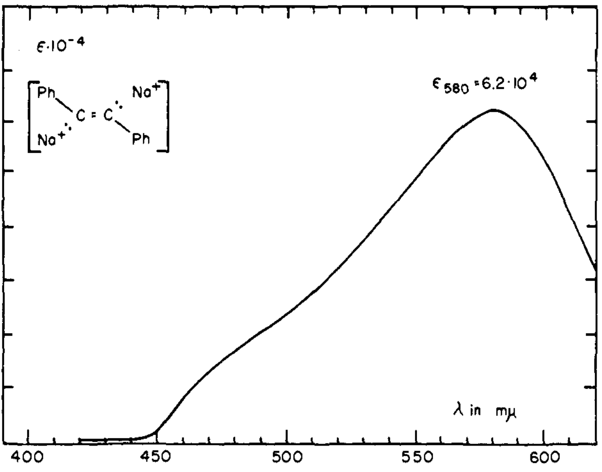

Figure 3. Spectrum of the DPA^{2-}, $2Na^+$ in THF at −94°.

Hence, under such conditions the final protonation, caused by the addition of methanol, yields *trans*-stilbene.

The reddish brown solution of $PhCH{:}\bar{C}Ph,Li^+$ reacts with sodium or lithium when contacted with the alkali metal at 25°. The spectrum of the resulting product proves it to be the dianion of stilbene; its absorption (λ_{max} 509 mμ) is identical with that reported in the literature[9] for $C_6H_5\bar{C}H{\cdot}\bar{C}HC_6H_5$. Eventual protonation of the reduced solution, after it is decanted from the alkali metal, yields quantitatively bibenzyl. It seems that $PhCH{:}\bar{C}Ph$ acquires an additional electron when contacted with alkali metal. The resulting radical dianion $(PhCH{:}\bar{C}Ph)\cdot^-$ is then rapidly protonated by THF and yields stilbene radical ion which reacts again with the metal and finally forms the dianion of stilbene.

Low-Temperature Reduction of DPA in THF by Metallic Sodium

DPA in THF solution is reduced when contacted with metallic sodium. The reaction was performed at −78 and at −94°. It proceeds through the formation of $DPA\cdot^-,Na^+$, and the solution removed from the sodium after about 5 min of contact shows only the characteristic spectrum of the radical anion. This species is stable if kept below −78°; it neither dimerizes nor decomposes under these conditions. A prolonged contact of 5×10^{-3} N DPA solution with the metal, for about 4–5 hr, leads to the formation of the dianion. The conversion could be as high as 95%. The spectrum of $DPA^{2-},2Na^+$ solution is shown in Figure 3, λ_{max} 580 mμ, ϵ 6.4×10^4. In contradistinction to DPA^{2-}, $2Li^+$, the sodium salt is soluble in THF, even at −94°.

Protonation of the sodium salts was performed at −77 and at −93° by adding a large excess of methanol to their THF solution. The results are summarized in Table II. The ratio alkali:DPA was obtained by titration of aliquots of the protonated solution. The

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[8] K. H. Buschow and G. J. Hoijtink, *J. Chem. Phys.*, 40, 2501 (1964).

[9] E. R. Zabolotny and J. F. Garst, *J. Amer. Chem. Soc.*, 86, 1645 (1964).

Table II. Protonation of the Sodium Salts of $DPA\cdot^-$ and DPA^{2-} [a]

		Calcd % salts[c]		Products, mol %[d]		
Temp, °C	Alkali:DPA, *r*[b]	% $DPA\cdot^-$	% DPA^{2-}	DPA	*trans*-Stilbene	Bibenzyl
−77	1.42 (exptl)	58	42	45 48	25 23	30 26
	1.6 (calcd)	38.5	61.5			
−93	1.52 (exptl)	48	52	57.5	12.3	31
	1.49 (calcd)	52	48			
−77	1.95 (exptl)	~10	~90	37	34	29
		Protonation of $DPA\cdot^-,Na^+$ in the Absence of DPA^{2-}				
−78	1	100	0	67	16	17
			Calcd	67		

