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References and Notes

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Chemical Consequences of Hydride Addition to Aromatic Olefins

Itshak Granoth,* Yoffi Segall, Haim Leader, and Rivka Alkabets

Department of Chemistry, Israel Institute for Biological Research, Ness-Ziona, Israel

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The scope and synthetic applications of hydride addition to aromatic olefins have been studied. Many aromatic olefins are reduced by $LiAlH_4$ in tetrahydrofuran (THF), 1,2-dimethoxyethane, *p*-dioxane, or diglyme at 65–150 °C. Hydride addition to 1,1-diarylethylenes is accelerated by THF and other solvents, as compared with diethyl ether, and by electron delocalizing or cyclic, relatively rigid, aromatic groups. Substituents which increase the electron density at the double bond, or form steric hindrance, decelerate the hydride addition. *o*-MeO and especially *o*-Me_2N groups accelerate the reaction, probably by coordination with the lithium ion and displacing solvent molecules in both the transition state and the generated carbanions. 2,2-Diarylpropanes are efficiently obtained from 1,1-diarylethylenes, $LiAlH_4$, and anisole in THF, while 1,1-diarylethanes are produced in diglyme at 140–150 °C. A novel specific carbon–carbon bond formation is utilized for the diarylpropanes synthesis, involving methylation of the intermediate carbanions by anisole. Anthracene and phenanthrene are reduced by $LiAlH_4$ in diglyme, the former giving eventually 9,9,10,10-tetramethyl-9,10-dihydroanthracene. *cis*-Stilbene undergoes competing reduction and isomerization to *trans*-stilbene when heated with $LiAlH_4$ in diglyme; the latter ultimately gives 1,2-diphenylethane.

It has generally been accepted[1,2] that nonfunctionalized aromatic olefins do not react with $LiAlH_4$. The hydride addition to dibenzofulvene[3] has been interpreted as evidence for the high polarity of the exocyclic double bond of this special olefin. Transformation of cinnamyl alcohols to phenylcyclopropanes,[4] 1-phenylpropyne to *n*-propylbenzene,[4f] cinnamaldehyde to dihydrocinnamyl alcohol, and reduction of some unsaturated azabicyclic systems,[5] effected by $LiAlH_4$, have indicated that suitable functionalization of an olefin might enable hydride addition across a carbon–carbon double bond to occur. However, these latter reactions have been shown to be specific examples of intramolecular reactions.[4e] Recently, it has been found that aromatic compounds bearing an exocyclic double bond, such as substituted 9-methylenexanthenes[6] and methylenebenzanthrene,[7] react with $LiAlH_4$ under mild conditions. Furthermore, alternate aromatic olefins, such as 1,1-diphenylethylene,[8,9] are converted by $LiAlH_4$ in THF to the corresponding benzylic carbanions. Possible synthetic applications of these carbanions have briefly been outlined.[8,10] Similar findings have been reported[11] for the reduction of some aromatic olefins with sodium bis(2-methoxyethoxy)aluminum hydride. We now wish to present new data[12] concerning the scope of hydride addition to aromatic olefins, substituent and solvent effects, and some synthetic applications associated with this reaction.

Substituent and Geometry Effects. We have studied the hydride addition to aromatic olefins using $LiAlH_4$ in several ethereal solvents and temperatures. Reaction progress was followed by ^1H NMR spectroscopy and final products were isolated, purified, and characterized by standard techniques.

Generally, substituents which increase the electron density at the double bond or cause steric hindrance decelerate the hydride addition to an aromatic olefin. Electron-delocalizing, and cyclic, relatively rigid aromatic groups accelerate the reaction. Half-lives of some representative olefins in the presence of $LiAlH_4$ in refluxing THF (65 °C) are given in Table I. The hydride addition to 1,1-di-*o*-anisylethylene (**2**) is considerably faster than it is to 1,1-di-*p*-anisylethylene (**3**) in refluxing THF. A similar ortho effect is exhibited by 1-(*o*-anisyl)-1-phenylethylene[10] and especially 1-(*o*-dimethylaminophenyl)-1-phenylethylene ($T_{1/2}$ **31**/$T_{1/2}$ **30** = 40).

This rate-enhancing phenomenon exhibited by *o*-MeO[13] and *o*-Me_2N might be associated with the hydride attack (the "activated complex") as well as the stabilization of the generated carbanion (the "product"). The *o*-MeO group, e.g., might replace a solvent molecule[14,18] in the transition state, thus placing the hydride closer to the double bond and consequently enhancing the reaction rate. Similarly, intramolecular stabilization could be extended to the carbanion by

Table I. Half-Lives (h) of Olefins in the Presence of Excess $LiAlH_4$ at 65 °C in THF

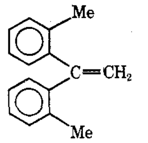
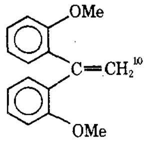
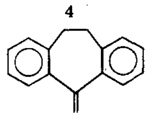
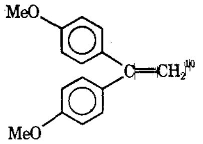
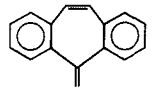
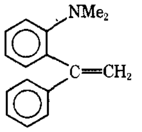
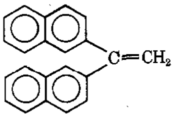
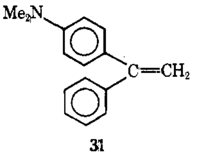
$Ph_2C{=}CH_2$[10] 1	0.33 ± 0.03	 4	1.60 ± 0.1
 2	1.50 ± 0.1	 5	0.20 ± 0.02
 3	30 ± 2	 6	0.14 ± 0.01
 30	0.21 ± 0.01	 7	0.03 ± 0.008
 31	8.5 ± 0.5		

