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REDUCTIVE METALATION OF UNSATURATED COMPOUNDS: THE EFFECT OF ALLYLIC PROTONS

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SUMMARY

Reductive metalation by alkali metals of hydrocarbons containing labile protons can be accompanied by proton transfer from the hydrocarbon to the derived radical anion and/or dianion. The extent of this reaction as a function of reaction conditions has been studied with *trans*-1,2-diphenylpropene (I). Three alkali metals, Li, Na and K, and two solvents, diethyl ether (DEE) and tetrahydrofuran (THF) were examined.

No significant proton transfer was observed with the Li/DEE, Li/THF or Na/DEE system; the product (III) being the vicinal dianion of (I). In the case of Li/DEE, the limited solubility of the dianion prevented complete conversion of (I) to (III) except in dilute solutions.

With Na/THF, substantial amounts of proton transfer occurred to form the substituted allylic anion (V) from (I). The extent of this reaction could be controlled by varying the temperature and was largely suppressed at 0°.

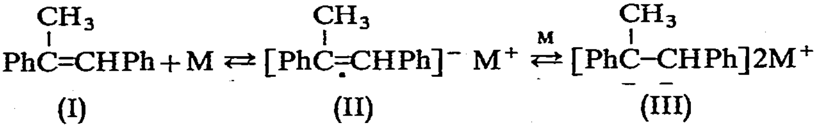
Extensive proton transfer resulted with K/THF. However, in this case the allylic anion (V) so formed was further reduced with dimerization to the tetra-anion of 1,2,5,6-tetraphenylhexane, (IX).

The chemical behaviour of alkali metal organometallic compounds is characterized[1] by a sensitivity towards labile protons. While this property makes alkyllithium compounds valuable metalation agents[2], it is responsible for a variety of side reactions in the preparation and reactions[3] of many organosodium and organopotassium compounds.

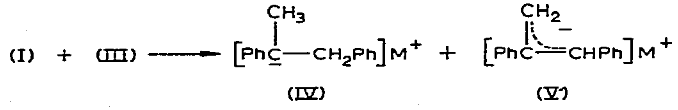
Specifically, it might be anticipated that the formation of organo-alkali metal vicinal dianions by the reductive metalation of unsaturated hydrocarbons[4] would be complicated by the presence of labile protons in the hydrocarbon. Qualitatively, by-products generated by the reaction of such labile protons with the organometallic derivative have been observed[5,6]. However, there remains a need for determining more precisely the extent of this reaction and its dependence on the reaction conditions.

For this reason, the reaction between alkali metals and 1,2-diphenylpropene (I) has been studied. This particular hydrocarbon was selected since it is known to react with alkali metals[7,8] and the lability of the allylic protons has been documented by a number of investigators[9-11]. Additionally, the chemical behaviour[3,4] of the related hydrocarbon, stilbene, provided a useful reference point for distinguishing those effects due to the allylic protons of (I).

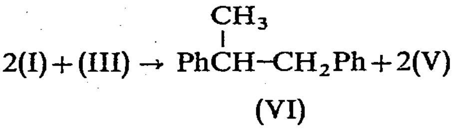
The following reactions might be expected to occur during the reductive metalation of (I);



$$\underset{(I)}{Ph\overset{CH_3}{\overset{|}{C}}=CHPh}+M \rightleftarrows \underset{(II)}{[Ph\overset{CH_3}{\overset{|}{C}}\dot{=}CHPh]^-}\ M^+ \overset{M}{\rightleftarrows} \underset{(III)}{[Ph\overset{CH_3}{\overset{|}{\bar{C}}}-\bar{C}HPh]2M^+} \qquad (1)$$



$$(I)+(III) \longrightarrow \underset{(IV)}{[Ph\overset{CH_3}{\overset{|}{\bar{C}}}-CH_2Ph]M^+} + \underset{(V)}{[Ph\overset{CH_2}{\overset{|}{C}}=CHPh]^-M^+} \qquad (2)$$



$$2(I)+(III) \rightarrow \underset{(VI)}{Ph\overset{CH_3}{\overset{|}{C}}H-CH_2Ph}+2(V) \qquad (3)$$

Eqn. (1) describes the usual formation of a radical anion (II) and/or a vicinal dianion (III). The second and third equations show metallation of the alkene (I) by the dianion to produce an allylic anion (V) and a mono-anion (IV)* or the hydrocarbon 1,2-diphenylpropane, (VI).

