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# Carbon-Skeletal [1,2] Anionic Rearrangements and the π-Orbital Overlap Constraint: The Question of Nucleophilic Attack versus Electron Transfer[1]

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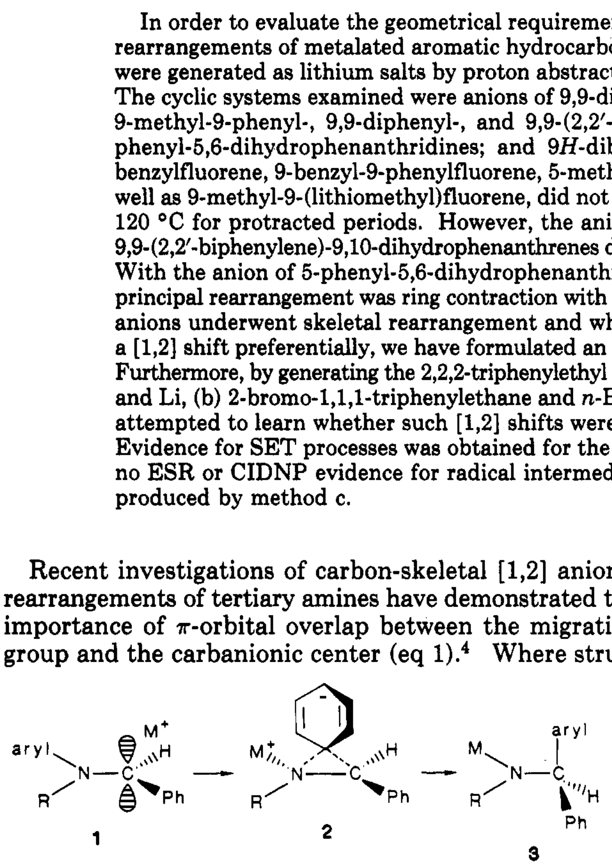
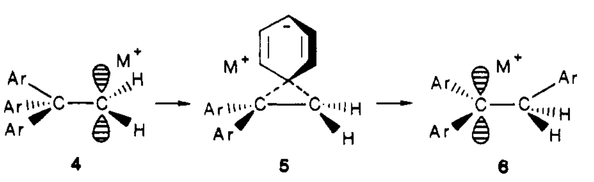
*Received August 9, 1988*

In order to evaluate the geometrical requirements and the actual electronic nature of apparent [1,2] anionic rearrangements of metalated aromatic hydrocarbons, amines, and ethers, cyclic structural types of such anions were generated as lithium salts by proton abstraction from C–H bonds by RLi or by C–Cl bond cleavage by Li. The cyclic systems examined were anions of 9,9-dimethyl-, 9-methyl-9-benzyl-, and 9-benzyl-9-phenylfluorenes; 9-methyl-9-phenyl-, 9,9-diphenyl-, and 9,9-(2,2′-biphenylene)-9,10-dihydrophenanthrenes; 5-methyl- and 5-phenyl-5,6-dihydrophenanthridines; and 9*H*-dibenzo[*b*,*e*]pyran. The anions generated from 9-methyl-9-benzylfluorene, 9-benzyl-9-phenylfluorene, 5-methyl-5,6-dihydrophenanthridine, and 9*H*-dibenzo[*b*,*e*]pyran, as well as 9-methyl-9-(lithiomethyl)fluorene, did not undergo skeletal rearrangement when heated between 40 and 120 °C for protracted periods. However, the anions derived from the 9-methyl-9-phenyl-, 9,9-diphenyl-, and 9,9-(2,2′-biphenylene)-9,10-dihydrophenanthrenes did undergo rearrangement with a [1,2] shift of the 9-aryl group. With the anion of 5-phenyl-5,6-dihydrophenanthridine, some [1,2] shift of the 5-phenyl was observed, but the principal rearrangement was ring contraction with the formation of *N*-phenyl-9-fluorenylamine. By noting which anions underwent skeletal rearrangement and which competing migrating groups in a given anion underwent a [1,2] shift preferentially, we have formulated an appropriate geometrical view of the transition states involved. Furthermore, by generating the 2,2,2-triphenylethyl anion (as its lithium salt) from (a) 2-chloro-1,1,1-triphenylethane and Li, (b) 2-bromo-1,1,1-triphenylethane and *n*-BuLi, and (c) bis(2,2,2-triphenylethyl)mercury and *n*-BuLi, we attempted to learn whether such [1,2] shifts were truly nucleophilic or whether SET processes were involved. Evidence for SET processes was obtained for the generation of (2,2,2-triphenylethyl)lithium by method a, but no ESR or CIDNP evidence for radical intermediates was observable when (2,2,2-triphenylethyl)lithium was produced by method c.

Recent investigations of carbon-skeletal [1,2] anionic rearrangements of tertiary amines have demonstrated the importance of π-orbital overlap between the migrating group and the carbanionic center (eq 1).[4] Where structural constraints in **1** prevent the anion from attaining some form of a bridging intermediate **2**, without undue strain, the rearrangement fails to take place. Although there is no doubt about the anionic nature of the initial rearranging amine **1** and the final rearranged product **3**, the actual mechanism of such so-called anionic rearrangements has not been clearly established. In the absence of evidence to the contrary,[4] the amine rearrangement depicted in eq 1 has been assumed to involve the carbanion **2** as the crucial intermediate. Such a carbanion mechanism has also been assumed for the [1,2] shifts observed in hydrocarbon anions, a reaction known as the Grovenstein–Zimmerman rearrangement[5] (eq 2). The driving force of the reaction is the formation of the delocalized anion **6** from a more localized one, **4**, and the migratory tendencies of the aryl groups were reconciled with the ability of the bridging aryl group to stabilize its negative charge (**5**).[6] However, recent studies on the reactions of β-phenyl-β-2- and -4-pyridylethyl halides with alkali metals (the usual method for generating the starting anion **3** in the Grovenstein–Zimmerman rearrangement[6]) have adduced evidence for the role of radical anions in these reactions.[7]

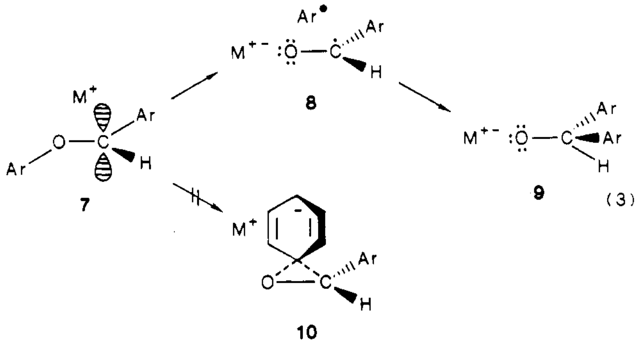


(1)



(2)

In contrast with such anionic rearrangements of amines and of hydrocarbons, the anionic rearrangements of metalated ethers (Wittig rearrangement[8]) have been shown to involve free radicals (eq 3).[8-10] In fact, for some rear-



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(1) Rearrangement of Organometallic Compounds. 25. Part 24: *J. Org. Chem.* **1987**, *52*, 4437.

(2) Present address: Eastman Kodak Company, Rochester, NY 14692.

(3) Present address: Sudarshan Chemical Company, Pune, India.

(4) Eisch, J. J.; Dua, S. K.; Kovacs, C. A. *J. Org. Chem.* **1987**, *52*, 4437.

(5) (a) Grovenstein, E., Jr. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 313. (b) Zimmerman, H. A.; Zweig, A. *J. Am. Chem. Soc.* **1961**, *83*, 1196.

(6) Grovenstein, E., Jr.; Wentworth, G. *J. Am. Chem. Soc.* **1967**, *89*, 2348.

(7) Eisch, J. J.; Kovacs, C. A.; Chobe, P.; Boleslawski, M. P. *J. Org. Chem.* **1987**, *52*, 4427.

(8) Wittig, G.; Löhmann, L. *Justus Liebigs Ann. Chem.* **1942**, *550*, 260.

(9) Lansbury, P. T.; Pattison, V. A. *J. Org. Chem.* **1962**, *27*, 1933.

(10) Schöllkopf, U.; Eisert, M. *Justus Liebigs Ann. Chem.* **1963**, *664*, 76.

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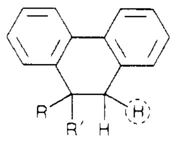
rangements it was shown that a bridging intermediate on the order of **10** would be highly improbable: the facile rearrangement of metalated 6*H*-dibenzo[*b*,*d*]pyran to yield benzyhydrol (as its metal salt) would not be comprehensible, if such a severely strained configuration resembling **10** had to be an intermediate.[11]

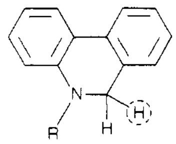
In light of the remaining mechanistic uncertainties in these [1,2] anionic rearrangements, the present study sought to scrutinize a select series of lithiated hydrocarbons, amines, and ethers and their tendency to undergo skeletal rearrangement. By choice of geometric and electronic structural factors and by close monitoring of experimental conditions, we hoped to determine whether the $\pi$-overlap requirement were a general constraint for all three types of rearrangements (eq 1–3) and whether any further evidence could be obtained for the importance of radical intermediates in these reactions.

## Results

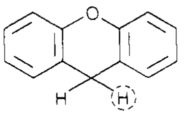
**Selection of Carbanion Substrates.** In order to learn whether the $\pi$-overlap requirement would be a general constraint in skeletal rearrangement, we chose cyclic hydrocarbon, amine, and ether substrates, in which the starting carbanion would be constrained by the ring of which it was a member (encircled H in **11**–**16**).



**11**: R = Me, R′ = Ph
**12**: R = R′ = Ph
**13**: R,R′ = 2,2′-biphenylene

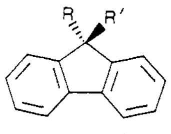


**14**: R = Me
**15**: R = Ph

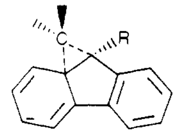


**16**

In a variant of such constrained carbanions, we also investigated a system where the carbanion could be freely oriented but the aryl ring being tested for rearrangement was now constrained (**17**–**19**). Were much bridging required for rearrangement (**20**), great strain would be encountered.