Table II. Half-Lives (h) of Olefins in the Presence of Excess $LiAlH_4$ at 150 °C in Diglyme

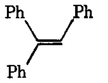
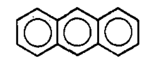
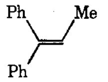
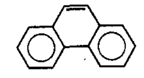
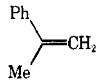
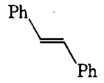
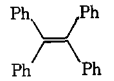
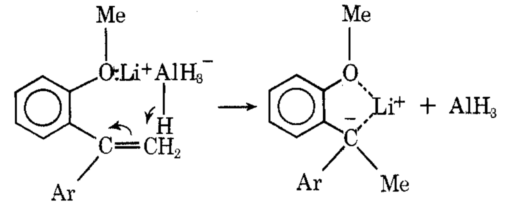
 8	1.0 ± 0.1	 12	0.40 ± 0.03
 9	1.2 ± 0.1	 13	14 ± 1
 10	1.2 ± 0.1		
 11	1.5 ± 0.1	 14	18 ± 1

Table III. Half-Lives (h) of 1,1-Diphenylethylene in the Presence of Excess $LiAlH_4$ in Some Ethereal Solvents at 17 °C

Tetrahydrofuran	2.5 ± 0.1	*p*-Dioxane	22 ± 2
1,2-Dimethoxyethane	3.5 ± 0.1	Diethyl ether	>>50
Diglyme	6.5 ± 0.2	Anisole	No reaction after 50 h

formation of a contact ion pair, such as the one shown in eq 1 (see also later). The more pronounced ortho effect of the Me_2N group, as compared with MeO, further substantiates the above interpretation, since the former is a stronger base than the latter.


(1)

Analogous contact ion pairs structures have been suggested[14] for 9-(ω-methoxyethyl)- and 9-(ω-dimethylaminoethyl)fluorenyllithium salts in THF.

The data in Table I also suggest that the hydride addition rate is markedly influenced by the geometry of the olefins. It should be noted that the steric factor is twofold. Apart from the straightforward steric hindrance to the hydride attack, the aromatic ring in the transition state should be properly oriented in order to effectively stabilize the generated carbanion. Orthogonal alignment of the aromatic ring with respect to the carbanion provides maximum resonance stabilization of the negative charge.[15]

Another example of the geometry effect is offered by the stilbene isomers. *cis*-Stilbene is reduced to 1,2-diphenylethane by $LiAlH_4$ in diglyme faster than *trans*-stilbene when the reaction is started at 20 °C and gradually heated to 150 °C. This is in accord with the reported[16] vinyl isotopic exchange for *cis*-stilbene, proceeding at a rate ca. 10 times faster than the exchange for *trans*-stilbene. However, the hydride addition to *cis*-stilbene is complicated by the base-catalyzed[17] cis–trans isomerization. This hydride-induced isomerization becomes faster than the hydride addition to *cis*-stilbene at 150 °C in diglyme; the half-life time with a large excess of $LiAlH_4$ at 28 °C in diglyme is 4 h.

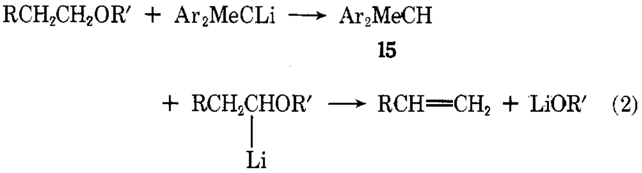
The rate of hydride addition to aromatic olefins is sensitive to the substituents on the aromatic rings. Moreover, substituents on the double bond might even inhibit the reaction, as is the case with α-*tert*-butylstyrene and 1,1-diphenyl-2-methylpropene. The substituents on the double bond induce both steric and electronic effects which are not easily distinguishable. However, some of the more hydride-resistant olefins can be reduced by $LiAlH_4$ in diglyme at 140–165 °C. Comparative data are shown in Table II.

While cumene is easily prepared in a good yield by the $LiAlH_4$ reduction of α-methylstyrene (**10**) in diglyme, styrene itself is almost completely polymerized by the hydride in either THF or diglyme. Phenanthrene and especially anthracene represent aromatic hydrocarbons which can be reduced by $LiAlH_4$ in diglyme to the corresponding 9,10-dihydro derivatives. However, anthracene yields eventually 9,9,10,10-tetramethyl-9,10-dihydroanthracene (see later). Tetraphenylethylene (**14**) suffers a reductive cleavage,[11] under our reaction conditions, and eventually methylation to yield mainly 2,2-diphenylpropane, together with 1,1-diphenylethane and 1,1-diphenylcyclopropane as by-products. 1,1,2,2-Tetraphenylethane and diphenylmethane are intermediates in this reaction.[11] Consequently, it appears that the approaching hydride is capable of polarizing a nonpolar double bond conjugated with an aromatic ring, probably with the solvent participation.

Solvent Effects and Synthetic Applications. It has already been noted[9,10] that hydride addition to 1 is considerably faster in THF than it is in diethyl ether. We have now examined the relative rate of this reaction in several ethereal solvents. The half-lives of 1 in the presence of a large excess of $LiAlH_4$ in several solvents under a dry nitrogen atmosphere at 17 °C are given in Table III. Hydride addition to 1 is fastest in THF, while diethyl ether and especially anisole are less suitable or even inhibit the reaction, in the latter solvent.

