Competitive Pathways in the Reaction of 1-Phenyl-1-butyne with Alkali Metals in Various Solvents

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The reaction of 1-phenyl-1-butyne (I) with alkali metals (sodium and potassium) has been investigated in tetrahydrofuran (THF), diethyl ether (DEE), and n-octane. Hydrolysis of the reaction mixtures yielded (a) products resulting from the reductive metalation at the triple bond of I, 1-phenylbutane (II), 1-phenyl-1-butene (III), and its positional isomer 1-phenyl-2-butene (IV); (b) hydrocarbons due to the propargylic rearrangement of I, 1-phenyl-1,2-butadiene (V) and 1-phenyl-2-butyne (VI); (c) olefinic and acetylenic hydrocarbons of higher molecular weight (VII, VIII, and IX) corresponding to the addition of ethylenic units. The appearance and the relative amounts of the products are strongly dependent on the nature of the metal and somewhat less on the solvent. This fact is discussed in light of the formation of both deuterated and nondeuterated hydrocarbon products upon deuterolysis of the reaction mixtures, and our results are compared with those reported in the literature.
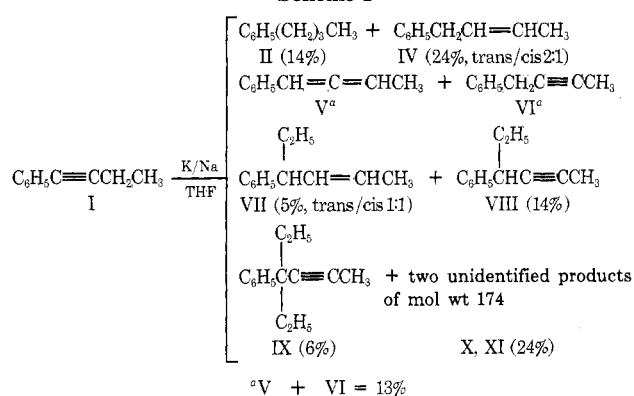
In the course of the study of the noncationic rearrangement of homopropargylic derivatives[1] the competitive reactions that we observed between species formed during that process and the alkali metal present in the medium led us to study the behavior of 1-phenyl-1-butyne (I) under such conditions. We wish to report the results of this investigation, which complement recent observations made by Szwarc in the reaction of *tert*-butylphenylacetylene with metallic potassium.[2a]

Results

Reaction of 1-Phenyl-1-butyne (I) with K/Na Alloy. In THF (Run 1).
When 1-phenyl-1-butyne (I) was added to a stirred suspension of K/Na alloy in THF at room temperature a strongly exothermic reaction took place. After hydrolysis with a methanol–water mixture, analysis by vapor phase chromatography (vpc) showed the presence of at least ten products, which were collected in a first fraction (corresponding to a 30–40% yield) by distillation at 25–50° under vacuum (0.05 mm). Further distillation at higher temperature afforded a constant-boiling fraction (120°, 0.05 mm), corresponding to a 5–10% yield of dimers, as indicated by mass spectrometric analysis (mol wt 258–262). These dimers were not further investigated. The polymeric residue of the distillation corresponded to a 40–50% yield from the starting material I. Catalytic hydrogenation over Pd/C of a sample of the crude undistilled reaction mixture led to a mixture of only four volatile products (dimeric and polymeric materials were not analyzed). These compounds as well as the compounds formed in run 1 were isolated by preparative vpc as pure compounds or as mixtures,[2b] and their structures were determined by means of ir, mass spectral, and nmr data (see Experimental Section). This analysis indicated the following product distribution (see Schemes I and II and Table I).

Of the 51% 1-phenylbutane in the reduction product, 14% is present from the initial reaction of I with K/Na in THF, and 24% results from the reduction of 1-phenyl-2-butene (IV). The remaining 13% of II was attributed to the hydrogenation products of 1-phenyl-1,2-butadiene (V) and 1-phenyl-2-butyne (VI), which were present in the product mixture from run 1 but which had the same retention time as other products, thus precluding accurate analytical determination. Furthermore, mass spectrometric analysis of the mixture[2b] did not show the presence of other isomeric products which could have yielded 1-phenylbutane (II) upon catalytic hydrogenation.