[a] Solvent, THF; protonating agent, methanol (large excess). [b] Calculation of *r* from the composition of the products: $100r = 2(\%\ \text{stilbene}) + 4(\%\ \text{bibenzyl})$. [c] Calculation of the per cent of $DPA\cdot^-$ and DPA^{2-} from the composition of the products: $\%\ DPA^{2-} = (\%\ \text{stilbene}) + 3(\%\ \text{bibenzyl}) - (\%\ DPA)$. [d] No *cis*-stilbene was detected in the products.

composition of the products was determined by vpc using a silicone column, and it is given in mole per cent calculated with respect to DPA originally introduced into the reactor. The protonation yields *trans*-stilbene; no *cis* isomer was detected. The reliability of the results is checked by calculating the ratio alkali:DPA from the composition data. Each bibenzyl is counted as an equivalent of four alkalis and each stilbene accounts for 2 equivalents. Alternatively, it is possible to calculate the per cents of $DPA\cdot^-$ and DPA^{2-} from the observed composition of the products. The mass balance combined with charge balance leads to the equation

$$\%\ DPA^{2-} = \%\ \text{stilbene} + 3(\%\ \text{bibenzyl}) - \%\ DPA$$

It should be stressed, however, that the latter check is very sensitive to small errors in per cent of bibenzyl. Values calculated in this way are included in Table II. It seems that the analysis of the bibenzyl produced at −77° was too high. The more refined analysis of the products produced at −93° gave good agreement between the observed and the calculated data.

Inspection of Figure 1 shows that a maximum at 450 mμ and an inflection point at 440 mμ appear close to each other in the spectrum of $DPA\cdot^-$. We may assume, therefore, that the difference in the optical density at 450 and 440 mμ measures the concentration of $DPA\cdot^-$ in the mixture of the radical ion and dianion (see Figure 2). On this basis, the amount of $DPA\cdot^-$ at − 93° was determined to be 45%, implying that the solution contains 55% of DPA^{2-}. This result agrees well with that derived from the alkali titration.

Addition of LiCl dissolved in THF to a solution of $DPA^{-2},2Na^+$ at −78° converts the sodium salt into a red precipitate which on protonation yields only *cis*-stilbene. Apparently the reaction

$$DPA^{2-},2Na^+ + 2LiCl \rightarrow DPA^{2-},2Li^+ + 2NaCl$$

converts the sodium salt into the insoluble lithium salt.

Although the solution of $DPA^{2-},2Na^+$ is relatively stable at −93°, its protonation by THF (see the previous discussion of $DPA^{2-},2Li^+$) becomes rapid as the temperature is raised. Eventually the monoprotonated species $PhCH{=}\bar{C}Ph,Na^+$ is formed from the dianion, while the radical ions $DPA\cdot^-,Na^+$ disappear due to their dimerization. The latter reaction was investigated by Dadley and Evans[3] and will be discussed later. The protonation with methanol of the solution brought up to the ambient temperature produced *trans*-stilbene (56% of the original DPA) and *cis,cis*-1,2,3,4-tetraphenylbutadiene (28% of the original DPA). The amount of the stilbene formed in this process (56%) is fairly close to the amount of DPA^{2-} present in the original solution as calculated from the alkali:DPA ratio (1.52%).

Protonation of the solution of pure $DPA\cdot^-,Na^+$, containing no DPA^{2-}, led again to the formation of bibenzyl as well as stilbene. The results are included in Table II, and the directly determined per cent of DPA was compared with the one calculated on the assumption that each bibenzyl is equivalent to three DPA's and each stilbene to one DPA. The experimental and calculated results again agree well.

Mechanism of Formation of Bibenzyl

The appearance of bibenzyl in the products of protonation of $DPA\cdot^-$ or DPA^{2-} raises the question of the mechanism leading to its formation. It may be that the protonation is relatively slow and the products of the reactions compete with the protonating agents for the unreacted $DPA\cdot^-$ or DPA^{2-}. Thus, the radicals such as $PhCH{:}\dot{C}Ph$, or even stilbene, may react with $DPA\cdot^-$ (or DPA^{2-}) and be converted through a rapid electron-transfer process into carbanions ($PhCH{:}\bar{C}Ph$) or radical ions ($PhCH{:}CHPh\cdot^-$) leaving DPA as the other product. The protonation of the resulting carbanions or radical ions leads eventually to bibenzyl, *e.g.*