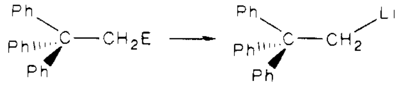


**17**: R = Me; R′ = ClCH$_2$
**18**: R = Me; R′ = PhCH$_2$
**19**: R = Ph; R′ = PhCH$_2$



**20**

Finally, a variety of reactions were undertaken, in order to generate (2,2,2-triphenylethyl)lithium by alternative routes (eq 4). Since the reaction of the chloro derivative **23** with lithium metal in THF was shown to produce radical anions (cf. infra), it was important to produce **25** from reagents not involving free alkali metal. Accordingly, an unsuccessful attempt was made to lithiate 1,1,1-triphenylethane (**21**) by *n*-butyllithium in THF and thus produce **25**. However, two other approaches to **25** did prove successful: (1) bromine–lithium exchange between 2-bromo-1,1,1-triphenylethane (**22**) and *n*-butyllithium in THF;[12] and (2) mercury–lithium exchange between bis(2,2,2-triphenylethyl)mercury (**24**) and *n*-butyllithium in THF.[13]

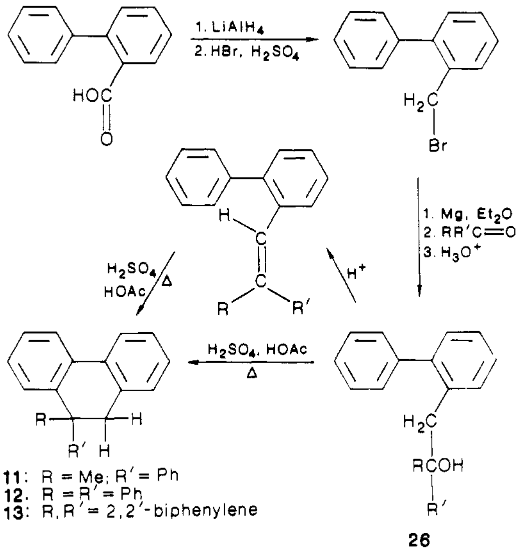


(4)

**21**: E = H
**22**: E = Br
**23**: E = Cl
**24**: E = HgCH$_2$CPh$_3$

**25**

### Scheme I

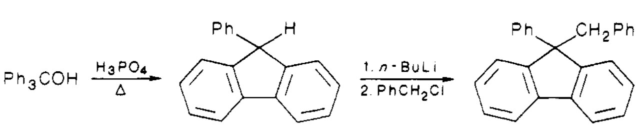


**11**: R = Me; R′ = Ph
**12**: R = R′ = Ph
**13**: R,R′ = 2,2′-biphenylene

**26**

**Synthesis of 9,9-Disubstituted 9,10-Dihydrophenanthrenes.** The requisite dihydrophenanthrenes, **11**–**13**, were synthesized from 2-biphenylcarboxylic acid by the sequence of reactions depicted in Scheme I. The carbinols **26** could be subjected to cyclization directly with concentrated sulfuric acid, or the olefin intermediate **27** could be formed by mild, acid-catalyzed dehydration.

**Synthesis of 9,9-Disubstituted Fluorenes.** 9-(Chloromethyl)-9-methylfluorene (**17**) and 9-benzyl-9-methylfluorene (**18**) were both prepared from fluorene, via 9-methylfluorene, by the sequence of reactions depicted in Scheme II. 9-Benzyl-9-phenylfluorene (**19**) was obtained by the acid-catalyzed cyclization of triphenylmethanol to 9-phenylfluorene[14] and the customary base-promoted benzylation (eq 5).



(5)

**Synthesis of 5-Substituted 5,6-Dihydrophenanthridines.** 5-Methyl-5,6-dihydrophenanthridine (**14**) was prepared from phenanthridine by quaternization and reduction (eq 6). 5-Phenyl-5,6-dihydrophenanthridine (**15**) was prepared from 5-phenylphenanthridin-6(5*H*)-one (**28**) by reduction with LiAlH$_4$; the latter was formed from phenanthridin-6(5*H*)-one (**29**) by a known sequence of reactions[15] (eq 7). Both dihydrophenanthridines **14** and **15** were extremely prone to air oxidation and hence had

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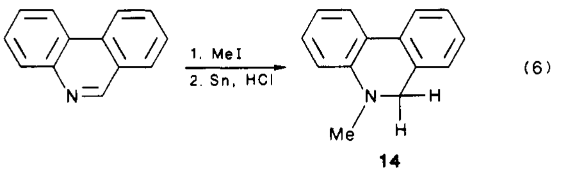
[11] Eisch, J. J.; Kovacs, C. A.; Rhee, S. G. *J. Organomet. Chem.* **1974**, *65*, 289.

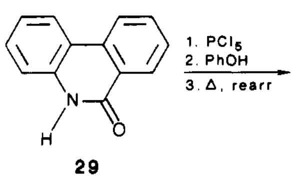
[12] Jones, R. G.; Gilman, H. *Organic Reactions*; Adams, R., Ed.; John Wiley & Sons: New York, 1951; Vol. 6, p 339.

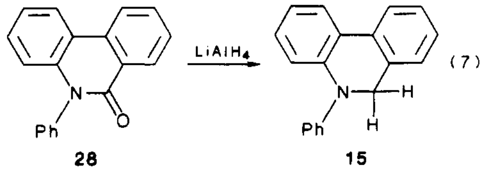
[13] Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1941**, *63*, 1443.

[14] Kliegl, A. *Chem. Ber.* **1905**, *38*, 287.

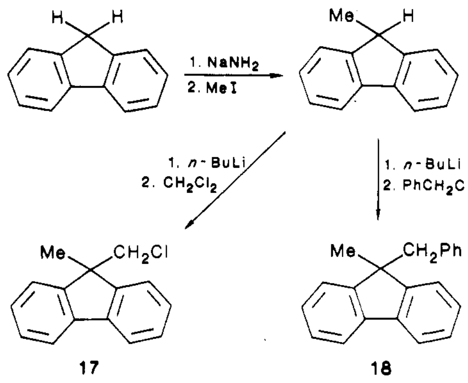
[15] von Hoft, E.; Rieche, A.; Schaltze, H. *Justus Liebigs Ann. Chem.* **1966**, *697*, 181.



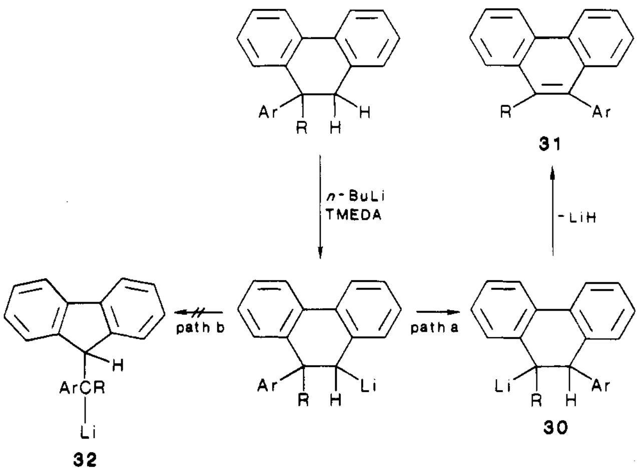




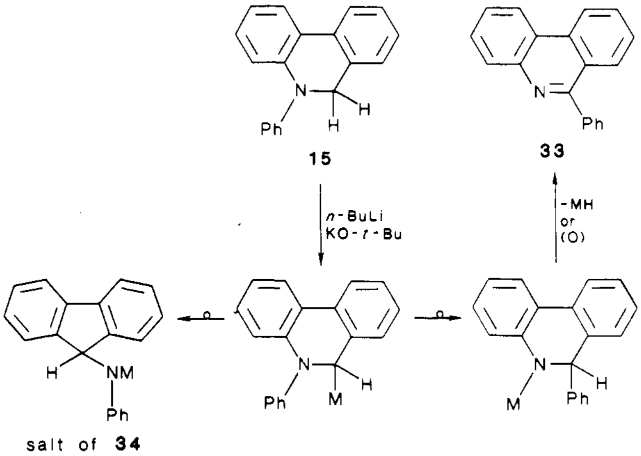
## Scheme II



## Scheme III



## Scheme IV



to be purified and allowed to react under an inert atmosphere.

**Rearrangements. 9,9-Disubstituted 9,10-Dihydrophenanthrenes.** All three of these hydrocarbons could be induced to rearrange when they were heated with *n*-butyllithium in a solution of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA). It is significant to note that only the 9-aryl substituent underwent migration (path a); no migration of the biphenylyl substituent, and concomitant ring contraction, was observed (path b, **32**) (Scheme III).

In the case of **12**, evidence for the formation of monolithiated **30** (R, Ar = Ph) was obtained by quenching the reaction mixture with $D_2O$ and isolating *trans*-9-deuterio-9,10-diphenyl-9,10-dihydrophenanthrene. These rearrangements were relatively slow in refluxing TMEDA, the 9-methyl-9-phenyl derivative **11** being the least reactive. Under these conditions, extensive aromatization of **30** into **31** occurred by apparent elimination of lithium hydride.

**5-Substituted 5,6-Dihydrophenanthridines.** Treatment of 5-methyl-5,6-dihydrophenanthridine (**14**) with an excess of *n*-butyllithium in THF over a 24-h period led to no rearrangement. However, a combination of *n*-butyllithium and potassium *tert*-butoxide at the reflux temperature of hexane did induce rearrangement of 5-phenyl-5,6-dihydrophenanthridine (**15**). In contrast with the aforementioned dihydrophenanthrenes, however, migration of phenyl from nitrogen to the adjacent $C_6$ carbon was the minor part of rearrangement (10% of 6-phenylphenanthridine (**33**)). The principal course of rearrangement was that involving the biphenylyl substituent and leading to ring contraction; a 70% yield of *N*-phenyl-9-fluorenylamine (**34**) was realized (Scheme IV).