This solvent effect implies that THF provides a better solvation of the transition state complex associated with the hydride-induced polarization of the double bond and/or a better stabilization of the intermediate benzylic carbanions. This is consistent with our observations[8] that the highly reactive 9-methylenexanthenes and also the dibenzofulvenes do react with $LiAlH_4$ in diethyl ether. This view is in accord with a recent report[18] which has revealed the formation of solvent separated ion pairs and triple ions for $LiAlH_4$ in THF, but larger aggregates of contact ion pairs appear to be formed for $LiAlH_4$ in diethyl ether. The solvent separated ion pairs of $LiAlH_4$ in THF would presumably be the more reactive species. It has also been suggested[4d] that intramolecular hydride transfer from aluminum to an olefinic carbon is facilitated by stronger Lewis bases, probably through coordination with aluminum. Furthermore, evidence has been presented[18] for the ability of the oxygen of the methoxy group to coordinate the lithium ion and displace solvent molecules in ethereal solutions of $LiAl(OMe)_2H_2$. This also substantiates our interpretation concerning the *o*-MeO and Me_2N effects discussed above.

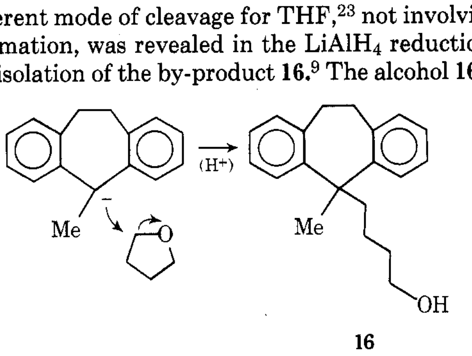
The solvent for the hydride addition reaction is sometimes dictated by the olefin. However, the solvent and temperature might determine the reaction products. Proton abstraction from the solvent is a well-known[19,20] side reaction of benzylic carbanions, regardless of their mode of formation. This reaction is usually described[21,22] as α-metalation of the ether (solvent), followed by olefin and lithium alkoxide, e.g., formation as shown in eq 2.



$$RCH_2CH_2OR' + Ar_2MeCLi \longrightarrow \underset{\mathbf{15}}{Ar_2MeCH} + \underset{\displaystyle Li}{RCH_2CHOR'} \longrightarrow RCH{=}CH_2 + LiOR' \quad (2)$$

The deprotonation reaction, leading to 1,1-diarylethanes **15**, is almost as fast as the hydride addition reaction in diglyme at 150 °C. The blood-red benzhydrylic carbanions, initially formed, were decolorized rapidly by proton abstraction from the diglyme, confirmed by the absence of deuterium in the products after D_2O quenching of the reaction mixture. Deprotonation of refluxing *p*-dioxane by these carbanions is ca. 10^2 slower and that of refluxing THF is the slowest. It may well be mainly a temperature effect. The fast deprotonation of diglyme by the carbanions was used to a good advantage for the preparation of pure **15**. This was especially important in the case of the anisylethylenes, where partial demethylation of the MeO groups by the carbanions accompanied the hydride addition reaction in THF (see also later).

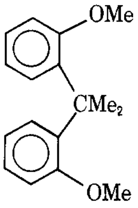
A different mode of cleavage for THF,[23] not involving enolate formation, was revealed in the $LiAlH_4$ reduction of **5** through isolation of the by-product **16**.[9] The alcohol **16** could



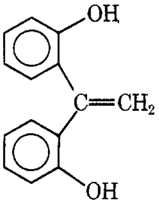
(3)

16

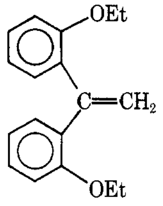
have been formed by a nucleophilic attack of the corresponding carbanion (or anion radical[27]) on the α carbon of THF as shown in eq 3. Stabilization of the intermediate alkoxide would support this type of reaction. Indeed, during the hydride addition to the anisylethylenes, e.g., **2**, in THF, an appreciable quantity of 2,2-di-*o*-anisylpropane (**17**) is formed together with 1,1-di-*o*-hydroxyphenylethylene (**18**), after hydrolysis. This nucleophilic displacement of alkoxide, leading to a carbon–carbon bond formation, does not occur with phenetole derivatives. Thus, **19** yields only the corresponding 1,1-diarylethane upon refluxing with $LiAlH_4$ in either THF or *p*-dioxane for 24 h.



17

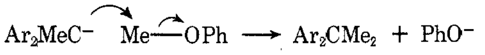


18



19

The above specific demethylation reaction was used for syntheses of 2,2-diarylpropanes, such as **17**. While hydride addition to the aromatic olefins does not occur in anisole,[4d] it takes place in a THF–anisole mixture. The intermediate carbanions demethylate the anisole, giving eventually the corresponding 2,2-diarylpropanes.

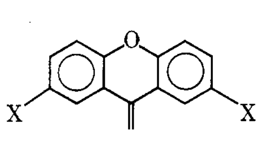


$$Ar_2MeC^- \quad Me{-}OPh \longrightarrow Ar_2CMe_2 + PhO^- \quad (4)$$

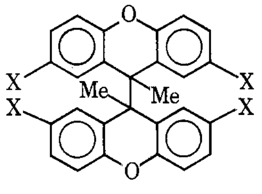
Partial demethylation of diglyme by some of the more crowded carbanions, competing with deprotonation, has also been found at elevated temperatures and relatively long reaction times. Consequently, 30% of 1,2,2-triphenylpropane and 17% of 2,2-diphenylbutane were obtained in the reductions of **8** and **9** in diglyme at 150 °C, in addition to 70% of 1,1,2-triphenylethane and 83% of 1,1-diphenylpropane, respectively. Especially facile methylation by diglyme was found in the case of anthracene (9,9,10,10-tetramethyl-9,10-dihydroanthracene being the major product after 2 h at 150 °C).

Other useful synthetic applications have also been briefly explored. Quenching the hydride addition reaction with solid CO_2 leads to a carboxylic acid. Specifically labeled compounds are obtained by using $LiAlD_4$ instead of $LiAlH_4$ in the reactions described above. Alternatively, reductions with either $LiAlH_4$ or $LiAlD_4$ in THF followed by D_2O quenching lead to the corresponding mono- or dideuterated derivatives. However, highly pure α-deuteration (by D_2O quenching) should be carried out in THF-d_8, thus avoiding contamination through proton abstraction from THF.