The occurrence of the proton transfer can be assessed by a determination of alkali metal uptake, by protonation of the organometallic compound coupled with product analysis and by deuteration coupled with product isolation and spectroscopic examination of the products for deuterium content. If only reaction (1) occurred, the organometallic compound would contain on the average 2 g-atoms of metal per mole of initial alkene, the only organic product would be (VI) and this product would be doubly deuterated when deuterium oxide was used. If reaction (II) proceeded to completion, the product would average 1 g-atom of metal per mole of initial alkene, the organic product would be a 1/1 mixture of (VI) and diphenylpropene (mixture of three isomers) and all products would be singly deuterated. Should reaction (3) proceed to completion the metal content would be 0.67 g-atom per mole of initial alkene, the products would be a 1/2 ratio of (VI) and the isomeric diphenylpropenes and only the latter would be found deuterated after deuterolysis.

It should be stressed that this assessment is focused upon the metalation of the alkene (I) by the alkali metal products derived from it during reductive metalation. It cannot provide information on the equilibrium between the radical anion (II) and the dianion (III) since (II) undoubtedly behaves on protonation[12,13] as an equimolar mixture of the dianion (III) and the alkene (I). Since Garst[8] has examined the equilibrium between (II) and (III) and concluded that the dianion (III) is favoured, we have elected to represent the proton transfer as involving the dianion (III).

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* The equation shows the tertiary anion but the isomeric secondary anion is also possible.

RESULTS

In this study the extent of proton transfer was evaluated as a function of the reducing agent (Li, Na, or K) and the reaction medium diethyl ether (DEE) or tetrahydrofuran (THF). Table 1 summarizes the effect of these parameters on the equilibrium composition of the organometallic compound and the composition of the protonation products.

TABLE 1

REACTION OF *trans*-1,2-DIPHENYLPROPENE WITH ALKALI METALS

Metal, M	*Solvent*	*M/mole of (I)*	*Product composition*[a]				
			(VI)	*cis-(I)*	*(VII)*[b]	*trans-(I)*	*Dimer*
Li	DEE	0.5	24	13	1	62	
Li	THF	2.0	100	t[c]	t	t	
Na	DEE	2.0	99	<1	t	<1	
Na	THF	1.6	72	3	1	24	
K	THF[d]	1.5	55	<1		<1	45

[a] Average of at least 3 determinations. [b] 1,3-Diphenylpropene. [c] Trace. [d] No reaction occurred in DEE.

Both the sodium/DEE and lithium/THF reactions proceeded by eqn. (1). The protonolysis product was almost entirely (VI) and, on deuterolysis, (VI) proved to be doubly deuterated. Similar observations were made on (VI) isolated from the lithium/DEE reaction. Since the *trans*-(I) obtained on deuterolysis of this last reaction was found to be deuterium free, this again represented a reaction proceeding by eqn. (1) but with an equilibrium less favorable to the organometallic product.

In the case of sodium/THF, the reductive metalation was accompanied by proton transfer. Thus, the organosodium compound averaged 1.6 g-atoms of metal per mole while the *trans*-(I) isolated from this experiment contained between one and two deuteriums per mole. That more than reactions (1) and (2) had occurred was shown by the mass spectrum of the deuterated (VI) which had appreciable peaks at *m/e* 196 and 198 but a relatively small peak at 197. Thus (VI) was a mixture of non-, mono- and di-deuterated material with the non- and di-deuterated hydrocarbon predominating. Reaction (3) was therefore proceeding at least as fast as reaction (2). In a control experiment, the dianion (3) generated by lithium in THF was treated with half the equivalent amount of D_2O. Again, the mass spectrum showed the *m/e* 198 and 196 peaks exceeding the 197 peak.