$$DPA\cdot^- + CH_3OH \longrightarrow PhCH{:}\dot{C}Ph + CH_3O^-$$

$$DPA\cdot^- + PhCH{:}\dot{C}Ph \longrightarrow DPA + PhCH{:}\bar{C}Ph$$

$$PhCH{:}\bar{C}Ph + CH_3OH \longrightarrow PhCH{:}CHPh + CH_3O^-$$

$$DPA\cdot^- + PhCH{:}CHPh \longrightarrow DPA + PhCH{:}CHPh\cdot^-$$

$$PhCH{:}CHPh\cdot^- + CH_3OH \longrightarrow PhCH_2\dot{C}HPh + CH_3O^-$$

$$DPA\cdot^- + PhCH_2\cdot\dot{C}HPh \longrightarrow PhCH_2\cdot\bar{C}HPh + DPA$$

$$PhCH_2\cdot\bar{C}HPh + CH_3OH \longrightarrow PhCH_2CH_2Ph + CH_3O^-$$

The electron transfer from a radical ion to a radical is known to be very fast and it may compete efficiently with the protonation.[10] This is not surprising because the electron affinity of radicals is very high. One may expect also that the electron transfer to stilbene could compete efficiently with the protonation because its electron affinity is probably larger than that of DPA.[11]

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(10) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, 78, 116 (1956).

(11) Electron affinity of stilbene was determined by the polarographic studies of Laitinen and Wawzonek.[12] Their value leads to ea = 0.32 V in our scale, while the electron affinity of DPA is 0.27 V. However,

To test the proposed mechanism the following experiment was performed. A THF solution of $DPA\cdot^-,Na^+$ kept at −78° was divided in two parts. One (solution I) was protonated by adding a THF solution of methanol, the other (solution II) by adding a THF solution of methanol and stilbene. The concentrations of the substrates and of the resulting products are given in Table III, which includes also the material and charge balances as well as the internal checks. The inspection of the data summarized in the table is revealing. Although the concentration of stilbene was always low in solution I, *i.e.*, it did not exceed at any time 0.7×10^{-4} *M*, most of the reduced product was present as bibenzyl. This implies that stilbene competes very efficiently with methanol for the unreacted $DPA\cdot^-,Na^+$. Therefore, one expects that in solution II virtually *all* of the $DPA\cdot^-$ should react with stilbene because its concentration was more than tenfold higher than that in solution I. However, the data show that instead of 4.6×10^{-4} only 0.85×10^{-4} of the added stilbene was reduced.

Table III. Protonation of $DPA\cdot^-,Na^+$ in THF at −78°[a]

Substrates, *M*	Products, *M*
Protonation by CH_3OH in THF in the Absence of Stilbene	
$[DPA\cdot^-]_0$, 8.8×10^{-4}	[DPA], 5.85×10^{-4}
$[CH_3OH]_0$, 4.8×10^{-3}	[*trans*-Stilbene], 0.72×10^{-4}
	[Bibenzyl], 1.82×10^{-4}
Material balance 8.8×10^{-4}	8.39×10^{-4}
Charge balance 8.8×10^{-4}	8.72×10^{-4}
Protonation by CH_3OH in the Presence of Stilbene in THF	
$[DPA\cdot^-]_0$, 9.2×10^{-4}	[DPA], 6.9×10^{-4}
[*trans*-Stilbene]$_0$, 9.45×10^{-4}	[*trans*-Stilbene], 8.6×10^{-4}
$[CH_3OH]_0$, 3.65×10^{-3}	[Bibenzyl], 2.4×01^{-4}
Material balance 18.65×10^{-4}	17.9×10^{-4}
Charge balance[b] 9.2×10^{-4}	7.9×10^{-4}

[a] Internal checks: [DPA] = 3[bibenzyl] + [stilbene]. In the absence of added stilbene, 5.85 compared with 5.46 + 0.72 = 6.18; in the presence of added stilbene,[b] 6.9 compared with 7.2 − 0.85 = 6.35. [b] The largest experimental error may occur in the amount of consumed stilbene which is obtained as a small difference of two large numbers (9.45 − 8.6). Error of 5% in [stilbene]$_0$ and in [stilbene] may reduce Δ(stilbene) from −0.85 to −0.4. This improves the charge balance (8.8 as compared with 9.2) and the internal check (6.8 as compared with 6.9).