Scheme I

$$\text{C}_6\text{H}_5\text{C}{\equiv}\text{CCH}_2\text{CH}_3 \xrightarrow[\text{THF}]{\text{K/Na}}$$
I

C₆H₅(CH₂)₃CH₃ + C₆H₅CH₂CH=CHCH₃
II (14%)   IV (24%, trans/cis 2:1)

C₆H₅CH=C=CHCH₃ + C₆H₅CH₂C≡CCH₃
Vᵃ   VIᵃ

C₆H₅CHCH=CHCH₃ + C₆H₅CHC≡CCH₃ (with C₂H₅ groups)
VII (5%, trans/cis 1:1)   VIII (14%)

C₆H₅CC≡CCH₃ (with two C₂H₅ groups) + two unidentified products of mol wt 174
IX (6%)   X, XI (24%)

ᵃ V + VI = 13%

The 20% of 3-phenylhexane (XXI) found after the catalytic hydrogenation cannot be fully accounted for by the hydrogenation of the 5% of 4-phenyl-2-hexene (VII) present in the product from run 1. Mass spectrometric analysis of that mixture,[2b] however, showed the presence of only one other product (VIII, mol wt 158) which could reasonably have led to 3-phenylhexane (XXI). Compound VIII could not be isolated pure owing to the presence of impurities of the same retention time, making difficult the interpretation of its nmr spectrum as well as an accurate determination of the amount of VIII produced in run 1. Based on this discussion, the structure of VIII was assigned as 4-phenyl-2-hexyne. (See Experimental Section for a discussion of the data obtained for VIII.) The formation of only one compound of mol wt 176 (XXIII, 25%) after catalytic hydrogenation of the mixture from run 1 showed that the two unidentified products of mol wt 174 (25%) must be two positional olefinic isomers, but unfortunately no other information could be obtained concerning their structures.
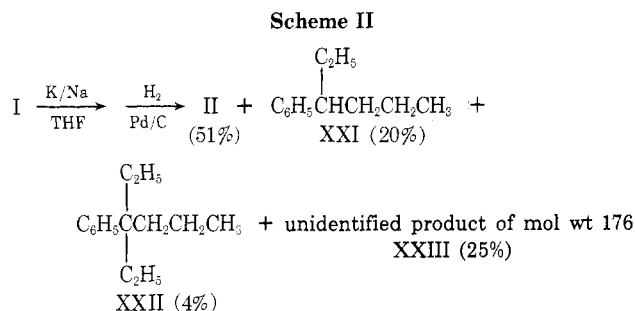
The amount of compound XXII obtained was too small for nmr analysis, but the mass spectrum[2b] of XXII showed that it had a molecular weight of 190. The structure 3-phenyl-3-ethylhexane was assigned to XXII based on the following considerations: (1) only one product from run 1 (IX, mol wt 186) could reasonably have led to 3-phenyl-3-ethylhexane; (2) the per cent of compound IX (6%) in the product mixture of run 1 is consistent with the 4% of compound XXII observed after hydrogenation.

In Diethyl Ether (DEE) (Run 2).
When the reaction was carried out in DEE instead of THF it was somewhat slower and 1-phenylbutane (II) and *cis*- and *trans*-1-phenyl-2-butene (IV) were the main products isolated after

Table I
Relative Distribution[a] of the Products Formed in the Reaction of I with Alkali Metals

Run	Metal	Solvent (temp, °C)	II	trans-III	cis-III	trans-IV	cis-IV	V[b]	VI[b]	Higher mol w products
1	K/Na	THF (50)	14			16	8	13[c]		49[d]
2	K/Na	DEE (37)	13	3		40	30	4	10	Trace
3	K/Na	n-Octane (25)	35	3		40	22			Trace
4	Na	THF (25)	Trace	32	28	8	5	11	16	Trace
5	Na	THF (0)	Trace	60	12			20	8	Trace
6	Na	DEE (25)	2	54	29	10	5			
7	Na	n-Octane (120)	3	60	22	10	5			Trace

[a] Values given are in per cent and were determined by vpc analysis of the reaction mixtures. Reproductibility of the result was satisfactory within the error limits of ±4%, except for the amount of V and VI (see footnote b). [b] Compounds V and VI are unstable in the reaction medium, and their percentages in the mixture may vary from run to run. [c] Since V and VI were obtained in mixtures with other products, their percentages were calculated from the amount of phenylbutane formed by catalytic hydrogenation of the reaction mixture as described in the text. [d] This value represents the sum of the percentages of products VII, VIII, IX, X, and XI, but does not include the percentages of the dimeric species also formed during the reaction.