Protonation of the organopotassium compound produced approximately equal amounts of 1,2-diphenylpropane (VI) and a dimeric hydrocarbon $C_{30}H_{30}$. Since the (VI) isolated after deuterolysis contained on the average one deuterium per mole, proton transfer had proceeded more extensively here than with sodium. Initially, it was felt that the dimer was formed by reductive dimerization* of (I) and

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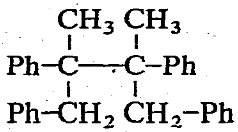
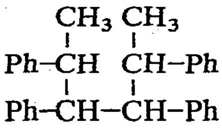
* While reductive dimerization has not been reported for 1,2-diphenylpropene, it has been observed for 1,1-diphenylethylene. For a definitive study of this latter reaction see ref. 14.

therefore should have structure (VII) or (VIII). However, spectroscopic data did not



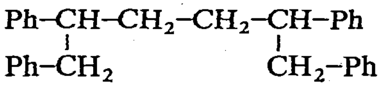
$$\begin{array}{c}\mathrm{CH_3\ \ CH_3}\\ \mathrm{Ph{-}C{-}C{-}Ph}\\ \mathrm{Ph{-}CH_2\ \ CH_2{-}Ph}\end{array}$$

(VII)



$$\begin{array}{c}\mathrm{CH_3\ \ CH_3}\\ \mathrm{Ph{-}CH\ \ CH{-}Ph}\\ \mathrm{Ph{-}CH{-}CH{-}Ph}\end{array}$$

(VIII)



$$\begin{array}{l}\mathrm{Ph{-}CH{-}CH_2{-}CH_2{-}CH{-}Ph}\\ \mathrm{Ph{-}CH_2\qquad\qquad\qquad CH_2{-}Ph}\end{array}$$

(IX)

support either of these structures since it was evident that methyl groups were not present in the dimer. Structure (IX) was compatible with the spectroscopic data and independent synthesis of the hydrocarbon confirmed this assignment.

The dimer (IX) isolated from the deuterolysis of the organopotassium compound was found to contain four deuteriums which, from the NMR and mass spectra, were located one on each of the four benzylic carbon atoms.

The rate of electron transfer between a radical anion and a receptive hydrocarbon is known[15] to be extremely fast. In the case of electron transfer from an alkali metal to an unsaturated compound, the surface area of the metal is an additional and very important factor. Under the conditions used in these experiments, the metal was in a massive form and the limited surface area must be an important factor in the rate of reduction of (I). It might be expected that the electron transfer reaction would be appreciably less sensitive to temperature changes than the proton transfer [formation of (V)] since the latter occurs in solution. This suggested that the temperature of the reaction between (I) and sodium might be one means of controlling the extent of the formation of the allylic anion (V).

In a series of experiments at various temperatures, the reaction between (I) and sodium (THF as solvent) was examined by means of the previously described criteria. As may be seen from Table 2, the extent of proton transfer was markedly affected by changes of temperature. At 0° very little occurred so that reaction (1) dominated and essentially a dianion was formed. The deuterium content of the *trans*-(I) recovered after deuterolysis demonstrated that proton transfer was not entirely suppressed. At temperatures above 50°, the proton transfer reactions (2) and (3) have proceeded to a large extent.

TABLE 2

REACTION OF *trans*-1,2-DIPHENYLPROPENE WITH SODIUM

Temp. (°C)	*Compn. of organo-sodium compd.*[a]	*Product analysis*[b]				*D per mole in*[c]	
		(VI)	*cis-(I)*	*(VII)*	*trans-(I)*	*(VI)*	*trans-(I)*
0	1.9	90	3	<1	7	1.9	0.5
23	1.6	72	3	1	24	1.6	0.6
40	1.4	57	8	8	27		
49	1.2	51	5	2	42	1.1	0.8
55	1.2	50	5	2	43	1.0	0.7
65[d]	0.94	42	6	2	50	1.0	1

[a] g-Atoms of Na per initial moles of (I). [b] Analysis by VPC. [c] Analyzed by NMR of isolated products. [d] At reflux.

In an effort to compare the lability of the methyl protons of an aromatic methyl group with that of the allylic protons of (I), the behaviour of *p*-methylstilbene towards alkali metals was examined. The reaction proved to be relatively uncomplicated, a dianion was smoothly and rapidly generated in THF by sodium metal. Deuteration provided no products indicative of metalation of the aromatic methyl group. With potassium as the reducing metal much the same observation was made. However, in this case, the equilibrium between the hydrocarbon and its derived anion was less favorable.

DISCUSSION

Generally, the solution equilibria between alkali metals and many acceptors lies far to the right. Diphenyl is a notable exception[16] and in this case it has been observed that lithium is more effective[16]* in forming the organometallic compound than is sodium and that solvents with increased cation solvating[16,18] ability shift the equilibrium to the right.