**2-(2-Biphenylyl)-1,1-diphenylethene (35).** A curious isomerization encountered in this study is worthy of comment because it is relevant to the possible, but undetected, ring contraction depicted in Scheme III (path b). When **35** was heated with *n*-butyllithium in TMEDA for 72 h and then hydrolyzed, a 20% yield of 9-(diphenylmethyl)fluorene (**36**) was isolated. The formation of **36** can be understood as arising by lithiation at the 2'-biphenylyl position[16] and the intramolecular addition of **37** to the ethenyl group to form a salt of **36**. This salt undergoes further lithiation to the dilithium salt of **36**, **38**. That **38** was the precursor to **36**, which was isolated after hydrolysis, was shown by hydrolyzing with $D_2O$; in this case, dideuteriated **36**, namely, **39**, was isolated (Scheme V).

This finding supports the view that were an anion such as **37** involved in the rearrangement of 9,9-diphenyl-9,10-dihydrophenanthrene (Scheme III, Ar, R = Ph), then 9-(diphenylmethyl)fluorene (**36**) should have been formed. Since **36** was in fact not observed in the rearrangement product of **12**, the intermediacy of **37** can be ruled out.

**Attempted Rearrangements. Xanthene.** 10-Xanthyllithium (**40**) can readily be generated from xanthene and *n*-butyllithium.[17] However, despite employing THF or TMEDA media over prolonged periods, no rearrangement of any kind (such as that depicted in

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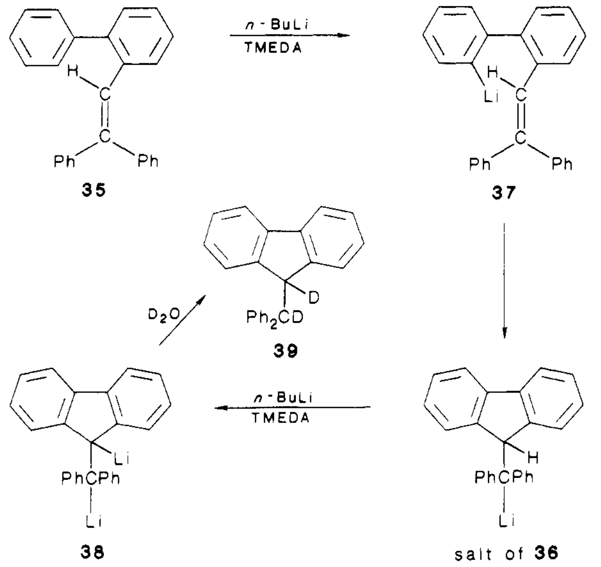
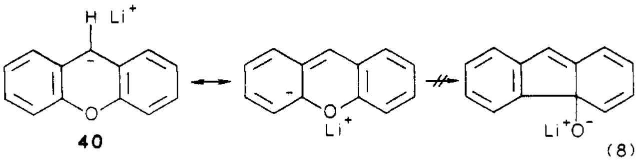
(16) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107.

(17) Cusic, J. W. U.S. Patent 2,368,006; *Chem. Abstr.* **1945**, *39*, 3630.

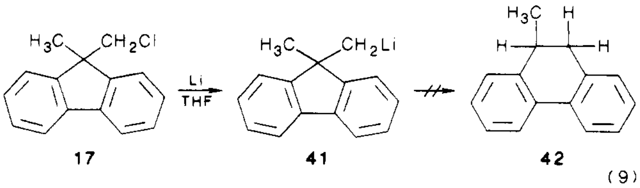
**Scheme V**



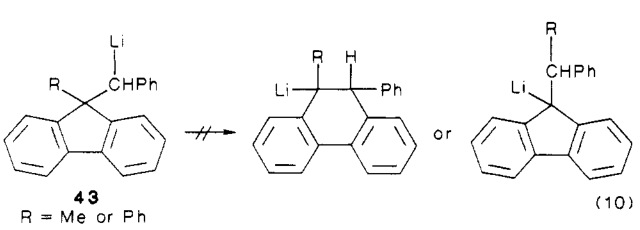
eq 8) could be detected. Possibly the planarity of **40** interferes with the overlap of the rings' $\pi$-electrons.


(8)

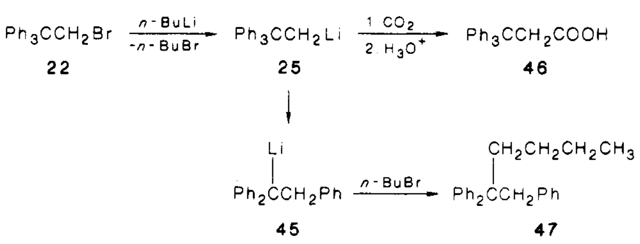
**9,9-Disubstituted Fluorenes.** 9-(Chloromethyl)-9-methylfluorene (**17**) was converted into its lithio derivative (**41**) by use of lithium metal in THF. Despite prolonged standing at 25 °C or heating at 45 °C, no rearrangement to 9-methyl-9,10-dihydrophenanthrene (**42**) was observed (eq 9). It is significant to note that the open-chain analogue of **41**, (2,2-diphenylpropyl)lithium, does rearrange under precisely these conditions.[18]


(9)

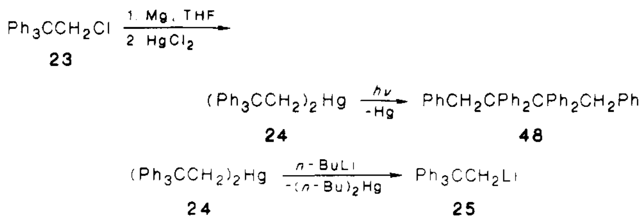
9-Benzyl-9-methylfluorene (**18**) and 9-benzyl-9-phenylfluorene (**19**) were individually lithiated at the benzylic carbon (**43**) by $n$-butyllithium in THF or an $n$-butyllithium–potassium *tert*-butoxide combination. However, prolonged heating of **43** led to no rearrangement (eq 10). Again, the open-chain analogues of **43**, 1,2,2,2-tetraphenylethyl metallics, do undergo skeletal rearrangement.[19]


(10)

**Scheme VI**

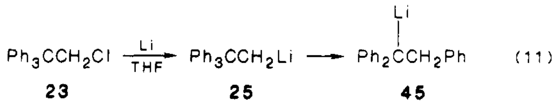


**Scheme VII**



Although no rearrangement took place, it is important to mention that at higher temperatures (70 °C) 9-benzyl-9-phenylfluorene and $n$-butyllithium did yield the cleavage product, 9-phenylfluorene (**44**).

**Rearrangements of 2,2,2-Triphenylethyl Derivatives.** As is well-known from previous work,[20] the reaction of 2-chloro-1,1,1-triphenylethane (**23**) with lithium metal leads to the formation of (2,2,2-triphenylethyl)lithium (**25**) and (1,1,2-triphenylethyl)lithium (**45**), the latter being the rearrangement product of **25** (eq 11). In this study we monitored the reaction of **23** with metal lithium in THF by ESR spectroscopy at −50 °C and by $^1H$ NMR spectroscopy at 0 °C. The ESR spectra of the reaction solutions displayed strong signals of a width of 25–30 G that persisted throughout the reaction when maintained below −50 °C. A moderately resolved hyperfine pattern of five lines having a spacing of 5 G was observed in the ESR signal below −60 °C. The ESR signal weakened as the solution warmed up, so that examination of the reaction solutions by $^1H$ NMR spectroscopy at >0 °C showed no broadening of the signals, which paramagnetic components might be expected to cause.



$$\underset{23}{Ph_3CCH_2Cl} \xrightarrow[THF]{Li} \underset{25}{Ph_3CCH_2Li} \longrightarrow \underset{45}{Ph_2\overset{Li}{C}CH_2Ph} \qquad (11)$$

Because radicals were undoubtedly present throughout the foregoing reaction (eq 11), the question arose whether the rearrangement necessarily involves radical intermediates. To answer this, we sought to generate **25** by avoiding obvious sources of electrons, like lithium metal. In one approach, 2-bromo-1,1,1-triphenylethane (**22**) was treated with $n$-butyllithium in THF at 0 °C. Workup with carbon dioxide gave two products, **46** and **47**. The formation of **47** indicates that **25** had been generated by bromine–lithium exchange and had rearranged to **45**. This benzylic lithium reagent then coupled readily with $n$-butyl bromide to produce **47**. The nonbenzylic lithium reagent **25** does not couple rapidly with $n$-butyl bromide and hence would survive to undergo carbonation and yield the unrearranged acid **46** (Scheme VI).

Because of the reaction's complexity, a cleaner method of generating **25** and monitoring its rearrangement spec-

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[18] Zimmerman, H.; Zweig, A. *J. Am. Chem. Soc.* **1961**, *83*, 1196.

[19] Crimmins, T. F.; Murphy, W. S.; Hauser, C. R. *J. Org. Chem.* **1966**, *31*, 4273.

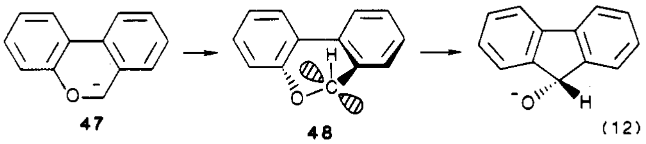
[20] Grovenstein, E., Jr.; Williams, L. P. *J. Am. Chem. Soc.* **1961**, *83*, 412.

troscopically was sought. A suitable method proved to be the interaction of bis(2,2,2-triphenylethyl)mercury (**24**) with *n*-butyllithium. The necessary **24** was prepared from (2,2,2-triphenylethyl)magnesium chloride (which does *not* rearrange) and mercury(II) chloride. The mercury compound is light-sensitive and eventually yields mercury and 1,2,2,3,3,4-hexaphenylbutane (**48**) (Scheme VII). From **24**, the unrearranged **25** could smoothly be generated with *n*-butyllithium at −60 °C and the reaction monitored to completion over 4 h by ESR spectroscopy. Periodic spectral scans of up to 1000 G in width failed to detect any ESR absorptions whatsoever. In a parallel rearrangement monitored by $^1$H NMR spectroscopy at 40 °C, no broadening of signals or CIDNP emissions were detected during the course of reaction.