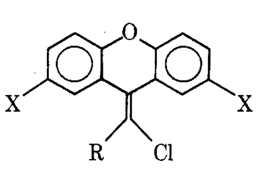
The reactions of $LiAlH_4$ with 9-methylenexanthenes **20–22** without exclusion of air lead to dimerization of the intermediate carbanions to **23–25**, respectively. These dimerization reactions might proceed through oxygen-induced electron transfer in the carbanions to anion radicals.[22,24,25] A side reaction involving dimer formation (2,2,3,3-tetraphenylbutane) in the $LiAlH_4$ reduction of **1** has also been found.[8] The tendency of stabilized anion radicals to dimerize has been reported.[26]



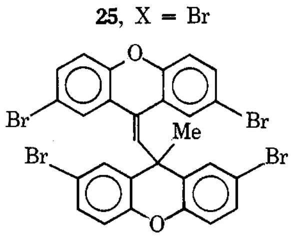
20, X = H
21, X = Me
22, X = Br



23, X = H
24, X = Me
25, X = Br



26, X = F; R = H
27, X = F; R = Me
28, X = Br; R = H



29

We have already described[6] two examples of hydride addition to **26** and **27** eventually yielding a condensation product, such as **29**. We now can add **28** to this reaction type, noting that diethyl ether should be used as the solvent, thus preventing partial hydrogenolysis of the aromatic bromide, occurring in THF. It has been suggested[6] that the final condensation step leading to the olefins such as **29** is a nucleophilic displacement of chloride by an intermediate carbanion. In view of the possible anion radical nature of the intermediates obtained upon hydride addition to aromatic olefins, the radical anion substitution mechanism[27] might be involved in the above displacement reaction.

Experimental Section

All melting and boiling points are uncorrected. Organic solutions were dried over $MgSO_4$ and Na_2CO_3. The ^1H NMR spectra were determined at 60 MHz with a JEOL C-60 HL spectrometer in CCl_4 solution, unless otherwise stated. The chemical shift values are expressed in δ values (ppm) relative to Me_4Si internal standard.

The mass spectra were obtained with an Hitachi (Perkin-Elmer) Model RMU-6. Unless otherwise stated all reactions involving $LiAlH_4$ or organometallic intermediates were performed under a dry nitrogen atmosphere. Elemental analyses found values for all the new compounds were within ±0.3% of the calculated values.

Compounds **1**, **8–14**, *cis*-stilbene, and styrene were commercially available. They were purified either by careful fractional distillation or recrystallization. 9-Methylenexanthenes were prepared as described elsewhere.[28] 1,1-Diarylethylenes were prepared from aryl Grignard[29] reagents or aryllithium reagents[30] which were obtained by the methods described in the references cited, and acetophenone or ethyl acetate, followed by dehydration with acetic anhydride. Alternatively, a diaryl ketone was added to an alkyl Grignard reagent, and the crude product was similarly dehydrated. The following two procedures are representative examples.

1,1-Bis(*o*-ethoxyphenyl)ethene (19). An *n*-hexane solution of *n*-butyllithium (140 ml of 2 N) was added dropwise to a stirred solution of 36.6 g of phenetole in 100 ml of dry THF and 120 ml of dry diethyl ether. The resulting mixture was refluxed for 2 h and cooled and then 12.8 g of ethyl acetate (distilled over P_2O_5) was added during 30 min, followed by 1-h reflux. Usual workup gave a solid residue, a sample of which melted at 136° (EtOH). This crude alcohol, thus obtained, was refluxed for 5 h with 100 ml of acetic anhydride and then evaporated under reduced pressure.

The crude product yielded 26.5 g of **19** after recrystallization from EtOH: mp 99 °C; mol wt 268 (mass spectrum); δ 0.98 (6 H, t, Me), 3.64 (4 H, q, CH_2), 5.28 (2 H, s, vinyl CH_2), 6.40–7.10 (8 H, m, ArH).

5-Methylene-5*H*-dibenzo[*a,d*]cycloheptene (6). Methylmagnesium iodide was prepared from 17 g of MeI and 2.9 g of finely divided Mg in 100 ml of diethyl ether. 5*H*-Dibenzo[*a,d*]cyclohepten-5-one (20.6 g) in 50 ml of dry THF was added to the clear solution of the Grignard reagent, at 7–10 °C, with external cooling. The resulting solution was refluxed for 1 h and hydrolyzed with a cold aqueous solution of NH_4Cl. The usual workup gave the expected carbinol (mp 112–114 °C), which was refluxed for 2 h with 100 ml of acetic anhydride. Evaporation under reduced pressure and recrystallization from 95% EtOH yielded 15 g of **6**, mp 118 °C.[31]

Half-Lives Measurements Procedure. The required solvent (30 ml) and $LiAlH_4$ (1.0 g) were equilibrated with magnetic stirring at a suitable temperature under a positive nitrogen pressure, and then 2.0 g of an olefin was added. At various time intervals, a 0.5-ml aliquot of the reaction mixture was pipetted into 20 ml of chilled hydrochloric acid (1 N), or sodium hydroxide (3 N) in the case of an amino olefin, to quench the reaction. Extraction with CCl_4, drying over Na_2CO_3, evaporation, and dissolution in 0.5 ml of CCl_4 containing 1% Me_4Si were followed by an NMR analysis. When diglyme was used as the solvent, the CCl_4 extract was dried over neutral alumina. Each half-life measurement was repeated at least twice.

1,1-Diphenylethane and 2,2,3,3-Tetraphenylbutane. 1,1-Diphenylethylene (**1**, 5.0 g), $LiAlH_4$ (2.0 g), and 50 ml of dry THF were refluxed for 3 h, cooled, and decomposed slowly by adding to ice-cold 1 N hydrochloric acid (200 ml). Extraction with $CHCl_3$ followed by standard workup yielded 4.0 g of 1,1-diphenylethane:[11] bp 85 °C (0.3 mmHg); δ 1.53 (3 H, d, Me, $J = 7.0$ Hz), 4.01 (1 H, q, CH, $J = 7.0$ Hz), 7.03 (10 H, s, Ph).