Superficially, the behavior of (I) towards alkali metals contrasted with that of biphenyl in that lithium was less effective than sodium. However, this appeared due to a limited solubility of the organometallic compound in DEE. Decreasing the initial concentration of (I) resulted in a steadily increasing conversion of (I) to the organometallic compound. From this data it was possible to estimate the solubility as 0.037 moles/kg of solution [assuming the product was the dianion (III)]. When this concentration was reached, (III) coated the surface of the lithium and prevented further reaction. Below this concentration, conversion of (I) to (III) was complete.

The extent of proton transfer between (I) and its derived organometallic derivatives increases with the atomic weight of the cation and is greater in THF than in DEE. This corresponds to observations made in related studies. For example, Bank[19] has concluded that solvent separated ion pairs (*i.e.* Li salts) are less reactive in protonation than contact ion pairs (*i.e.* Na and K salts). Possibly this is due to the greater localization of the anionic charge which occurs in solvent separated ion-pairs while in contact ion pairs this charge is more localized and hence the anionic center more basic. The larger dielectric constant of THF (relative to DEE) stabilizes the transition state for proton transfer by facilitating charge separation.

The formation of 1,2-diphenylpropane, (VI), which is a mixture of di-, mono- and non-deuterated hydrocarbons deserves comment. Hoijtink[20] has cited examples in which the monoanion has disproportionated to the dianion plus the reduced hydrocarbon [*i.e.* (IV) → (VI) + (III)]. While this would explain our observations, a simpler explanation is that the rate of reaction (3) exceeds that of reaction (2). In other words, the monoanion (IV) is protonated faster than the dianion (III). This is not surprising if one accept the view[8,21,22]** that steric factors in the dianion (III) favor a twisted conformation about the bond joining the benzylic carbons. Each half of the dianion may be considered as a benzylic anion with a reactivity approximating to that of anion (IV).

Additionally, the sodium salts are probably contact ion pairs[18,21a,23] in THF.

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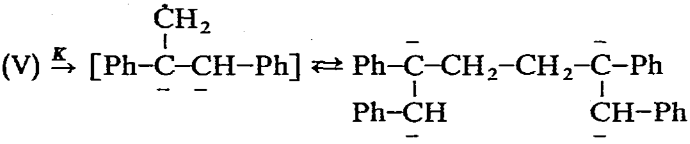
* A dianion can also be formed from naphthalene and Li but not Na[17].

** Some controversy has arisen recently over this twisted dianion structure[22].

Thus the intimate presence of the sodium cation at one anionic center of the dianion would hinder the approach of the alkene (I) to the other anionic site. In contrast, the monoanion (IV) with a hydrogen replacing the second sodium cation has a more accessible anionic center and can be expected to be more reactive than the dianion.

The reaction of (I) with potassium is particularly interesting because of the dimeric products, (IX), formed. That dimerization of 1,3-diphenylpropene [arising from the equilibria shown in eqn. (1)] was not the source of (IX) was indicated by the isolation of a tetradeuterated dimer on deuterolysis. Dimerization of 1,3-diphenylpropene should yield a dideuterated form of (IX). In addition, a control experiment with 1,3-diphenylpropene and potassium produced a complex series of products some of which have VPC retention times corresponding to (IX). The exact composition of these products is under examination but certainly this dimerization differs from that of (I).

In order to rationalize the formation of the dimer (IX), it must be assumed that the allylic anion (V) has a low lying vacant MO capable of accepting an electron to form a dianion radical such as (X) which equilibrates with its dimer, the tetra-anion (XI). Protonation of (XI) generates the observed dimer (IX) while deuteration provides a corresponding tetradeuterated dimer.

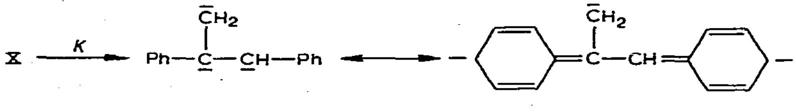


$$(V) \xrightarrow{K} [Ph-\overset{\dot{C}H_2}{\underset{-}{C}}-\underset{-}{C}H-Ph] \rightleftarrows Ph-\overset{-}{\underset{Ph-\underset{-}{C}H}{C}}-CH_2-CH_2-\overset{-}{\underset{\underset{-}{C}H-Ph}{C}}-Ph$$

(X) (XI)

The formation of radical dianions is not without precedent. Bauld[24] has found, both theoretically and experimentally, that a surprising number of anions have low-lying MO's and can be reduced to radical dianions and even trianions.