## Discussion

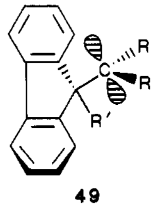
From a consideration of which of the foregoing carbanions **11–19** undergo rearrangement, we can conclude whether π-orbital overlap is a generally important constraint for [1,2] rearrangements involving carbon–oxygen and carbon–carbon sites, as well as carbon–nitrogen centers (eq 1). Furthermore, the case for such π-orbital overlap can be strengthened by observing the migratory aptitudes for competing rearrangements in cyclic systems **11–15**.

For the carbon–oxygen system, the great difference in the behavior of the isomeric dibenzopyrans is illuminating: the anion of 6*H*-dibenzo[*b*,*d*]pyran (**47**) rearranges very rapidly at 0 °C (eq 12);[11] the anion of 9*H*-dibenzo[*b*,*e*]pyran is very stable and shows no tendency whatsoever to rearrange. This contrast in reactivity is consistent with the nonplanar conformation possible with **47**, which permits the carbanion orbital to overlap with the biphenylyl π-orbitals (**48**) and thus anticipate bonding. Such overlap would seem far less accessible to the planar xanthene anion **40**.

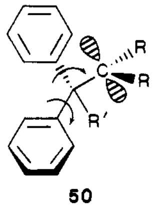


**47** **48** (12)

For the carbon–carbon case, the failure of 9-fluorenylmethyl anions (**49**), derived from **17–19**, to rearrange, even though their open-chain analogues do so readily (2,2-diphenylpropyl anions, **50**), suggests that the bridging necessary to permit π-orbital overlap (**20**) is too strained to be formed. The rotation of the aryl rings possible in **50** would make the formation of the requisite bridging intermediate (**5**) of lower energy.



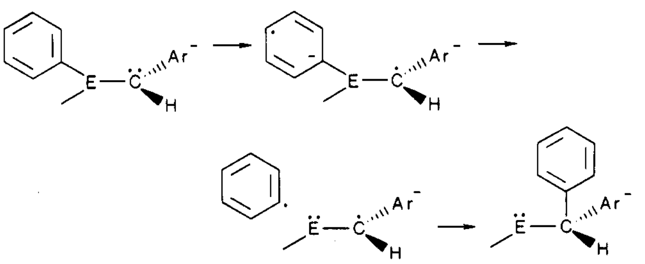
**49**

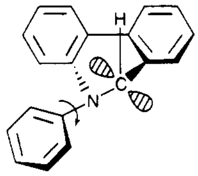


**50**

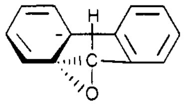
Since it therefore appears that π-orbital overlap is important in all such skeletal carbanionic rearrangements, such overlap should also be decisive in determining group migratory aptitudes, as those observed with dihydrophenanthridines (**14**, **15**) and dihydrophenanthrenes (**11–13**). With 5-phenyl-5,6-dihydrophenanthridine (**15**), the biphenylyl group migrated about 7 times faster than the phenyl group. This outcome can be attributed to the relatively rigidly held biphenylyl group in the ring system, compared with the freely rotating phenyl group. The former constraint would thus aid overlap with the carbanionic site (**51**).

**Scheme VIII**





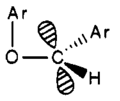
**51**



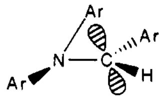
**52**

With the dihydrophenanthrenes, however, no migration of the biphenylyl group whatsoever was observed (Scheme III, path b); only the 9-aryl substituent underwent rearrangement. In light of the behavior of the phenanthridine system **51**, the reason for this difference may be the extent of bridging required for the migrating group in carbon–oxygen, carbon–nitrogen, and carbon–carbon systems. As has already been discerned, it is highly unlikely that 6*H*-dibenzo[*b*,*d*]pyran undergoes rearrangement (eq 12) via a fully symmetrically bridged intermediate **52**. Such a dibenzocyclopentadiene epoxide-like structure should be very strained and as difficult to form as that needed for the carbon–carbon case (**20**), where no rearrangement occurs.

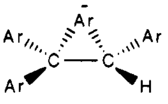
For this reason, it is appealing to suggest that as one goes from the carbon–oxygen to the carbon–nitrogen to the carbon–carbon rearrangement, the bridging involved may become more symmetrical (**53–55**). By demanding less bridging in the transition state, the 6*H*-dibenzo[*b*,*d*]pyran (**47**) and 5-phenyl-5,6-dihydrophenanthridine (**51**) could still allow π-orbital overlap between the carbanion and the biphenylyl π-cloud without encountering excessive ring strain. With the 9,10-dihydrophenanthrenes, the strain involved in forming a symmetrical intermediate can be minimized by migration of the 9-aryl substituent and avoiding the migration of the biphenylyl group.



**53**



**54**

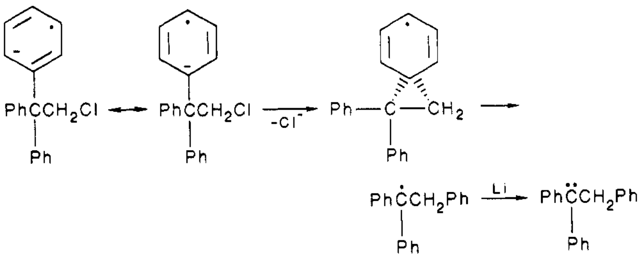


**55**

If one proposes a longer range interaction of a carbanion and an aryl group's π-orbitals, as in **53** and **54**, there still remains the question of whether this interaction is nucleophilic substitution ($S_N2$) or single-electron transfer (SET). In the nucleophilic view, new bonding is initiated between the carbanion and the antibonding π-orbitals of the migrating aryl group. In an SET process, the carbanion would donate an electron to the aryl's antibonding orbitals, creating a biradical. If such intermediates were involved, these rearrangements would proceed, not via carbanions, but by way of radical-anion cleavage and radical recombination pathways (Scheme VIII).

A choice between an $S_N2$ and an SET mechanism can only be made when signs of unpaired electrons are ob-

Scheme IX

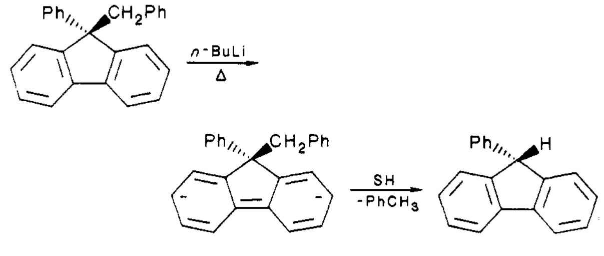


served in such rearrangements. In a previous study of the carbon–nitrogen rearrangement and the present study of the carbon–carbon case, the triphenylethyl anion, such rearrangements have been monitored by ESR and $^1$H NMR spectroscopy in the search for long-lived or short-lived organic free radicals. Since no radicals were observed, we have no firm basis for suggesting radical involvement in these cases. Nevertheless, simply on the basis of this negative evidence, it is also not established that such rearrangements must be carbanionic $S_N2$ processes.

But there are definite indications of radical involvement in some of these rearrangements. First of all, in the Grovenstein–Zimmerman rearrangement, as commonly carried out,[21] β-arylethyl chlorides are treated with alkali metals in donor solvents. It is generally assumed that initially β-arylethyl metallics are generated and that these then rearrange. This assumption has only been experimentally established in a few cases, however, and in many other instances, only the final rearranged products have been characterized.

Recent studies with alkali metals and β-phenyl-β-2- and -4-pyridylethyl chlorides[7] and this present study with lithium metal and 2,2,2-triphenylethyl chloride (**23**) have shown that ESR-active organic radicals are generated during these reactions and persist until the chloride is completely consumed. The signal observed with **23**, a hyperfine pattern of five lines with a splitting of 5 G, is consistent with the type of radical anion formed by the 1,1,1-triphenylethane system, where the electron is largely localized on the ortho and meta positions of one benzene ring.[22] Such an intermediate could then lead to rearranged products as in Scheme IX. This SET mechanism would accommodate all of the known migratory aptitudes of such processes.

Finally, there are spectroscopy indications of free-radical formation in the anionic rearrangement of 6*H*-dibenzo[*b*,*d*]pyran (**47**) and other ethers,[8–11] and the fragmentation of 9-benzyl-9-phenylfluorene (**19**) under conditions of attempted rearrangement suggests SET by *n*-butyllithium to the biphenylene system[23] (eq 13).



(13)

In conclusion, it is conceivable that the greater electron affinity of the biphenylyl groups[24] in **19** and **47**, compared with the phenyl group, not only fosters SET processes but increases the lifetime of the intermediate radical anions. Ongoing work with the 4-biphenylylethyl anion is testing this hypothesis.[25]

## Experimental Section

**Instrumentation.** All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on either a Perkin-Elmer 457 or 238B grating spectrophotometer, and the samples were prepared in solution, as KBr pellets, or as mineral oil mulls. The proton nuclear magnetic resonance spectra ($^1$H NMR) were measured with a Varian spectrometer, Model EM360. The values are reported on the $\delta$ scale in parts per million with reference to internal tetramethylsilane, followed by the relative proton intensities and the coupling constants (*J*) in hertz. Mass spectra were determined either with a MS/902 CIS 2 instrument equipped with a V6 Datasystem 2040 computerized recorder or with a Varian MAT spectrometer, Model CH5. Vapor-phase chromatographic analysis (VPC) and isolations were carried out on an F&M chromatograph, Model 720, equipped with a 6 ft × 0.25 in. column of 10% SE-30 silicone gum rubber on Chromosorb P. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

**Inert Reaction Media.** All preparations and reactions involving air- and moisture-sensitive organometallic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen, with adherence to published procedures.[26] Solvents of reagent grade were used in all reactions. Peroxides were removed from diethyl ether and tetrahydrofuran (THF) by passing such solvents through a column of neutral alumina under nitrogen. The eluted solvents were then allowed to reflux over $LiAlH_4$ for 5 h and then distilled. Alkane solvents were likewise allowed to reflux over and then to be distilled from $LiAlH_4$. Aromatic hydrocarbons (benzene, toluene, and mesitylene) were washed consecutively with concentrated $H_2SO_4$, water, aqueous NaOH, and aqueous NaCl before being dried over anhydrous $MgSO_4$. Finally, they were allowed to reflux over $CaH_2$ for 6 h before being distilled.