The nonvolatile residue from the distillation yielded 0.5 g of 2,2,3,3-tetraphenylbutane, after recrystallization from EtOH: mp 122 °C;[32] δ 1.96 (6 H, s, Me), 6.80–7.35 (20 H, m, Ph); mass spectrum *m/e* (rel intensity) 362 (19, M^+), 168 (100, $C_{13}H_{12}^+$), 167 (23), 166 (20).

1,1-Diphenyl-2-deuterioethane. **1** (2.0 g) and $LiAlD_4$ (0.5 g) in THF (20 ml) were treated as above, giving 1.5 g of the desired product: bp 87 °C (0.5 mmHg); δ 1.56 (2 H, dt, CH_2D, $J_{HH} = 7.0$, $J_{HD} = 1.5$ Hz), 4.05 (1 H, t, CH, $J = 7.0$ Hz), 7.10 (10 H, br s, Ph); mass spectrum *m/e* (rel intensity) 183 (29, M^+), 167 [100, $(M - CH_2D)^+$], 165 (26, $C_{13}H_9^+$), 154 (24, $C_{12}H_{10}^+$).

1,1-Bis(*p*-methoxyphenyl)ethane. $LiAlH_4$ (0.5 g), **3** (2.0 g), and 20 ml of diglyme were heated for 5 min at 140 °C, cooled, and decomposed with 100 ml of ice-cold 1 N hydrochloric acid. The product was extracted with $CHCl_3$, yielding, after recrystallization from EtOH, 1.7 g: mp 67 °C;[33] δ 1.57 (3 H, d, MeCH, $J = 7.0$ Hz), 3.76 (6 H, s, MeO), 4.02 (1 H, q, CH, $J = 7.0$ Hz), 6.73 (4 H, d, ArH, $J = 9.0$ Hz), 7.05 (4 H, d, ArH, $J = 9.0$ Hz); mass spectrum *m/e* (rel/intensity) 242 (31, M^+), 227 [100, $(M - Me)^+$].

1,1-Bis(*p*-methoxyphenyl)-2-deuterioethane. $LiAlD_4$ (0.5 g), **3** (2.0 g), and 20 ml of diglyme were treated as above, giving 1.6 g of deuterated product: mp 66 °C (EtOH); δ 1.53 (2 H, dt, CH_2D, $J_{HH} = 7.0$, $J_{HD} = 1.5$ Hz), 3.62 (6 H, s, MeO), 4.00 (1 H, t, CH, $J = 7.0$ Hz), 6.65 (4 H, d, ArH, $J = 9.0$ Hz), 6.98 (4 H, d, ArH, $J = 9.0$ Hz); mass spectrum *m/e* (rel intensity) 243 (28, M^+), 227 [100, $(M - CH_2D)^+$].

5-Methyl-5*H*-dibenzo[*a,d*]cycloheptene. Diglyme (20 ml) and $LiAlH_4$ (1.0 g) were held at 140 °C when 2.0 g of **6** were added. After 2 min, the reaction mixture was rapidly cooled and 15 ml of ethyl acetate was added, followed by 50 ml of 1 N hydrochloric acid. Extraction with 2 × 50 ml of *n*-hexane yielded 1.5 g of a 1:1 mixture of geometrical isomers, mp 56 °C (MeOH).[34] A, δ 1.28 (3 H, d, Me^{ax}, $J = 7.0$ Hz), 4.07 (1 H, q, CH^{eq}, $J = 7.0$ Hz), 6.78 (2 H, s, CH=CH), 7.14 (8 H, m, ArH); B, δ 1.81 (3 H, d, Me^{eq}, $J = 7.0$ Hz), 3.42 (1 H, q, CH^{ax}, $J = 7.0$ Hz), 7.00 (2 H, s, CH=CH), 7.14 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 206 (33, M^+), 191 [100, $(M - Me)^+$].

Hydride Addition to 1,1-Bis(*o*-methoxyphenyl)ethene (2) in THF. **2** (4.0 g), $LiAlH_4$ (2.0 g), and 100 ml of dry THF were refluxed for 24 h, cooled, and carefully decomposed with 200 ml of hydrochloric acid. The products were extracted with $CHCl_3$ which was washed with aqueous NaOH. The organic extract yielded 2.0 g of 2,2-bis(*o*-methoxyphenyl)propane: mp 93 °C (EtOH); δ 1.68 (6 H, s, MeC), 3.28 (6 H, s, MeO), 6.60–7.40 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 256 (60, M^+), 241 [67, $(M - Me)^+$], 133 (41), 121 (100), 105 (65), 91 (50), 77 (28).

The NaOH solution was acidified and extracted with $CHCl_3$, giving 0.4 g of 1,1-bis(*o*-hydroxyphenyl)ethene (**18**): mp 134 °C (CCl_4); δ 5.35 (2 H, br s, HO, exchangeable with D_2O), 5.58 (2 H, s, CH_2), 6.80–7.30 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 212 (29, M^+), 195 [100, $(M - OH)^+$].

2,2-Diphenylpropane. **1** (5.0 g), $LiAlH_4$ (2.0 g), THF (50 ml), and anisole (50 ml) were refluxed for 4 h, cooled, and then decomposed as above, including washing of the extract with aqueous NaOH, from which phenol could be isolated. Distillation gave 4.5 g of 2,2-diphenylpropane:[11] bp 90 °C (0.3 mmHg); δ 1.61 (6 H, s, Me), 7.14 (10 H, s, Ph); mass spectrum *m/e* (rel intensity) 196 (30, M^+), 181 [100, $(M - Me)^+$].