The large discrepancy between the expected and observed amounts of consumed stilbene calls for modification of the proposed mechanism. Apparently in THF and at −78° the ion pairs $DPA\cdot^-,Na^+$ associate and form aggregates of at least three or four pairs. Protonation of $DPA\cdot^-$ in an aggregate is followed by an extremely fast, intraaggregate electron transfer and produces a $PhCH{:}\bar{C}Ph,Na^+$ pair which is retained in the agglomerate. Its protonation by the next molecule of methanol appears to be faster than of $DPA\cdot^-$ and, before the resulting stilbene has a chance to diffuse out of the agglomerate, it becomes reduced, again by the rapid intraaggregate electron transfer. Thus, a $PhCH{:}CHPh\cdot^-,Na^+$ ion pair is formed and its protonation eventually leads to the formation of bibenzyl.

We imply in our mechanism that carbanions such as $PhCH{:}\bar{C}Ph$ and $PhCH_2\cdot\bar{C}HPh$ are protonated faster than $DPA\cdot^-$. This is plausible because the carbanions should be more basic than the diphenylacetylene radical anion. However, we are forced also to assume a faster protonation of the stilbene radical ion than of $DPA\cdot^-$ and the reason for such behavior is not clear. It may be that the agglomerate has a structure in which the partially protonated ions, or radical ions, are located on its surface and therefore are more accessible to further protonation than the $DPA\cdot^-$ radical ions which reside in its interior.

The proposed model accounts for the preferential formation of bibenzyl and explains why the intermolecular reduction of stilbene is relatively ineffective. The latter reduction probably arises on encounter of stilbene with the unassociated $DPA\cdot^-,Na^+$ or perhaps even on its encounter with a cluster, but these intermolecular processes are bound to be slower than the intraaggregate reduction.

It is probable that similar aggregates are formed by $DPA^{2-},2Na^+$ and the mechanism proposed above might account then for the formation of bibenzyl from the dianions. Therefore, why is bibenzyl not formed from $DPA^{2-},2Li^+$? The latter is insoluble in THF at −78° and the protonation probably takes place only in solution and not in the crystal. The minute amount of $DPA^{2-},2Li^+$ present in the saturated solution is at too low concentration to allow for aggregation. Thus, only these molecules are protonated and the formed stilbene does not benefit from the intraaggregate electron transfer.

Reaction of DPA with Sodium Biphenylide ($Na^+,B\cdot^-$) in THF

In tetrahydrofuran (THF), like in HMPA, the electron transfer from $Na^+,B\cdot^-$ to DPA proceeds quantitatively and too fast to be observed when flow techniques are applied. Similar results were reported by Dadley and Evans[3] who studied the reaction between sodium phenanthrenide and DPA in THF. At not too low temperature the resulting $DPA\cdot^-,Na^+$ ion pairs dimerize and form the disodium salt of 1,2,3,4-tetraphenylbutadiene dianion. Its spectrum (see Figure 2) is obtained by mixing in a flow system the solution of $B\cdot^-,Na^+$ with a small excess of DPA, also dissolved in THF, and recording the light absorption of the resulting mixture. It shows only one peak in the visible range, namely, λ_{max} 467 mμ, ϵ 1.1×10^4. If the mixing is poor an additional peak appears at about 400 mμ indicating that some other species is formed due to the interaction of the reagents with the products. Moreover, a peak at 620 mμ develops if the solution is kept for a longer time. These additional peaks are shown in Figure 7 of Dadley and Evans' paper[3] which depicts the spectrum of the supposedly pure dimeric dianion. Their main absorption at about 470 mμ is, nevertheless, virtually identical with that observed by us.