An additional feature of the reaction with potassium is the composition of the deuterated 1,2-diphenylpropane formed in the reaction. The mass spectrum showed the presence of nondeuterated (*m/e* 196), dideuterated (*m/e* 198), smaller amounts of monodeuterated (*m/e* 197) hydrocarbons and, in addition, a trideuterated hydrocarbon (*m/e* 199). A comparison of the mass spectrum of this hydrocarbon mixture with that of the nondeuterated and di-deuterated samples showed that the only other significant difference was the presence of a *m/e* 107 fragment in addition to the 105 and 106 fragments expected. It must be concluded that the third deuterium atom is located in the hydrocarbon chain of (VI) rather than in the phenyl groups.



(XII)

Conceivably, the dianion radical (X) can be reduced by potassium to a trianion (XII) which can gain some stabilization by delocalization of the benzylic anionic charges. Alternatively, reduction of the radical center of (X) can occur during reaction with deuterium oxide in the manner suggested for the reaction of naphthalene radical anion[12,15]. However, no product has been detected which would represent the oxidation co-product of this last reaction.

EXPERIMENTAL

Melting points are uncorrected and were determined on a Mel-temp apparatus. The NMR spectra were recorded on a Varian T-60 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Line positions are ppm downfield from TMS (δ). IR spectra were recorded on a Beckman IR-10 spectrometer and mass spectra on a Perkin–Elmer RMU-6E single focusing mass spectrometer operated at 70 eV. Several spectra were also recorded on an AEI MS-30 double beam, double focusing mass spectrometer with perfluorokerosene in the reference beam so as to confirm the assignment of peak positions. Analyses were performed by the M-H-W Laboratories, Garden City, Michigan.

Gas chromatography was conducted on a Varian Aerograph 1520 instrument. For the analytical determinations, a 5 ft. by 1/8 in. column packed with 10% Carbowax 20M on 100/120 mesh Chromosorb W was used at 160° with flame ionization detectors. For those samples containing dimers, a column of the same dimensions packed with 3% SE 30 on 100/120 mesh Varaport 30 was used with the following temperature-time profile: 4 min at 160°, 4 min heating at 12°/min, final temp. 230°.

Preparative gas chromatography was conducted with a 5 ft. by 1/4 in. column packed with 10% Carbowax 20 M on 60/80 mesh Chromosorb W with a He flow of 60 ml/min.

General procedure

At room temperature, the hydrocarbon (0.01 mol) was dissolved in 100 ± 10 ml of the ethereal solvent which had been purified and dried by distilling from $LiAlH_4$. The solution was shaken with an excess of alkali metal until reaction was complete. The reaction time was determined by preliminary experiments in which aliquots of the reaction solution were quenched in water and the liberated base titrated with standardized acid. Equilibrium metal uptake was reached in the following times (metal, solvent, time(h)); Li, DEE, 2.5; Li, THF, 7; Na, DEE, 7; Na, THF, 2; K, THF, 4.5. Reaction times in preparative runs were not permitted to exceed* these times by more than 1 h.

The solution was then transferred from the excess metal to a second nitrogen-filled flask, cooled to −60° and, with vigorous stirring, treated with excess methanol (protonation) or D_2O (deuterolysis)**. After warming to room temperature, the mixture was diluted with water and the products isolated by ether extraction.

For the reactions conducted at temperatures differing from 23°, sodium and (I) were reacted in a magnetically stirred flask immersed in a thermostatically controlled water bath. Equilibrium metal uptake occurred in a minimum of 1 h (above 50°) to a maximum of 3.5 h (at 0°). The final solution was transferred to a second flask and treated as described (see Table 2).

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* Slates and Szwarc[25] have shown that "negligible killing takes place within a few hours" of THF solutions of radical anions and dianions of a variety of hydrocarbons and normally used overnight preparative runs.

** This procedure was adopted to obviate the vigorous exothermic reaction (often with local overheating) which occurs at room temperature.

Gas chromatographic analyses were performed on the dried ether extracts while VPC separations were performed on the residue left after removal of the solvent.

In the case of the experiments with potassium, the organic residue was treated with 10 ml of cold pentane. The solid which separated was filtered, dried and recrystallized from ethanol. The IR and NMR spectra were identical to those of authentic (IX) and a mixture m.p. was not depressed. The pentane filtrate contained the 1,2-diphenylpropane which was isolated by distillation.