Alcohols, such as ethanol and methanol, were refluxed over CaO for 4 h and then distilled. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was stored over NaOH pellets overnight, refluxed over fresh slices of sodium metal, and then distilled. The final TMEDA was stored over activated Linde 4A Molecular Sieves under nitrogen. Pyridine was stored over KOH pellets (20 g/kg) for 2 weeks; then it was distilled from a mixture of KOH pellets and Linde 5A Molecular Sieves.

**Reaction Procedures.** The organolithium reagents were either purchased or prepared by known procedures.[27] All such reagents were analyzed just before every use by established titrimetric

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[21] Grovenstein, E., Jr.; Lu, P. C. *J. Org. Chem.* **1982**, *47*, 2928.

[22] 2,2-Diphenylpropane forms a radical anion with alkali metals in DME whose ESR spectrum indicates that the electron spin is localized on one phenyl ring, namely, a five-component hyperfine pattern with a binomial distribution of intensity and a splitting of 4.9 G. Such a pattern is consistent with the interaction of the unpaired electron with the four equivalent ortho and meta protons of one ring. Cf.: Grandberg, I. I.; Golubev, V. B.; Khrolova, O. R. *Zh. Strukt. Khim.* **1967**, *8*, 1021.

[23] Panek, E. J. (*J. Am. Chem. Soc.* **1973**, *95*, 9460) has observed the quantitative formation of the biphenyl radical anion by the treatment of biphenyl with *n*-butyllithium in hexamethylphosphoramide (HMPA) solution.

[24] Biphenyl forms a stable radical anion at 10 °C when treated with potassium metal in THF (Nishiguchi, H.; Nakai, Y.; Nakamura, K.; Ishizu, K.; Deguchi, Y.; Takaki, H. *J. Chem. Phys.* **1964**, *40*, 241). Benzene and the alkylbenzenes form stable radical anions only at temperatures much below room temperature (−80 °C). Cf.: Tuttle, T. R., Jr.; Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 5342.

[25] The generation of (2-(4-biphenylyl)ethyl)lithium by the treatment of bis(2-(4-biphenylyl)ethyl)mercury with *n*-butyllithium in THF at 0 °C proceeds smoothly, since treatment of the reaction solution with $D_2O$ yields 4-(2-deuterioethyl)biphenyl. Furthermore, treatment of the mercury precursor with *n*-butyllithium or potassium *tert*-butoxide in HPMA generates a red solution of the biphenylylethyl anion, which displays a 25-G broad, unresolved ESR signal below −60 °C. Although an unambiguous assignment of this signal to a 2-(4-biphenylyl)ethyl radical cannot yet be made, this observation does show that radical anions can be generated in such systems even though free alkali metal is not involved (Eisch, J. J.; Boleslawski, M. P.; Doetschman, D. C., unpublished studies, 1988).

[26] Eisch, J. J. *Organometallic Syntheses*; Academic: New York, 1981; Vol. 2, pp 3–37.

[27] Eisch, J. J. *Organometallic Syntheses*; Academic: New York, 1981; Vol. 2, pp 89–100.

methods.[28] All reactions conducted in the range 50–120 °C were carried out in a constant-temperature bath of paraffin oil. A Wood's metal bath with an insulating mantle was used for higher temperatures. Temperatures below 0 °C were maintained with dry-ice slurries in various solvents or liquid-nitrogen–solvent slushes.[29]

Hydrolytic workup of reactions generally involved the slow addition of 5% aqueous HCl solution, subsequently making the mixture basic with aqueous KOH solution and then extracting the organic product into diethyl ether. The solvent was removed after drying over anhydrous $MgSO_4$. The residue was examined by thin-layer (TLC), column (CC), or gas (VPC) chromatography.

**Starting Materials.** The following reagents were obtained from commercial sources and were analyzed by chromatographic and spectroscopic methods, in order to ascertain their purity. Where required, they were purified by chromatography, distillation, or recrystallization: xanthene, 2-biphenylcarboxylic acid, 9-fluorenone, triphenylmethane, fluorene, triphenylmethanol, and phenanthridine.

**Substrates for Rearrangements. Phenanthridines.** 5-Methyl-5,6-dihydrophenanthridine (**14**) was prepared by the reduction of phenanthridine methiodide by tin and hydrochloric acid;[30] it is most sensitive to air oxidation and has to be stored under nitrogen. 5-Phenyl-5,6-dihydrophenanthridine (**15**) was prepared in a published five-step synthesis from 9-fluorenone;[31] it is also moderately sensitive to oxygen and must be handled under nitrogen or argon. For this reason, the sample prepared and studied in this work was reanalyzed and its spectral properties were recorded under argon: mp (under Ar) 103–105 °C (lit.[31] mp (in air) 94–96 °C); $^1H$ NMR ($CDCl_3$) $\delta$ 4.7 (s, 2 H, $CH_2$), 6.87–7.90 (m, 13 H, arom); MS, *m/e* 257 ($M^+$); IR $\nu_{max}$ (KBr) absence of NH, C=O bands.

Anal. Calcd for $C_{19}H_{15}N$: C, 88.71; H, 5.83. Found: C, 88.62; H, 5.98.

**9,10-Dihydrophenanthrenes. 9,9-Diphenyl-9,10-dihydrophenanthrene (12).** 2-Biphenylcarboxylic acid was converted into 2-(bromomethyl)biphenyl by the published sequence of forming 2-(hydroxymethyl)biphenyl with $LiAlH_4$[32] and then generating the bromide with an $HBr–H_2SO_4$ mixture.[33] A 1.24-g (5 mmol) sample of the bromide in 20 mL of anhydrous diethyl ether was allowed to react at 0 °C with 360 mg (15 mg-atom) of magnesium turnings to produce the corresponding Grignard reagent (initiation with $I_2$). After 4-h stirring at 0 °C, the Grignard reagent was treated with 728 mg (4 mmol) of benzophenone, whereupon heat was evolved and the solution turned yellow. The mixture was heated under reflux for 12 h and then hydrolyzed with an aqueous $NH_4Cl$ solution. The separated organic layer was dried over anhydrous $CaSO_4$ and evaporated to give a yellow syrup, whose $^1H$ NMR spectrum resembled an 85:15 mixture of 2-(2-biphenylyl)-1,1-diphenylethanol and 1,2-bis(2-biphenylyl)ethane. This mixture was dehydrated directly by being heated for 12 h in 25 mL of benzene, which contained 40 mg of *p*-toluenesulfonic acid. The benzene solution was washed with dilute aqueous $NaHCO_3$ solution and then dried. This organic extract was chromatographed on a silica column and eluted with a hexane–benzene gradient to yield 58% of 2-(2-biphenylyl)-1,1-diphenylethene (**27**): mp 99–101 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.3 (s, H, =CH), 7.4–8.5 (m, 19 H, arom); MS, *m/e* (relative intensity) 332 ($M^+$, 96), 254 (38), 167 (100). The side product, 1,2-bis(2-biphenylyl)ethane, was identified by its mass spectrum: 334 ($M^+$, 24), 167 (100), 152 (32), 43 (71).

Anal. Calcd for $C_{26}H_{20}$: C, 93.97; H, 6.02. Found: C, 93.69; H, 6.28.

A 1.0-g sample of the ethene in 100 mL of glacial acetic acid containing 0.4 mL of concentrated $H_2SO_4$ was heated at reflux for 72 h. The cooled mixture was diluted with 200 mL of ether and this solution extracted repeatedly by water and by aqueous $NaHCO_3$ solution. The ether layer was dried over anhydrous $MgSO_4$ and then evaporated. The residue was recrystallized from glacial acetic acid to provide 850 mg (85%) of 9,9-diphenyl-9,10-dihydrophenanthrene: mp 148–149.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 3.64 (s, 2 H, $CH_2$), 6.6–7.7 (m, 18 H, arom); MS, *m/e* (relative intensity) 332 ($M^+$, 40), 255 (100), 239 (26), 165 (41).

Anal. Calcd for $C_{26}H_{20}$: C, 93.97; H, 6.02. Found: C, 93.85; H, 5.97.

**9-Methyl-9-phenyl-9,10-dihydrophenanthrene (11).** As described above, a 1.23-g (5 mmol) portion of 2-(bromomethyl)biphenyl was converted into its Grignard reagent. Then 480 mg (4 mmol) of acetophenone was added in one portion and the resulting reaction mixture heated at reflux for 24 h. Usual workup led to a crude residue of 1-(2-biphenylyl)-2-phenyl-2-propanol. Without isolation of the alcohol, the residue was dissolved in 30 mL of glacial acetic acid containing 0.5 mL of concentrated $H_2SO_4$. The solution was heated for 72 h at reflux and then worked up as in the preparation of **12**. The organic residue was chromatographed on a silica gel column and a petroleum ether–ethyl acetate gradient used for elution. The oily product (**11**) was isolated in a 51% yield and had the following spectral properties: $^1H$ NMR ($CDCl_3$) $\delta$ 1.65 (s, 3 H, $CH_3$), 2.75–3.5 (quintet, 2 H, $CH_2$), 6.35–7.75 (m, 13 H, arom); MS, *m/e* (relative intensity) 270 ($M^+$, 70), 255 (100); IR (neat) 3106, 2838, 1497, 1484, 1452 $cm^{-1}$.

Anal. Calcd for $C_{21}H_{18}$: C, 93.33; H, 6.66. Found: C, 93.21; H, 6.73.

**Spiro[fluorene-9,9′-(9,10-dihydrophenanthrene)] (13).** As described above, a 1.3-g (5.5 mmol) sample of 2-(bromomethyl)biphenyl was converted into its Grignard reagent. Then 720 mg (4 mmol) of 9-fluorenone was added in one portion and the resulting reaction mixture heated at reflux for 12 h. Usual hydrolytic workup and acid-catalyzed cyclization of the crude alcohol with $H_2SO_4$ in glacial acetic acid gave crude **13**, which was separated by column chromatography on silica gel (petroleum ether–benzene eluent) to yield 960 mg 58% of **13**: mp 193–193.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 3.3 (s, 2 H, $CH_2$), 6.45–8.0 (m, 16 H, arom); MS, *m/e* (relative intensity) 330 ($M^+$, 34), 165 (100).