The kinetics of the dimerization was thoroughly investigated by Dadley and Evans.[3] Unfortunately, the extinction coefficient of $DPA\cdot^-,Na^+$ reported by these workers is twice as low as that found in our studies. Therefore, we checked our value by converting a known amount of $B\cdot^-,Na^+$ into $DPA\cdot^-,Na^+$ and then again by converting the resulting $DPA\cdot^-,Na^+$

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according to Hoijtink's data[13] the electron affinity of stilbene is the same as that of naphthalene, *i.e.*, *lower* than the electron affinity of DPA. This discrepancy will be investigated.

(12) H. A. Laitinen and S. Wawzonek, *J. Amer. Chem. Soc.*, **64**, 1765, 2365 (1942).

(13) G. J. Hoijtink and P. H. Meir, *Z. Phys. Chem.* (Frankfurt am Main), 20, 1 (1959).

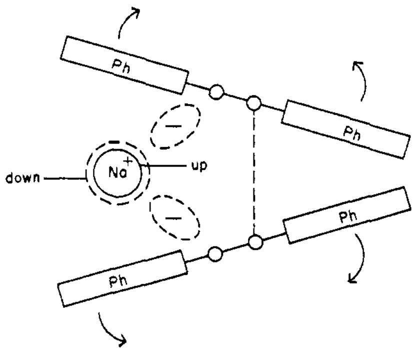

Figure 4. Schematic drawing of the dimerization of $DPA\cdot^-,Na^+$ radical ions.

into sodium anthracenide. The results fully confirmed our claim.

Close inspection of the spectrum of $DPA\cdot^-$ shown in Figure 3 of ref 3 reveals a peak at about 500 mμ not observed by us (see Figure 1). This suggests the presence of some other organosodium compound which could account for the low ϵ value of these workers.

The error in ϵ affects the bimolecular rate constant determined by Dadley and Evans; *i.e.*, the corrected constant should be twice as high as the reported one. The rate of the dimerization was reinvestigated in our laboratory by Mr. T. Staples, who used in his studies a Durrum flow spectrophotometer. His results obtained at 25° led to $k = 600\text{–}700\ M^{-1}\ \text{sec}^{-1}$ for the sodium salt, while the corrected value of Evans extrapolated to 25° is $300\ M^{-1}\ \text{sec}^{-1}$. This discrepancy may be caused by extrapolation if the reported activation energy is slightly in error.

Protonation of the dimeric dianion yields mainly *cis,cis*-1,2,3,4-tetraphenylbutadiene (about 65%) and smaller amounts of the other isomers. The identification of the isomers[14] was achieved by means of nmr using, for calibration purposes, samples of the pure isomers kindly supplied by Dr. H. H. Freedman, whom we thank for his help. Inspection of the models shows that the *cis,cis* isomer is formed if the two radical ions approach each other plane-to-plane with the counterions simultaneously associated with both carbanions as shown schematically in Figure 4. This finding verifies, therefore, the suggestion of Dadley and Evans.[3] The tendency of both counterions to be associated simultaneously with both lone pairs of electrons is particularly pronounced for Li^+ (see the preceding discussion of the $DPA^{2-},2Li^+$), and this accounts for the nearly exclusive formation of the *cis,cis* dimer when the reduction is performed with metallic lithium.[15]

When a THF solution of DPA is mixed at −60° with two equivalents of $B\cdot^-,Na^+$ the instantly formed $DPA\cdot^-,Na^+$ radical anions react slowly with the excess of the electron donor. The dimerization of $DPA\cdot^-,Na^+$ is exceedingly slow at this temperature, and it does not interfere with the observed reaction. The simultaneous disappearance of both radical ions was observed spectrophotometrically by recording the spectrum of the mixture at 20-min intervals. The characteristic maxima of $\mathbf{B}\cdot^-,Na^+$ and $DPA\cdot^-,Na^+$ fade in a manner which indicates that the rates of consumption of both species are equal. Eventually the recorded spectrum shows only the absorption of the products, and in the range 280–600 mμ its shape is identical with that of $PhCH{:}\bar{C}Ph,Na^+$ shown in Figure 2. At shorter wavelengths the spectrum of biphenyl appears.