The organolithium compound was prepared with four different initial concentrations of (I) and these results are summarized in Table 3. Alkali metal uptake was complete in 2–2.5 h in all cases and in those runs in which conversion remained incomplete, the concentration of organolithium compound [assuming it to be (III)] was 0.037 molal.

TABLE 3

REACTION OF *trans*-1,2-DIPHENYLPROPENE WITH LITHIUM

Initial moles of (I)	*g of DEE*	*g-atoms Li per mole (I)*	*Molality of (III)*	*Molality of (VI)*	*Product analysis*		
					cis-(I)	*(VII)*	*trans-(I)*
0.001	63.0	2.08	0.0167	99	<1		1
0.004	60.0	1.11	0.0367	53	11	<1	36
0.010	69.0	0.50	0.0363	24	13	1	62
0.015	56.8	0.28	0.0370	16	16	<1	68

1,2-*Diphenylpropane*

1,2-Diphenylpropane* showed the following mass spectrum. *m/e* (rel. intensity): 196(16), 106(15), 105(100), 104(28), 91(14), 77(16).

The doubly deuterated hydrocarbon isolated from the reactions with lithium and with sodium in DEE or THF (at 0°) showed NMR ($CDCl_3$); δ 1.23 (s, 3, CH_3), 2.7–3.0 (broad d, 1, CHD), 7.0–7.3 ppm (m, 10, aromatics); mass spectrum *m/e* (rel. intensity): 198(13), 107(17), 106(100), 105(37), 92(14).

The 1,2-diphenylpropane isolated from those experiments conducted at 25° with sodium and THF was a mixture chiefly of di- and non-deuterated (VI) with some mono-deuterated hydrocarbon also present. The NMR spectrum showed a complex multiplet for the methyl protons and this was interpreted as being the superposition of the methyl singlet from the doubly deuterated hydrocarbon and the multiplet from the non-deuterated. Integration of the benzylic protons established the presence of an average of 1.6 H. The mass spectrum resembled that of the doubly deuterated hydrocarbon except for the larger relative intensities of the 196, 105 and 91 peaks due to the non-deuterated hydrocarbon. Table 2 summarizes the data obtained from similar experiments at various temperatures.

The 1,2-diphenylpropane formed on deuteration of the potassium adduct showed, NMR ($CDCl_3$): δ 1.2–1.4 (m, 3, CH), 2.7–3.2 (m, 2, benzylic H), 7.0–7.4 ppm (m, 10, aromatics). Mass spectrum *m/e* (rel. intensity): 199(7), 198(11), 196(3), 107(71), 106(100), 105(76), 92(40), 91(14).

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* The NMR spectrum has been reported, see ref. 26.

trans-1,2-*Diphenylpropene*

trans-1,2-Diphenylpropene[27] showed a mass spectrum *m/e* (rel. intensity): 195(15), 194(88, M^+), 193(14), 180(15), 179(100), 178(48), 165(13), 116(12), 115(16), 103(18), 91(16), 89(19), 77(18), 51(19).

This alkene when isolated from the sodium/THF experiments (at 20–65°) showed essentially the same mass spectrum with the 195 peak greatly exaggerated. No significant differences were noted in the NMR spectrum except in the area of the methyl resonances which decreased from 2.5 to 2H as the reaction temperature increased.

Suitable control experiments demonstrated that the hydrocarbon itself did not exchange with D_2O at room temperature in the presence of base. Thus deuterium is not gained (or lost) by the alkene during work-up.

Tetraphenylhexane

The tetraphenylhexane isolated after deuterolysis of the organopotassium compound showed NMR ($CDCl_3$): δ 1.60 (s, 4, CH_2–CH_2), 2.8 (broad s, 2, PhCHD), 6.8–7.4 ppm (m, 20, aromatics); mass spectrum, *m/e* (rel. intensity): 394(1, M^+), 302(8), 225(19), 224(100), 183(40), 168(20), 167(16), 119(22), 118(17), 106(30), 105(65), 104(19), 93(22), 92(96), 91(31).