Anal. Calcd for $C_{26}H_{16}$: C, 94.54; H, 5.45. Found: C, 94.28; H, 5.70.

**9,9-Disubstituted Fluorenes. 9-Benzyl-9-methylfluorene (18).** 9-Methylfluorene was prepared by forming 9-fluorenylsodium from fluorene and sodium amide and then methylating this sodio derivative with methyl iodide, mp 45–46 °C.[34] Then 9.05 g (50 mmol) of 9-methylfluorene in 100 mL of a 7:3 (v/v) mixture of anhydrous tetrahydrofuran and diethyl ether was stirred under nitrogen at 25 °C while 25 mL of 2.2 M *n*-butyllithium in hexane was added dropwise. After 60 min of reaction, 6.3 g (60 mmol) of benzyl chloride in 30 mL of anhydrous ether was introduced dropwise. A further 4-h stirring period was followed by a hydrolytic workup. The separated and dried ($MgSO_4$) organic layer was freed of solvent and the residue recrystallized from 95% ethanol. A yield of 6.3 g (47%) of colorless prisms of **18** was attained, mp 92–93 °C, from 95% ethanol: $^1H$ NMR ($CDCl_3$) $\delta$ 1.33 (s, 3 H, $CH_3$), 2.82 (s, 2 H, $CH_2$), 6.25–7.18 (m, 13 H, arom).

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.45; H, 6.55.

**9-Benzyl-9-phenylfluorene (19).** A solution of 1.30 g (5.37 mmol) of 9-phenylfluorene in 10 mL of anhydrous tetrahydrofuran was stirred under nitrogen at 0 °C while being treated dropwise with 3.5 mL of 1.6 M *n*-butyllithium in hexane. The reaction mixture, which turned orange-red in color, was then stirred at 20 °C for 90 min and finally treated with 680 mg (5.37 mmol) of benzyl chloride at 0 °C. The resulting colorless mixture was further stirred for 2 h and hydrolyzed with a mixture of water and ethyl ether. The organic layer was separated, dried over $MgSO_4$, and evaporated to yield the crude product, 1.78 g (91%), mp 135–137 °C. Recrystallization from a hexane–methylene chloride pair gave colorless **19**: mp 137.0–137.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 3.72 (s, 2 H, $CH_2$) and 6.30, 6.73, and 7.18 (m, 18 H); MS, *m/e* 332, 241, 91.

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.78; H, 6.02.

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[28] Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.

[29] Weast, R. B., Ed. *Handbook of Chemistry and Physics*, 58th ed.; The Chemical Rubber Co., Cleveland, OH, 1977; p D-215.

[30] Finkelstein, J.; Linder, S. *J. Am. Chem. Soc.* **1950**, *72*, 3282.

[31] Durst, T. *Can. J. Chem.* **1977**, *55*, 44.

[32] Campbell, N. *Recl. Trav. Chim. Pays-Bas* **1948**, *67*, 489.

[33] Campbell, N.; Neale, R. F.; Wall, R. A. *J. Chem. Soc.* **1959**, 1409.

[34] Scherf, G. W. H.; Brown, R. K. *Can. J. Chem.* **1961**, *39*, 799.

**9-(Chloromethyl)-9-methylfluorene (17).** Under a nitrogen atmosphere, a cooled solution of 9.0 g (50 mmol) of 9-methylfluorene in 100 mL of a 7:3 (v/v) mixture of anhydrous tetrahydrofuran and diethyl ether was treated dropwise with 30 mL of 2.1 M *n*-butyllithium in hexane. After 60 min of reaction, the red solution was transferred under nitrogen to an addition funnel and added dropwise to 100 mL of methylene chloride at such a rate that the red color was immediately discharged. After stirring overnight, the reaction mixture was hydrolyzed and the separated organic layer dried over anhydrous $CaSO_4$ and freed of volatile components. The residue (12.6 g) was chromatographed on a two-section column (top, 15 cm of charcoal; bottom, 45 cm of silica gel) with cyclohexane as the eluent. The first eluate (6.2 g) was a blue oil; the second eluate amounted to 2.5 g of a colorless oil, which solidified (mp 35–38 °C). From ethanol this crystallized as pure **17**: mp 41–42 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.58 (s, 3 H, $CH_3$), 3.72 (s, 2 H, $CH_2Cl$), 7.15–7.83 (m, 8 H, arom); MS, *m/e* 230 (25), 228 (75).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73. Found: C, 78.95; H, 5.48.

**Arylethane Derivatives. 1,1,1-Triphenylethane (21).** A solution of 10.0 g (43 mmol) of triphenylmethane in 125 mL of anhydrous tetrahydrofuran was stirred at 0 °C, while 30 mL of 1.6 M *n*-butyllithium in hexane was added dropwise. The resulting red solution was stirred for 2 h, and then 10 mL of methyl iodide was introduced dropwise. When the red color had been completely discharged, the reaction mixture was hydrolyzed. The organic layer was separated, dried over anhydrous $CaSO_4$, and evaporated. The residue was recrystallized from 95% ethanol to yield 5.6 g (51%) of 1,1,1-triphenylethane (**21**): mp 93–95 °C;[35] $^1H$ NMR ($CCl_4$) $\delta$ 2.17 (s, 3 H, $CH_3$), 7.10 (s, 15 H, arom).

**2-Chloro-1,1,1-triphenylethane (23).** In a manner analogous to the preparation of **21**, 13.0 g (51 mmol) of triphenylmethane in 70 mL of a 5:2 (v/v) THF–$Et_2O$ mixture was lithiated with 33 mL of 1.6 M *n*-butyllithium in hexane.[36] After a 60-min reaction period, the red solution was transferred under nitrogen to an addition funnel and added dropwise to 100 mL of methylene chloride. The resulting colorless solution was stirred for 60 min before being quenched with 100 mL of water. The separated organic layer was dried over anhydrous $CaSO_4$ and freed of volatile components in vacuo. The resulting oil was crystallized from cyclohexane to give 8.0 g (53%) of **23**: mp 99–101 °C (lit.[36] mp 101–101.8 °C); $^1H$ NMR ($CCl_4$) $\delta$ 4.53 (s, 2 H, $CH_2$), 7.23 (s, 15 H, arom).

**2-Bromo-1,1,1-triphenylethane (22).** The same procedure given for **23** was adapted for the preparation of the bromo derivative **22**, except that methylene bromide was used. The usual workup yielded 50% of **22**: mp 90–91 °C (lit.[37] mp 93 °C); $^1H$ NMR ($CCl_4$) $\delta$ 4.41 (s, 2 H, $CH_2$), 7.21 (s, 15 H, arom).

**Bis(2,2,2-triphenylethyl)mercury (24). (CAUTION**: toxic mercury compounds). The chloride **23** was converted into the corresponding Grignard reagent (without skeletal rearrangement[38]) by allowing 16.9 g (58 mmol) of it to react with 3.2 g (130 mg-atom) of magnesium turnings in 150 mL of anhydrous THF. The red solution was further stirred for 1.5 h at 25 °C and then filtered under nitrogen from the remaining magnesium. To the stirred filtrate was added dropwise 5.4 g (20 mmol) of mercury(II) chloride in 100 mL of anhydrous THF. The reaction mixture was stirred for 35 h at 20–25 °C and then hydrolyzed with a saturated, aqueous $NH_4Cl$ solution. The separated organic layer was dried over anhydrous $CaSO_4$ and evaporated in vacuo. The residue was redissolved in benzene, the solution treated with animal charcoal, and the charcoal filtered off. The benzene filtrate was diluted with methanol and cooled to yield 8.6 g (60%, based on $HgCl_2$) of **24**: mp 181–182 °C; $^1H$ NMR ($CCl_4$) $\delta$ 2.05 (s, 2 H, $CH_2$), 7.12 (s, 15 H, arom).

Anal. Calcd for $C_{40}H_{34}Hg$: C, 67.17; H, 4.79. Found: C, 67.18; H, 4.85.

This mercury compound is light-sensitive: after 1 month of standing in diffuse light, a sample of **24** in tetrahydrofuran-$d_8$ deposited mercury droplets and formed 1,2,2,3,3,4-hexaphenylbutane: $^1H$ NMR (THF-$d_8$) $\delta$ 5.06 (s, 4 H, $CH_2$), 7.39 (s, 30 H, arom).

**Rearrangements. Xanthene (16) (Attempted).**[38] A solution of 3.64 g (20 mmol) of xanthene in 150 mL of a 2:1 mixture of anhydrous cyclopentane and *N,N,N′,N′*-tetramethylethylenediamine was treated with 57 mL of 1.4 M *n*-butyllithium in hexane. The deep red solution was stirred at 20–25 °C for 6 days. After hydrolytic workup, the separated and dried organic layer was evaporated to a solid organic residue, which by IR, $^1H$ NMR, and TLC analysis revealed only starting material.

**5-Methyl-5,6-dihydrophenanthridine (14) (Attempted).** A solution of 3.90 g (20 mmol) of this amine (very air-sensitive; must be stored after preparation under nitrogen) was dissolved in 40 mL of anhydrous THF and then treated at 20 °C with 35 mL of 1.5 M *n*-butyllithium in hexane. After 24 h at 20–25 °C, a hydrolytic workup in air gave a dried, organic layer that upon removal of volatiles left a residue, which by $^1H$ NMR and IR spectrometry showed the presence of only **14** ($^1H$ NMR ($CDCl_3$) $\delta$ 2.82 (s, 3 H), 4.13 (s, 2 H), and 6.65–7.8 (m, 8 H, arom)) admixed with a small amount of 5-methylphenanthridine-6(5*H*)-one ($^1H$ NMR ($CDCl_3$) $\delta$ 3.0 (s)).