Vpc, mass spectrographic, and spectrophotometric analyses prove that *trans*-stilbene and biphenyl in 1:1 ratio are the only products when the mixture, after completion of the reaction, is protonated with methanol. Moreover, protonation with deuterated methanol yielded *trans*-stilbene possessing only one olefinic deuterium. Hence, the spectrophotometric data and the results of deuteration conclusively show that the following reactions take place in the cold mixture of $DPA\cdot^-,Na^+ + B\cdot^-,Na^+$.

$$DPA\cdot^-,Na^+ + B\cdot^-,Na^+ \overset{K_I}{\rightleftharpoons} DPA^{2-},2Na^+ + B \qquad (I)$$

$$DPA^{2-},2Na^+ + THF \xrightarrow{k_p} PhCH{:}\bar{C}Ph,Na^+ + \ldots \qquad (II)$$

$$Ph\cdot CH{:}\bar{C}Ph,Na^+ \xrightarrow{CH_3OH} \textit{trans}\text{-stilbene} + \ldots$$

Equilibrium I is rapidly established but the concentration of $DPA^{2-},2Na^+$ is exceedingly low. The relatively slow protonation of $DPA^{2-},2Na^+$ by THF is therefore the rate determining step. The kinetic experiments were performed at much lower concentrations of the reagents than the previous experiments designed for isolation and identification of the products. Hence, the agglomeration was negligible in kinetic experiments and the overall process could therefore be first order in $DPA\cdot^-,Na^+$ and $B\cdot^-,Na^+$, its composite second-order rate constant being $k_{II} = k_pK_I$.

Kinetics of an analogous reaction, namely the interaction of $DPA\cdot^-,Na^+$ with sodium phenanthrenide or sodium naphthalenide, has been investigated recently by Dadley and Evans.[16] They studied these reactions in the temperature range −25–∼0° and, after correcting the results for the competing dimerization of $DPA\cdot^-$, Na^+, found the residual processes to be first order with respect to $DPA\cdot^-,Na^+$ and the electron donor, as expected on the basis of our mechanism. However, Dadley and Evans[16] interpreted their results in terms of a simple electron transfer, *e.g.*

$$\text{phenanthrene}\cdot^-,Na^+ + DPA\cdot^-,Na^+ \longrightarrow DPA^{2-},2Na^+ + \text{phenanthrene} \qquad (III)$$

claiming that such a reaction is unusually slow (at 0° $k = 87\ M^{-1}\ \text{sec}^{-1}$). According to their implicit assumption the equilibrium of process III strongly favors the products, while simple calculations show that the reverse is expected. The redox potentials of aromatic hydrocarbons in THF were determined[5,17] and correlated with those measured in HMPA.[6] On the basis of these data and the results of our present studies we calculate the difference in the redox potentials of DPA and phenanthrene to be ∼0.13 V, *i.e.*, the free energy change of the reaction

$$\text{phenanthrene}\cdot^-,Na^+ + DPA \rightleftharpoons \text{phenanthrene} + DPA\cdot^-,Na^+$$

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[14] H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, 87, 3019 (1965).

[15] F. C. Leavitt, F. A. Manuel, F. Johnson, L. U. Mothernas, and D. S. Lachman, *ibid.*, 82, 5099 (1960).

[16] A. D. Dadley and A. G. Evans, *J. Chem. Soc., B*, 107 (1968).

[17] G. J. Hoijtink, E. Boer, P. H. Meir, and W. P. Weijland, *Rec. Trav. Chim. Pays-Bas.*, 75, 487 (1956).

performed in THF at 25° is about -3 kcal/mol. It seems that this value also represents ΔH of the above process because the entropy change in such an electron transfer is probably negligible.

According to Hoijtink[17] the difference between the second and first reduction potentials of aromatic hydrocarbons in THF (Na$^+$ counterion) is 0.3–0.5 V. If this value is accepted for the DPA system, then the free energy change of the disproportionation

$$2\mathrm{DPA}\cdot^{-},\mathrm{Na}^{+} \rightleftharpoons \mathrm{DPA}^{2-},2\mathrm{Na}^{+} + \mathrm{DPA}$$

at 25° is in the range $+7$ to $+11$ kcal/mol. Therefore, the free energy change of reaction III is greater than 4 kcal/mol at 25°. Electron transfer III is likely to be endothermic and therefore the equilibrium concentration of DPA^{2-},2Na$^+$ is probably very low at the relevant temperatures. This has been assumed in our mechanism.