1,2,5,6-*Tetraphenyl*-2,5-*hexanediol*

Benzylmagnesium chloride prepared from 15 g (0.12 mol) of benzyl chloride in 100 ml of ether was treated with 12 g (0.051 mol) of dibenzoylethane[28] in 100 ml of anhydrous THF. After the addition was completed, the mixture was stirred for thirty minutes and hydrolyzed with aqueous ammonium chloride. The crude reaction product was isolated by ether extraction and treatment of this product with 50 ml of ether with cooling at −10° caused 7.6 g (35%) of 1,2,5,6-tetraphenyl-2,5-hexanediol to crystallize, m.p. 152.5–155°. Recrystallization from ether gave an analytical sample m.p. 155–157°; NMR ($CDCl_3$): δ 1.6–2.2 (m, 4, CH_2–CH_2), 2.91, 3.16 (ABq, J_{AB} 13 Hz, 4, Ph–$C\underline{H}_2$), 6.7–7.4 (m, 20, aromatic) (exchangeable peak exists in the 1.6–2.2 ppm region, 2, OH). (Found: C, 85.34; H, 7.10. $C_{30}H_{30}O_2$ calcd.: C, 85.27; H, 7.16%.)

The filtrate from the crude diol on storing several days at −10° deposited a second crop of material, 5.7 g, m.p. 78–89°. Recrystallization from ethanol provided a sample of the second diastereomer, m.p. 100–101°; NMR ($CDCl_3$): δ 1.80 (s, 4, CH_2–CH_2), 2.20 (s, 2, OH, exchanges with D_2O), 2.82, 3.08 (ABq, J_{AB} 14 Hz, 4, Ph–$C\underline{H}_2$), 6.7–7.4 ppm (m, 20, aromatics). (Found: C, 85.49, 85.43; H, 6.95, 7.03. $C_{30}H_{30}O_2$ calcd.: C, 85.27; H, 7.16%.)

1,2,5,6-*Tetraphenylhexane*

A mixture of 1 g of 1,2,5,6-tetraphenyl-2,5-hexanediol (m.p. 152–155°), 0.10 g of 10% palladium on charcoal, 120 ml of glacial acetic acid and 0.5 ml of 70% perchloric acid was shaken for ten hours under 50 lbf/in^2 of hydrogen pressure[29]. The mixture was filtered, and the filtrates diluted with water, neutralized with sodium bicarbonate and the product isolated by an ether extraction. The dried ether extract was concentrated to 40 ml and cooled to 10°. A white solid, m.p. 139.5–144.5°, separated. This was recrystallized from ethanol to give 0.45 g (44%), m.p. 142–144.5°; NMR ($CDCl_3$): δ 1.6 (broad s, 4, CH_2–CH_2), 2.74 (broad s, 6, Ph–CH_2–CH–), 6.8–7.4 ppm (m, 20, aromatics); mass spectrum *m/e* (rel. int.): 390(1, M^+), 299(23), 222(42), 221(92), 181(72), 167(57), 117(68), 105(25), 104(52), 103(47), 91(100). (Found: C, 92.42; H, 7.67. $C_{30}H_{30}$ calcd.: C, 92.26; H, 7.74%.)

trans-4-Methylstilbene

trans-4-Methylstilbene[30] reacted rapidly with sodium using THF as the reaction solvent. Titration of aliquots showed the average composition to be 2 g-atoms of sodium per mole and the only product formed on protonation was 4-methylbibenzyl, NMR ($CDCl_3$): δ, 2.30 (s, 3, CH_3), 2.87 (s, 4, CH_2–CH_2), 7.1–7.3 ppm (m, 9, aromatics); mass spectrum *m/e* (rel. int.): 196(65), 106(32), 105(100), 91(58).

On deuteration, the 4-methylbibenzyl had an NMR ($CDCl_3$): δ 2.30 (s, 3, CH_3), 2.87 (s, 2, CHD–CHD), 7.1–7.3 ppm (m, 9, aromatics); mass spectrum *m/e* (rel. int.) 198 (M^+, 21), 106(100), 105(34), 92(16).

The reductive metallation of *trans*-4-methylstilbene by potassium proceeded to an average composition of 0.75 g-atom of potassium per mole of alkene and the products of protonation were the recovered alkene (65%) and 4-methylbibenzyl (35%). The latter was found to be doubly deuterated when the organopotassium compound was treated with D_2O while the former was deuterium free.