**5-Phenyl-5,6-dihydrophenanthridine (15).** A solution of 1.28 g of **15** (5.0 mmol) in 100 mL of dry hexane, cooled in an ice bath, was treated with 12 mL of 1.35 M of *n*-butyllithium in hexane. The resulting pale yellow solution was treated with 560 mg (5.0 mmol) of potassium *tert*-butoxide, whereupon the solution became fluorescent blue. After the mixture was heated at reflux for 4 days, the reaction mixture was treated with an aqueous solution of $NH_4Cl$. The organic layer, augmented by ethyl ether, was separated, dried over anhydrous $MgSO_4$, and evaporated under vacuum. The $^1H$ NMR spectrum of the residue revealed the presence of about 25% of **15**, 70% of *N*-phenyl-9-fluorenylamine (**34**), and some 6-phenylphenanthridine (**33**). This mixture was subjected to column chromatography on alumina with a hexane–methylene chloride gradient. The first fractions yielded *N*-phenyl-9-fluorenylamine (65%), which after recrystallization from 95% ethanol melted at 123–124 °C (lit.[39] mp 123–124 °C): $^1H$ NMR ($CDCl_3$) $\delta$ 4.0 (s, br s, 1 H, NH), 5.7 (s, 1 H, CH), 6.7–7.7 (m, 13 H, arom). About 20% of unreacted **15** was recovered, as well as a small amount of oxidized starting material, 5-phenylphenanthridine-6(5*H*)-one, mp 116–117 °C. Finally, about 10% of 6-phenylphenanthridine was separated by rechromatography on alumina: mp 109–110 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.2–8.2.

**9,9-Diphenyl-9,10-dihydrophenanthrene (12).** A solution of 1.36 g (4.1 mmol) of **12** in 15 mL of freshly distilled, anhydrous TMEDA was treated with 5 mL of 1.7 M *n*-butyllithium. The resulting mixture was heated at reflux for 4 days. The dark red mixture was then hydrolyzed with an excess of 1 N aqueous HCl. Diethyl ether was added, and the separated organic layer was repeatedly extracted with 2 N aqueous HCl. The resulting ether layer was dried over anhydrous $MgSO_4$ and then evaporated to give the crude product, whose $^1H$ NMR spectrum showed the presence of **30** (R, Ar = Ph) (65%), **31** (R, Ar = Ph) (25%), and an unidentified component (10%). Column chromatography of this mixture on silica gel with an ether–benzene gradient gave pure *trans*-9,10-diphenyl-9,10-dihydrophenanthrene (mp 167–168.5 °C (lit.[40] mp 168–169 °C); $^1H$ NMR ($CDCl_3$) $\delta$ 4.3 (s, 2 H, CH) and 6.3–7.8 (m, 18 H, arom)) and pure 9,10-diphenylphenanthrene, mp 236–239 °C (lit.[41] mp 240 °C).

A similar reaction was conducted, but the first step in the hydrolytic workup was conducted with $D_2O$. The separated 9,10-diphenyl-9,10-dihydrophenanthrene (mp 165–167 °C) was shown by $^1H$ NMR ($\delta$ 4.3 (1 H, CH) and 6.3–7.8 (m, 18 H, arom)) and mass spectrometry (*m/e* (relative intensity) 334 (5.2), 333 (22), 332 (50)) to be largely monodeuteriated at $C_9$.

**2-(2-Biphenylyl)-1,1-diphenylethene (35).** A solution of 330 mg (1.0 mmol) of **35** in 7.5 mL of anhydrous TMEDA was treated with 2.5 mL of 1.6 M *n*-butyllithium in hexane. The resulting

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deep red solution was heated at reflux for 72 h and then hydrolyzed with an excess of aqueous 2 N HCl. Ether was added, and the organic layer was repeatedly extracted with aqueous 2 N HCl. The drying and evaporation of the organic layer gave a residue, whose $^1$H NMR spectrum indicated the presence of 80% of **35** and 20% of 9-(diphenylmethyl)fluorene (**36**). Column chromatography of this residue on silica gel with an ether–hexane gradient gave pure **36**: mp 212–214 °C (lit.[42] mp 216 °C); $^1$H NMR (CDCl$_3$) $\delta$ 4.1–5.0 (d of d, 2 H, 2 CH) and 6.55–7.75 (m, 18 H, arom).

From a similar reaction that was initially hydrolyzed with D$_2$O was isolated **36**, whose $^1$H NMR spectrum showed only aromatic protons. Accordingly, the saturated CH groups between 4.0 and 5.0 ppm were both deuteriated.

**9-Methyl-9-phenyl-9,10-dihydrophenanthrene (11).** A solution of 1.35 g (5.0 mmol) of **11** in 25 mL of anhydrous TMEDA was treated with 20 mL of 1.6 M *n*-butyllithium in hexane. The mixture was heated at reflux for 100 h and then quenched with aqueous 2 N HCl. The organic layer was increased with ethyl ether and then repeatedly extracted with aqueous 2 N HCl. The ether layer was dried over anhydrous MgSO$_4$ and then evaporated to provide a residue, whose $^1$H NMR spectrum showed the presence of 80% of starting **11** and 20% of 9-methyl-10-phenylphenanthrene. Column chromatography on silica gel with an ether–hexane gradient gave pure 9-methyl-10-phenylphenanthrene ($^1$H NMR (CDCl$_3$) $\delta$ 2.45 (s, 3 H) and 7.45–8.58 (m, 13 H, arom)).[43]

**Spiro[fluorene-9,9′-(9,10-dihydrophenanthrene)] (13).** A solution of 1.65 g (5.0 mmol) of **13** in 20 mL of anhydrous TMEDA was treated with 9 mL of 1.67 M *n*-butyllithium in hexane. During a 24-h reflux, the mixture became deep red; this color persisted through the overall 100-h reflux period. Hydrolytic workup as with **11** gave a crude reaction product, whose $^1$H NMR spectrum showed the presence of dibenzo[*g*,*p*]chrysene. (When the reaction was conducted at 50–60 °C for 100 h, instead of at reflux, only the dihydrodibenzo[*g*,*p*]chrysene was observed.) Chromatographic separation on silica gel gave either the aromatic hydrocarbon ($^1$H NMR (CDCl$_3$) $\delta$ 7.2–7.6 and 8.2–8.6)[44] or its dihydro derivative: $^1$H NMR (CDCl$_3$) $\delta$ 4.33 (s, 2 H, CH) and 6.5–8.8 (m, 16 H, arom).[45]

**9-(Chloromethyl)-9-methylfluorene (17) (Attempted).** A solution of 600 mg (2.6 mmol) of **17** in 35 mL of anhydrous THF was stirred with small, clean pieces of lithium (300 mg, 43 mg-atom). As the reaction began (shiny lithium surface), the stirred reaction mixture was cooled with a dry ice–acetone bath. After 90 min at this temperature, a 10-mL aliquot was hydrolyzed. From such a workup only 9,9-dimethylfluorene was found in the organic layer: mp 86–89 °C;[46] $^1$H NMR (CDCl$_3$) $\delta$ 1.45 (s, 6 H, CH$_3$), 7.2–7.45 (m, 6 H, arom), 7.63–7.82 (m, 2 H, arom).

The rest of the reaction mixture was stirred for 12 h at 20–25 °C, but hydrolytic workup again gave only 9,9-dimethylfluorene; no sign of 9-methyl-9,10-dihydrophenanthrene was observed.

Repetition of the reaction of **17** with lithium at 40–45 °C for 3.5 h (similar to the successful rearrangement of 1-chloro-2,2-diphenylpropane by lithium[18]) again gave only 9,9-dimethylfluorene, the unrearranged hydrocarbon.

**9-Benzyl-9-methylfluorene (18) (Attempted).** A solution of 1.25 g (0.5 mmol) of **18** in 25 mL of THF was treated with 10 mL of 2.1 M *n*-butyllithium in hexane. The red reaction mixture was stirred for 12 h at 20–25 °C and then hydrolyzed. The crude organic product was examined by TLC, IR, and $^1$H NMR spectral analysis and found to consist only of starting **18**.

A reaction conducted for 48 h at 20–25 °C also gave no sign of rearrangement.

**9-Benzyl-9-phenylfluorene (19) (Attempted).**[47] **(a) At 25 °C.** To a stirred suspension of 500 mg (1.65 mmol) of **19** and 184 mg (1.65 mmol) of potassium *tert*-butoxide in 10 mL of hexane under nitrogen was added 2.82 mL of 1.6 M *n*-butyllithium. The red-colored reaction mixture was stirred for 48 h at 25 °C and then worked up with water. Usual purification revealed the presence of only unchanged **19**.

**(b) At 70 °C.** The reaction described in part a was repeated, except that after the mixture was stirred for 24 h at 25 °C, the reaction was allowed to proceed for 24 h at 70 °C. Hydrolytic workup and analysis by HPLC (silica gel with hexane–CH$_2$Cl$_2$, 95:5 (v/v)) showed the presence of starting material and 9-phenylfluorene and the absence of fluorene, diphenylmethane, and 9-benzhydrylfluorene. Other unidentified components showed aliphatic CH$_2$ peaks in their MS patterns and $^1$H NMR spectra.

**1,1,1-Triphenylethane (21) (Attempted).** A stirred solution of 2.58 g (10 mmol) of **21** in 20 mL of THF was treated at −65 °C with 6.3 mL of 1.6 M *n*-butyllithium in hexane. The reaction mixture was stirred for 60 min at −65 °C and for 3 h at 0 °C. Treatment with gaseous CO$_2$ and hydrolytic workup gave no detectable triphenylacetic acid, only 92% of **21**. No other compound could be detected.

Similar results were obtained when the reaction was conducted in TMEDA at 0 °C.