2-Phenyl-2-(*p*-methoxyphenyl)propane. This compound was prepared as described above, using 1-phenyl-1-(*p*-methoxyphenyl)ethene (4.0 g), $LiAlH_4$ (2.0 g), THF (40 ml), and anisole (40 ml) and 6-h reflux: bp 115 °C (0.3 mmHg) (3.1 g); δ 1.58 (6 H, s, MeC), 3.64 (3 H, s, MeO), 6.50–7.15 (9 H, m, ArH); mass spectrum *m/e* (rel intensity) 226 (12, M^+), 211 [37, $(M - Me)^+$], 181 (30), 167 (28), 165 (27), 136 (32), 122 (91), 121 (100), 107 (36), 94 (25), 91 (45), 77 (61).

2,2-Bis(*o*-ethoxyphenyl)propane was similarly prepared from **19** (4.0 g), in 80% yield: mp 83 °C (EtOH); δ 0.84 (6 H, t, $MeCH_2$, $J = 7.0$ Hz), 1.65 (6 H, s, MeC), 3.52 (4 H, q, CH_2, $J = 7.0$ Hz), 6.45–7.40 (8 H, m, ArH).

5,5-Dimethyl-5*H*-10,11-dihydrodibenzo[*a,d*]cycloheptene. **5** (5.0 g), $LiAlH_4$ (2.0 g), THF (40 ml), and anisole (40 ml) were refluxed for 2 h, cooled, and decomposed with 200 ml of 1 N hydrochloric acid. The products were extracted with $CHCl_3$, washed with aqueous NaOH, dried over Na_2CO_3, and evaporated under reduced pressure. *n*-Hexane (15 ml) was added to the residue and upon cooling, 0.6 g of a solid separated and was filtered off. This solid, mp 102 °C (*n*-hexane), was identified as **5-methyl-5-(ω-hydroxybutyl)-5*H*-10,11-dihydrodibenzo[*a,d*]cycloheptene:** δ 0.90–1.60 (5 H, m, CH_2CH_2 + HO), 1.88 (3 H, s, Me), 2.10–2.37 (2 H, m, CH_2C), 2.72–3.70 (4 H, m, 10,11-CH_2CH_2), 3.50 (2 H, t, CH_2O), 7.05–7.53 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 280 (1, M^+), 207 [100, $(M - C_4H_9O)^+$].

The *n*-hexane solution yielded 4.0 g of the desired product as an oil: δ 1.85 (6 H, s, Me), 3.28 (4 H, s, CH_2), 6.90–7.50 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 222 (28, M^+), 207 [100, $(M - Me)^+$].

This compound was further characterized by its transformation to **5,5-dimethyl-5*H*-dibenzo[*a*,*d*]cycloheptene,** as follows. The above dihydro derivative (3.0 g), *N*-bromosuccinimide (2.5 g), dibenzoyl peroxide (70 mg), and CCl_4 (50 ml) were refluxed for 1.5 h. The bromination was accompanied by spontaneous dehydrobromination. The filtered solution was washed with aqueous $NaHCO_3$, and with $NaHSO_3$, followed by water. The desired product (2.3 g) was obtained after elution with petroleum ether (bp 40–60 °C) from a short neutral alumina (20 g) column. It solidified upon standing: mp 46 °C;[34] δ 1.65 (6 H, s, Me), 6.90 (2 H, s, CH=CH), 7.05–7.48 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 220 (31, M^+), 205 [00, $(M - Me)^+$].

1,1,2-Triphenylethane and 1,2,2-Triphenylpropane. 8 (2.0 g), $LiAlH_4$ (1.0 g), and diglyme (40 ml) were refluxed for 1.5 h. Careful acid hydrolysis and extraction with $CHCl_3$ yielded 1.9 g of a mixture from which 1,2,2-triphenylpropane crystallized upon addition of *n*-hexane (10 ml). Recrystallizations from *n*-hexane and then from EtOH gave 0.5 g of the pure compound: mp 115 °C;[35] δ 1.53 (3 H, s, Me), 3.40 (2 H, s, CH_2), 6.50–7.20 (15 H, m, Ph); mass spectrum *m/e* (rel intensity) (M^+ was not observed) 181 [100, $(M - PhCH_2)^+$], 167 (26), 103 (27). 1,1,2-Triphenylethane (1.1 g) was obtained from the original *n*-hexane solution upon evaporation and recrystallization from EtOH: mp 53 °C;[36] δ 3.30 (2 H, d, CH_2, $J = 8.0$ Hz), 4.15 (1 H, t, CH, $J = 8.0$ Hz), 7.15 (15 H, br s, ArH).

9,9,10,10-Tetramethyl-9,10-dihydroanthracene. Anthracene (2.0 g), $LiAlH_4$ (1.0 g), and diglyme (30 ml) were heated for 6 h at 150 °C, cooled, and decomposed with 200 ml of 1 N hydrochloric acid. The crystalline product was collected by filtration and yielded 1.7 g: mp 166–167 °C[37] after recrystallization from EtOH; δ 1.64 (12 H, s, Me), 7.00–7.50 (8 H, m, ArH).[24] NMR analysis of an aliquot of the reaction mixture, pipetted 0.5 h from the start, revealed that 9,10-dihydroanthracene was the major component of the reaction mixture at that time: δ 3.85 (4 H, s, CH_2), 7.15 (8 H, m, ArH).