It is instructive to discuss the reasons which led Dadley and Evans[16] to their conclusions. In the initial work[3] they noted that the interaction of metallic sodium with a THF solution of DPA (presumably at ambient temperatures) produces first a "green" species which later turns red. The spectra of the solution taken at different times were presented in Figure 2 of their first paper,[3] and our work, which will be reported in a forthcoming paper, fully confirms these observations. They also found the alkali to DPA ratio in the red solution to be 2:1, again a correct result, provided the red solution is removed from the sodium at the proper time. The red solution was found to be diamagnetic and to turn green on the addition of DPA. This, too, was confirmed by our studies, but the *green* solution has a spectrum different from that of DAP$\cdot^-$ or its dimer. Dadley and Evans assumed, however, that the red solution is that of DPA^{2-},2Na$^+$ and the green produced on the subsequent addition of DPA is that of the dimeric dianion.

The reaction of DPA with sodium at room temperature is most complex and its details will be reported later. However, the red solution is *not* that of DPA^{2-}, 2Na$^+$. The spectrum of the latter, shown in Figure 3 of this paper, can be studied only at low temperatures (see the preceding sections) and it is distinct from curve II depicted in Figure 2 of ref 3. The visual observations may be, therefore, misleading. Since Dadley and Evans did not report the spectrum of the products formed on interaction of DPA$\cdot^-$,Na$^+$ with sodium phenanthrenide or naphthalenide, one cannot check whether PhCH:$\bar{\mathrm{C}}$Ph,Na$^+$ (which is red) was indeed formed in their system, as our mechanism requires. The analysis of the protonated products, which was not performed by Dadley and Evans, would still lead to inconclusive results because both mechanisms predict the formation of stilbene It is necessary to use deuterated methanol in order to distinguish between the two alternatives. The simple electron-transfer mechanism proposed by Dadley and Evans demands the formation of PhCD:CDPh, whereas our mechanism calls for the formation of PhCH:CDPh. The latter was indeed found when DPA$\cdot^-$,Na$^+$ reacted in THF with B$\cdot^-$,Na$^+$ at -60°.

The other misleading factor which contributed to the difficulties of Dadley and Evans arose from their overestimation of the electron affinity of DPA. They explicitly stated on p 421 of ref 3 that the electron affinity of DPA is greater than that of chrysene (the reverse was demonstrated by this study). They argued that the dimerization of DPA$\cdot^-$ radical ions, and hence their formation, is observed when chrysene radical ions are the electron donors. However, the dimerization of DPA$\cdot^-$ continuously shifts the electron transfer to the right and the dimerization would be observed, therefore, provided that the electron affinity of the donor is not much greater than that of DPA.

Exothermic electron-transfer processes are fast (at 25° $k > 10^8\ M^{-1}\ \mathrm{sec}^{-1}$) and Dadley and Evans implied that the transfer phenanthrene$\cdot^-$,Na$^+$ (or naphthalene$\cdot^-$,Na$^+$) + DPA$\cdot^-$,Na$^+$ → phenanthrene (or naphthalene) + DPA^{2-},2Na$^+$ is exothermic. They argued, however, that the reaction between two negative species may be slow. An example of such a reaction is provided by the disproportionation of radical ions of tetraphenylethylene. Their sodium salts disproportionate extremely fast even at -40° (unpublished results from our laboratory).

Finally, a most interesting observation of Dadley and Evans calls for comments. They found[16] that lithium chrysene reacted extremely fast with DPA$\cdot^-$,Li$^+$; the rates were measurable for the sodium salts, and too slow to be observed when the potassium salt was used. These results were interpreted as an example of the counterion effect on the rate of electron transfer. In terms of our mechanism they indicate a large effect of counterion on the rate of proton transfer, an effect which is amplified by the low acidity of THF. Indeed, we found that DPA^{2-},2Li$^+$ rapidly reacts with THF at -60°, while the reaction of DPA^{2-},2Na$^+$ is slow at this temperature. The behavior of the potassium salt was not yet examined.

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