**2-Bromo-1,1,1-triphenylethane (22).** A solution of 35 mL of 1.6 M *n*-butyllithium in hexane was added to a stirred solution of 9.95 g (30 mmol) of **22** in 200 mL of anhydrous THF at 0 °C. After the resulting red solution was stirred for 6 h at 0 °C, dry, gaseous CO$_2$ was passed into the solution for 30 min. The reaction mixture was then poured into 500 mL of aqueous 2 N NaOH. The organic layer was diluted with ether, dried over anhydrous CaSO$_4$, and evaporated under reduced pressure. The residual 11.0 g of oil was passed through a silica gel column (90 × 5 cm) by using hexane as the eluent. The major fraction, 8.5 g, was a colorless oil that was homogeneous by the criterion of TLC on silica gel with benzene–hexane gradients: $^1$H NMR (CCl$_4$) $\delta$ 0.8–2.08 (m, 7 H, aliphatic), 2.40–2.78 (m, 2 H, aliphatic), 3.35 (s, 2 H, CH$_2$), 6.8–7.3 (m, 15 H, arom); MS, *m*/*e* 314. This compound is 1,2,2-triphenylhexane.

Anal. Calcd for C$_{24}$H$_{26}$: C, 91.67; H, 8.33. Found: C, 91.89; H, 8.10.

The aqueous layer from the reaction was acidified and extracted with ethyl ether. The ethereal layer was dried over solid CaSO$_4$ and evaporated to yield 900 mg of oil. Recrystallization from aqueous ethanol gave 3,3,3-triphenylpropionic acid, mp 173–176 °C (lit.[20] mp 179–180 °C). Its $^1$H NMR spectrum (CDCl$_3$) displayed a CH$_2$ singlet at 3.70 ppm.

**2-Chloro-1,1,1-triphenylethane (23) with Lithium Metal. (a) ESR Monitoring of the Reaction.** Under nitrogen, a three-necked, 500-mL flask provided with a magnetic stirrer and some crushed glass was charged with 250 mL of anhydrous THF and 700 mg (100 mmol) of freshly cut pieces of lithium metal. To this stirred mixture was added, at 25 °C, 4 mL of a solution of 10.0 g (34.3 mmol) of **23** in 25 mL of THF. After the reaction had started (coloration of solution and brightening of the lithium surface), the temperature of the reaction bath was lowered to and maintained at −65 °C. The balance of the solution of **23** was introduced dropwise. The resulting red solution was stirred at −65 °C while samples were removed periodically and transferred, under nitrogen, to an ESR tube. Such samples were immediately placed in the probe of an ESR spectrometer (Varian EPR spectrometer system, Model V4502), and by scanning over a 250-G range at −50 °C, a strong signal could be detected. Such signals persisted for over 2 h at this low temperature. When the temperature of the reaction mixture was allowed to rise to 0 °C, the sample showed a large signal envelope of 25–30 G. The signals displayed by reaction-mixture samples continued to be strong for 3 h. On cooling samples to −60 °C before ESR examination, the observed signals were diminished in intensity; however, rewarming the sample restored the signal intensity. During this period, a moderately resolved pattern of five lines, having a spacing of about 5 G, persisted. After a total reaction time of 4 h, the mixture was hydrolyzed with 50 mL of water. The organic fraction was taken up in ether, the ethereal layer separated and dried over MgSO$_4$, and the resulting organic solution freed of solvent in vacuo. The resulting oil (8.99 g, 100%) was examined by $^1$H NMR analysis (CDCl$_3$) and was found to contain only the 1,1,1-triphenyl- and 1,1,2-triphenylethanes.

**(b) $^1$H NMR Monitoring of the Reaction.** In a similar manner to that described in part a, a solution of 1.0 g of **23** in 10 mL of anhydrous THF was allowed to react with 500 mg (72

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mg-atom) of lithium pieces in 20 mL of THF at -65 °C. After 3 h, samples of the mixture were withdrawn and examined at 0 °C by $^1$H NMR spectroscopy. In the regions free of THF absorptions (2.0–3.2 and 3.9–8.0 ppm), the development of new signals was monitored at intervals of 15 s. Signals attributable to the reaction products were observed, but neither enhanced nor emission signals could be detected. After 5 h, the usual hydrolytic workup again led to the isolation of 1,1,1-triphenylethane and 1,1,2-triphenylethane.

**Bis(2,2,2-triphenylethyl)mercury (24) with *n*-Butyllithium. (a) Labeling of the (2,2,2-Triphenylethyl)lithium Intermediate (25).** Under nitrogen, a solution of 500 mg (0.69 mmol) of **24** in 30 mL of THF was treated below -65 °C with 2.5 mL of 1.6 M *n*-butyllithium in hexane. After 2 h at this temperature, the reaction mixture was treated with 2 mL of deuterium oxide (99.8%). Usual workup (cf. supra) gave 300 mg of oil, which was crystallized from ethanol to yield 200 mg of colorless 1,1,1-triphenylethane (**21**), mp 92–94 °C, which did not depress the melting point of an authentic sample. That this **21** was monodeuteriated on the methyl group was established by spectral measurements: MS, *m/e* (relative intensity) (at 70 eV) 259 (74), 243 (100), 185 (51), 165 (70), 77 (32); $^1$H NMR (CDCl$_3$) $\delta$ 2.2 (s, 2 H, CH$_2$), 6.9–7.4 (m, 15 H).

**(b) ESR Monitoring of the Rearrangement.** A solution of 50 mg of **24** and 0.5 mL of THF in an ESR tube equipped with a rubber septum was treated under nitrogen at -60 °C with 0.5 mL of 1.6 M *n*-butyllithium. After 30 min at -60 °C, the tube was placed in an ESR spectrometer probe maintained at -60 °C. Thereafter, spectral scans were taken at ranges of 1000 and 250 G for the following elapsed times and temperatures: 0.5 h, -60 °C; 1 h, 0 °C and 20 °C; and 2.5 h, 0 °C. No ESR signal could be detected in any of the spectral runs. After a total of 4 h with a maximum temperature of 0 °C, the reaction mixture was hydrolyzed and worked up. Spectral analysis indicated the presence of a mixture of 1,1,1- and 1,1,2-triphenylethanes.

**(c) $^1$H NMR Monitoring of the Rearrangement.** A similar reaction between 119 mg of **24** in 0.5 mL of tetrahydrofuran-$d_8$ and 0.3 mL of 1.6 N *n*-butyllithium at -65 °C was observed by $^1$H NMR spectroscopy at 40 °C. The two singlets at 2.05 and 7.12 ppm, which arise from **24**, quickly disappeared, and a new singlet grew in at 3.9 ppm. No emission signal could be observed. The aromatic proton region simultaneously changed from a singlet to three broad peaks, roughly split into triplets, at 5.8, 6.6, and 7.1 ppm. Usual hydrolytic workup showed that 1,1,2-triphenylethane was the major product.

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**Registry No.** **11**, 118716-46-4; **11** (lithium salt), 118716-54-4; **12**, 118716-47-5; **12** (lithium salt), 118716-55-5; **13**, 161-25-1; **13** (lithium salt), 118716-56-6; **14**, 30319-92-7; **15**, 13355-64-1; **15** (lithium salt), 118716-57-7; **16**, 92-83-1; **17**, 118716-48-6; **18**, 61076-90-2; **19**, 35377-96-9; **21**, 5271-39-6; **22**, 111584-33-9; **23**, 33885-01-7; **24**, 118716-50-0; **25**, 16536-63-3; **26** (R = R′ = Ph), 118716-43-1; **26** (R = CH$_3$, R′ = Ph), 118716-45-3; **27**, 118716-44-2; **28**, 13355-65-2; **31** (R, Ar = Ph), 602-15-3; **31** (R = Me, Ar = Ph), 33498-62-3; **33**, 2720-93-6; **34**, 31859-87-7; **36**, 4425-68-7; **39**, 118716-52-2; Ph$_3$CCH$_2$D, 118716-49-7; 2-(bromomethyl)biphenyl, 19853-09-9; benzophenone, 119-61-9; acetophenone, 98-86-2; 9-fluorenone, 486-25-9; 1,2-bis(2-biphenylyl)ethane, 96003-60-0; 9-methylfluorene, 2523-37-7; 9-phenylfluorene, 789-24-2; triphenylmethane, 519-73-3; 1,2,2,3,3,4-hexaphenylbutane, 118716-51-1; *trans*-9,10-diphenyl-9,10-dihydrophenanthrene, 25127-93-9; *trans*-9-deuterio-9,10-diphenyl-9,10-dihydrophenanthrene, 118722-50-2; dihydrodibenzo[*g,p*]chrysene, 5162-39-0; 1,2,2-triphenylhexane, 118716-53-3; 3,3,3-triphenylpropionic acid, 900-91-4.

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# Applications of Ammonium Formate Catalytic Transfer Hydrogenation. 6.[1] Analysis of Catalyst, Donor Quantity, and Solvent Effects upon the Efficacy of Dechlorination

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Dehalogenation reactions have important synthetic and environmental potential and can be achieved by a variety of chemical methods, including transfer hydrogenation. A catalytic transfer hydrogenation procedure utilizing ammonium formate as an in situ hydrogen donor has previously been used for the dechlorination of polychlorinated biphenyls and for the deuterium labeling of chlorinated peptides. In this study, a systematic evaluation of the effects of catalyst, donor quantity, temperature, and solvent on ammonium formate catalytic transfer hydrogenolyses of aryl chlorides has been undertaken. Results indicate that carbon was the most effective support among those surveyed, and a 3% palladium loading and 2 equiv of ammonium formate were adequate in terms of overall reaction rate and cost. Catalysts with low Pd content were found to benefit from an increase in temperature, as did reactions involving highly hydrophobic substrates. Alcohols proved to be more effective than polar aprotic (HMPA) and nonpolar (THF, dioxane) solvents. Thus, 1-chloronaphthalene was quantitatively dechlorinated in C$_2$ and C$_3$ alcohols in 2 h and in 4 h in HMPA. The reaction was only 51% complete in THF and 30% complete in 1,4-dioxane after 4 h. Improved reaction procedures emerging from these studies were then used for the dechlorination of a variety of mono- and polychlorinated aromatic compounds.

Hydrogenation is a convenient method for the dehalogenation of aryl halides because of its experimental simplicity, good yields, and high purity of products.[2] However, the low solubility of hydrogen gas in organic solvents presents a limitation that is best overcome by the employment of high-pressure reactors. This difficulty may also be circumvented through catalytic transfer hydrogenation (CTH), in which simple organic/inorganic molecules, such as cyclohexene,[3] cyclohexadiene,[4] formic acid,[5]

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