5-Methyl-5*H*-10,11-dihydrodibenzo[*a*,*d*]cycloheptene-5-carboxylic Acid. 5 (2.0 g), $LiAlH_4$ (0.5 g), and THF (40 ml) were refluxed for 40 min, cooled, and decomposed with solid CO_2. Acidification with 1 N HCl, filtration, dissolution in 1 N NaOH, and acidification of the clear basic solution yielded 1.1 g of the desired acid: mp 260 °C (EtOH); δ ($CDCl_3$) 2.15 (3 H, br s, Me), 2.85–3.43 (4 H, m, CH_2CH_2), 7.00–7.30 (8 H, m, ArH); mass spectrum *m/e* (rel intensity) 252 (17, M^+), 237 [40, $(M - Me)^+$], 207 [100, $(M - CO_2H)^+$], 192 (25), 191 (26), 129 (39), 91 (34).

Preparation of 9,9′-Dimethyl-9,9′-bixanthyls. The appropriate 9-methylenexanthene (2.0 g), $LiAlH_4$ (1.0 g), and 50 ml of THF (or diethyl ether for the 2,7-dibromoxanthenes) were refluxed for 2 h without exclusion of air. The usual workup gave the following compounds.

A. 9,9′-Dimethyl-9,9′-bixanthyl (23), mp 153 °C (EtOAc), was prepared in 75% yield from **20:** δ ($CDCl_3$) 1.68 (6 H, s, Me), 6.40–7.20 (16 H, m, ArH); mass spectrum *m/e* (rel intensity) 390 (2, M^+), 195 (62), 194 (100), 181 (60), 165 (37).

B. 2,2′,7,7′,9,9′-Hexamethyl-9,9′-bixanthyl (24), mp 145 °C (EtOH), was prepared in 60% yield from **21:** δ ($CDCl_3$) 1.52 (6 H, br s, 9,9′-Me), 2.16 (12 H, s, MeAr), 6.43 (4 H, br s, H-1,8), 6.86 (4 H, d, H-4,5), 7.04 (4 H, dd, H-3,6) ($J_{HH} = 7.0$ and 2.0 Hz, respectively); mass spetrum *m/e* (rel intensity) 446 (1, M^+), 223 (100, $M/2^+$), 222 (68, $C_{16}H_{14}O^+$), 209 (57, $C_{15}H_{13}O^+$).

C. 2,2′,7,7′-Tetrabromo-9,9′-dimethyl-9,9′-bixanthyl (25), mp 167 °C (EtOAc), was prepared from **22,** in 50% yield: δ ($CDCl_3$) 1.73 (3 H, s, Me), 1.80 (3 H, s, Me), 6.95–7.80 (12 H, m, ArH).

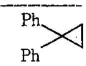
2,7-Dibromo-9-(2′,7′-dibromo-9′-methyl)xanthylmethylenexanthene (29). This compound, mp 202 °C (MeOH–EtOAc), was prepared by the usual procedure, under N_2 atmosphere, from **28,** in 50% yield: δ ($CDCl_3$) 1.78 (3 H, s, Me), 6.40 (1 H, s, H-11), 6.80–7.50 (11 H, m, Ar-H), 7.90 (1 H, d, H-1).

2-Phenylpropane. 10 (5.0 g), $LiAlH_4$ (2.0 g), and diglyme (40 ml) were heated for 3 h at 150 °C, cooled, and decomposed with 200 ml of 1 N HCl. Extraction with hexane (100 ml), drying over neutral alumina, and distillation gave 3.1 g of 2-phenylpropane: bp 152 °C; δ 1.24 (6 H, d, Me, $J = 7.0$ Hz), 2.39 (1 H, septet, CH, $J = 7.0$ Hz), 7.25 (5 H, br s, Ph).

Only a trace of phenylethane could be detected by ^1H NMR spectroscopy upon application of this procedure to styrene. Changing the solvent to THF mainly gave again polymerization of styrene.

Reduction of Tetraphenylethene (14) with $LiAlH_4$ in Diglyme. 14 (2.0 g), $LiAlH_4$ (1.0 g), and diglyme (30 ml) were heated at 150 °C. At various time intervals, a 1.0-ml aliquot of the reaction mixture was pipetted into 20 ml of chilled 1 N HCl. Extraction with CCl_4, drying over Na_2CO_3 and neutral alumina, evaporation, and dissolution in 0.5 ml of CCl_4 were followed by an NMR analysis. Representative results are given in Table IV.

Table IV. Products Formed from 14 and $LiAlH_4$ at 150 °C along the Reaction Coordinate

Time from start, h	Consumption of 14, %	Compd, mol %			
		Ph_2-$CHCHPh_2$	Ph_2CHMe	Ph_2CMe_2	
18	50	31	53	6	10
28	60	3	36	36	25
120	100	1	5	71	23

9,10-Dihydrophenanthrene. 13 (5.0 g), $LiAlH_4$ (2.5 g), and diglyme (30 ml) were refluxed for 36 h, cooled, and decomposed with 200 ml of 1 N HCl. Extraction with 2 × 50 ml of $CHCl_3$, drying over neutral alumina (20 g), and fractional distillation yielded 9,10-dihydrophenanthrene (3.5 g): bp 180 °C (25 mmHg); δ 2.84 (4 H, s, CH_2) 7.20–7.85 (8 H, m, ArH).