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REFERENCES

1 H. F. Ebel and A. Lüttringhaus (in Houben-Weyl Ed.), *Methoden der Organischen Chemie*, Vol. XIII, Georg Thieme Verlag, Stuttgart, 1970, p. 599.
2 U. Schöllkopf, ref. 1, p. 97.
3 A. G. Brook, H. L. Cohen and G. F. Wright, *J. Org. Chem.*, 18 (1953) 447.
4 (a) W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Chem. Ber.* 47 (1914) 473;
(b) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, 463 (1928) 1.
5 K. Ziegler, H. Colonius and O. Schäfer, *Justus Liebigs Ann. Chem.*, 473 (1929) 36.
6 (a) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, 479 (1930) 58;
(b) W. Schlenk and E. Bergmann, *ibid.*, 479 (1930) 78;
(c) J. W. Burley, R. Ife and R. N. Young, *Chem. Commun.*, (1970) 1256.
7 W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, 479 (1930) 42.
8 J. F. Garst, J. G. Pacifici and E. R. Zabolotny, *J. Amer. Chem. Soc.*, 88 (1966) 3872.
9 K. Ziegler, F. Crössmann, H. Kleiner and O. Schäfer, *Justus Liebigs Ann. Chem.*, 473 (1929) 1.
10 D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, 86 (1964) 5478.
11 G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 86 (1967) 1345.
12 (a) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, 93 (1971) 430;
(b) S. Bank and W. D. Closson, *Tetrahedron Lett.*, (1965) 1349;
(c) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Amer. Chem. Soc.*, 78 (1956) 116.
13 K. A. Bilevich and O. Yu. Okhlobystin, *Russ. Chem. Rev.*, 37 (1968) 954.
14 G. Spach, H. Monteiro, M. Levy and M. Szwarc, *Trans. Faraday Soc.*, 58 (1962) 1809.
15 L. M. Dorman, *Accounts Chem. Res.*, 3 (1970) 224.

16 (a) A. I. Shatenshtein, E. S. Petrov and E. A. Yakovleva, *J. Polym. Sci. Part C*, 16 (1962) 1729;
(b) R. V. Slates and M. Szwarc, *J. Amer. Chem. Soc.*, 89 (1967) 6043;
(c) K. Lühder, *Z. Chem.*, 9 (1969) 389.
17 J. Smid, *J. Amer. Chem. Soc.*, 87 (1965) 655.
18 M. Szwarc, in A. Streitwieser, Jr. and R. W. Taft (Eds.), *Progress in Physical Organic Chemistry, Chemistry of Radical-ions*, Vol. 6, Interscience publishers, 1968, p. 323.
19 S. Bank, *J. Org. Chem.*, 37 (1972) 114.
20 N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, 89 (1967) 209.
21 (a) R. C. Roberts and M. Szwarc, *J. Amer. Chem. Soc.*, 87 (1965) 5542;
(b) J. F. Garst, E. R. Zabolotny and R. S. Cole, *J. Amer. Chem. Soc.*, 86 (1964) 2257;
(c) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, 23 (1955) 514.
22 (a) D. H. Eargle, Jr., *J. Amer. Chem. Soc.*, 93 (1971) 3859;
(b) J. F. Garst, *J. Amer. Chem. Soc.*, 93 (1971) 6312.
23 J. B. Grutzner, J. M. Lawlor and L. M. Jackman, *J. Amer. Chem. Soc.*, 94 (1972) 2306.
24 N. L. Bauld, *J. Amer. Chem. Soc.*, 86 (1964) 2305.
25 R. V. Slates and M. Szwarc, *J. Phys. Chem.*, 69 (1965) 4124.
26 D. L. Ransley, *J. Org. Chem.*, 31 (1966) 3595.
27 I. Ho and J. G. Smith, *Tetrahedron*, 26 (1970) 4277.
28 J. P. Schaeffer, *J. Org. Chem.*, 25 (1960) 2027.
29 (a) A. M. Khan, F. J. McQuillin and I. Jardine, *Tetrahedron Lett.*, (1966) 2649;
(b) S. Misui, Y. Kudo and M. Kobayashi, *Tetrahedron*, 25 (1969) 1921;
(c) E. W. Garbisch, Jr., L. Schreader and J. J. Frankel, *J. Amer. Chem. Soc.*, 89 (1967) 4233.
30 O. H. Wheeler and H. N. Battle de Pabon, *J. Org. Chem.*, 30 (1965) 1473.