Registry No.—**1,** 530-48-3; **2,** 28358-60-3; **3,** 4356-69-8; **4,** 2919-19-9; **5,** 2732-90-3; **6,** 2975-79-3; **7,** 39799-27-4; **8,** 58-72-0; **9,** 778-66-5; **10,** 98-83-9; **11,** 103-30-0; **12,** 120-12-7; **13,** 85-01-8; **14,** 632-51-9; **17,** 56751-16-7; **18,** 56751-18-9; **19,** 56751-13-4; **20,** 55164-22-2; **21,** 55164-24-4; **22,** 55164-25-5; **23,** 55164-28-8; **24,** 60047-59-0; **25,** 60047-60-1; **28,** 55517-21-0; **29,** 60047-61-2; **30,** 10482-83-4; **31,** 22057-80-3; phenetole, 103-73-1; ethyl acetate, 141-78-6; 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one, 2222-33-5; 1,1-diphenylethane, 103-29-7; $LiAlH_4$, 16853-85-3; 2,2,3,3-tetraphenylbutane, 10496-82-9; 1,1-diphenyl-2-deuterioethane, 4416-97-1; $LiAlD_4$, 14128-54-2; 1,1-bis(*p*-methoxyphenyl)ethane, 10543-21-2; 1,1-bis(*p*-methoxyphenyl)-2-deuterioethane, 60047-62-3; 5-methyl-5*H*-dibenzo[*a*,*d*]cycloheptene, 56175-82-7; 2,2-diphenylpropane, 778-22-3; 2-phenyl-2-(*p*-methoxyphenyl)propane, 6623-93-4; 1-phenyl-1-(*p*-methoxyphenyl)ethene, 4333-75-9; 2,2-bis(*o*-ethoxyphenyl)propane, 60047-63-4; 5,5-dimethyl-5*H*-10,11-dihydrodibenzo[*a*,*d*]cycloheptene, 60047-64-5; 5-methyl-5-(ω-hydroxybutyl)-5*H*-10,11-dihydrodibenzo[*a*,*d*]cycloheptene, 60047-65-6; 5,5-dimethyl-5*H*-dibenzo[*a*,*d*]cycloheptene, 50356-63-3; 1,1,2-triphenylethane, 1520-42-9; 1,2,2-triphenylpropane, 16874-18-9; 9,9,10,10-tetramethyl-9,10-dihydroanthracene, 24269-10-1; 5-methyl-5*H*-10,11-dihydrodibenzo[*a*,*d*]cycloheptene-5-carboxylic acid, 60047-66-7; 2-phenylpropane, 98-82-8.

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Photoinduced Rearrangement and Related Reactions of Ethyl *N*-Phenylcarbamate

Divakar Masilamani and Robert O. Hutchins*

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Jack Ohr

Aero Materials Laboratory, Naval Air Development Center, Warminster, Pennsylvania 18974

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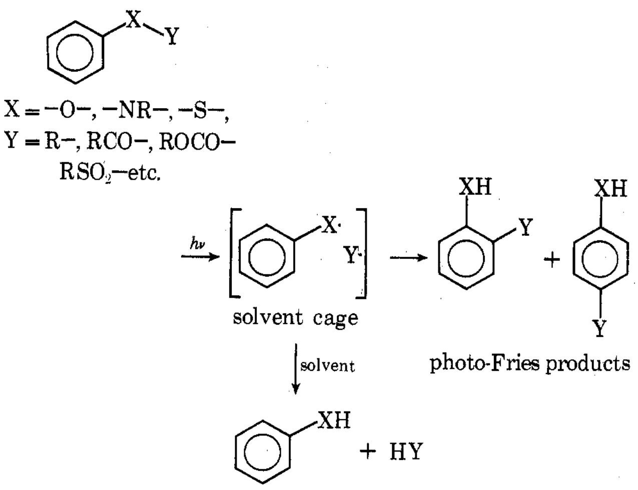
The photoinduced transformation of ethyl *N*-phenylcarbamate (**1**) to ethyl *o*-aminobenzoate (**2**), ethyl *p*-aminobenzoate (**3**), and aniline (**4**) is concentration dependent. At low concentrations, aniline is the exclusive nonpolymeric product. At higher concentrations of **1**, all three products are observed with **2** predominant, but the photoyield is reduced. The results are attributed to the formation of hydrogen-bonded aggregations at higher concentrations which favors similar rearrangement as observed in photo-Fries reactions and to the photolability of **3** and **4**.

Since the initial discovery of the photo-Fries rearrangement by Anderson and Reese in 1960,[1] similar reactions are found to be fairly general for aromatic systems linked to a carbonyl or sulfonyl group through a heteroatom, particularly O, N, or S. Scheme I depicts the overall reaction types observed along with the generally accepted mechanism involving initial light induced homolytic cleavage of the X–Y bond followed by rearrangement of the resulting biradical to the observed ortho and para products. In addition, cleavage products resulting from hydrogen atom abstraction by the intermediate radicals usually accompany the rearrangement products. However, the absence of crossover products[2c] has led to the suggestion[2a] that the rearrangements proceed by intramolecular 1,3 and 1,5 sigmatropic shifts, but this interpretation has been questioned.[3] On the other hand, the absence of crossover products from radicals may be explained if such intermediates are trapped in a solvent cage.[4] The degradation products resulting from hydrogen abstraction evidently result from escape of the radicals from the cage. This is consistent with the observation that the ratio of rearrangement to degradation products is enhanced in viscous solvents in which the cage should be more efficient.[5,6] In fact, no degradation products were observed at all in a polyethylene matrix.[7]

Scheme I



Our interest in the photodegradation of polyurethanes prompted this present investigation of the photochemistry of ethyl *N*-phenylcarbamate (**1**) as a model representative. Irradiation of **1** under a variety of conditions has been previously reported[8-12] to afford a combination of photoinduced rearrangements and photodegradation products as summarized in Table I. As seen, the percent conversion of **1** is consistently low and the ratio of degradation to rearrangement products appears to be nearly independent of solvent viscosity and irradiation time.

Recently, Schwetlick and co-workers[11,13,14] have examined the photoproducts carefully for a variety of *N*-phenylcarbamates and measured the quantum yields in different solvents. Their results were ascribed to a combination of N–C bond cleavage (Scheme I) and C–O bond cleavage which affords an amido radical which further dissociates to the anilino radical and carbon monoxide; the former eventually gives aniline and/or polymers.

A systematic analysis of the concentration dependence of the carbamates on the overall photoyields and relative ratios of the photoproducts has not been attempted. Such an investigation should provide clues as to the nature of the intermediates and whether the process is concerted or one involving biradical intermediates. Secondly, the photostabilities of the products have not been investigated. Recent work[16] on