Scheme II

$$I \xrightarrow[\text{THF}]{K/Na} \xrightarrow[\text{Pd/C}]{H_2} \underset{(51\%)}{II} + \underset{XXI\ (20\%)}{C_6H_5\overset{\overset{\displaystyle C_2H_5}{|}}{C}HCH_2CH_2CH_3} +$$

$$\underset{\underset{\displaystyle XXII\ (4\%)}{\overset{\overset{\displaystyle |}{C_2H_5}}{}}}{C_6H_5\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle |}{}}{C}}CH_2CH_2CH_3} + \text{unidentified product of mol wt 176} \\ \text{XXIII (25\%)}$$

hydrolysis of the mixture when no more starting material (I) was present (see Table I), although trans-1-phenyl-1-butene (trans-III) was shown to be an intermediate in the reaction. 1-Phenyl-1,2-butadiene (V), 1-phenyl-2-butyne (VI), and 3-phenyl-3-ethyl-4-hexyne (IX) could also be identified in the mixture.

In n-Octane (Run 3). In this solvent the reaction was much slower than in DEE or THF, as shown by rough kinetic studies. Here again 1-phenylbutane (II) and 1-phenyl-2-butene (cis- and trans-IV) were the main products isolated after hydrolysis of the reaction mixture (see Table I). trans-1-Phenyl-1-butene (trans-III) was demonstrated to be an intermediate in the reaction, as shown in Figure 1. Small amounts of products of higher molecular weight could also be detected.

In runs 1–3 hydrolysis of the mixture with deuterium oxide afforded non- and polydeuterated hydrocarbons, indicating the presence of the corresponding polymetalated species in the reaction mixture. In the reaction in n-octane (run 3), when deuterolysis was carried out after 1 half-life, mass spectral and nmr analysis of III and IV showed that these compounds were essentially mono-, di-, and trideuterated, but also that some tetra- (5–10%), penta- (2–4%), and nondeuterated (5–10%) products were present. Nmr data for cis- and trans-IV showed that all the deuterium atoms were located at the benzylic and vinylic carbon atoms, and the benzylic positions contained about twice as much deuterium as the olefinic positions. Deuterolysis of the mixture after 5 half-lives and analysis of the mass spectral and nmr data for cis- and trans-IV showed a decrease in the deuterium content compared with that observed after 1 half-life. Thus metal–hydrogen exchange reactions had occurred between metalated IV and other species present in the medium.

When the reaction was carried out in DEE and the mixture was quenched with deuterium oxide after 1 half-life, IV was a mixture of mono-, di-, tri-, and tetradeuterated hydrocarbons containing some penta- (5–7%) and nondeuterated (4–8%) products. The deuterium distribution was
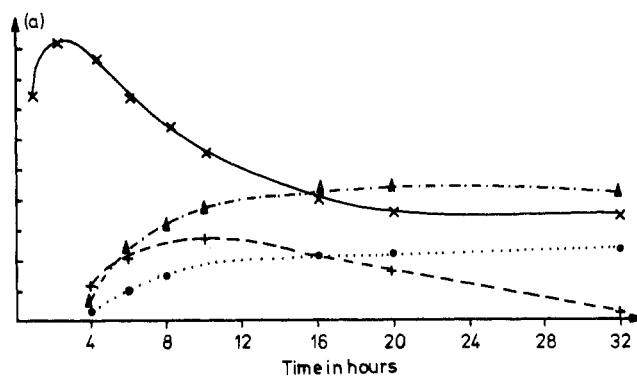

Figure 1. Formation of 1-phenylbutane (II), trans-1-phenyl-1-butene (III), and trans- and cis-1-phenyl-2-butene (IV) in the reaction of I with K/Na alloy in n-octane: ×, II; +, trans-III; ▲, trans-IV; ●, cis-IV; (a), absolute yields referred to diisoamyl ether as a standard.

approximately the same at the benzylic and olefinic positions, showing that the solvent can play quite an important role in determining the nature of the metalated species formed during the reaction. This difference is probably due to the formation of solvated ion pairs in ether but not in n-octane.

Reaction of 1-Phenyl-1-butyne (I) with Sodium. In THF (Runs 4 and 5). When sodium was used instead of a K/Na alloy a drastic change was observed in the product distribution formed from 1-phenyl-1-butyne (I). Addition of I to a stirred suspension of finely cut pieces of sodium caused a strong exothermic reaction, but in this case cis- and trans-1-phenyl-1-butene (III), 1-phenyl-1,2-butadiene (V), and 1-phenyl-2-butyne (VI) were the main products isolated after hydrolysis of the reaction mixture. The amount of 1-phenyl-2-butene (cis- and trans-IV) had fallen to a much lower value than in the reaction with the K/Na alloy, and 1-phenylbutane (II) and products of higher molecular weight were present only in small amounts. Moreover, when the reaction was carried out carefully at 0° (run 5) no trace of 1-phenyl-2-butene (IV) could be detected (see Table I).

In DEE (Run 6). When DEE was used instead of THF the reaction was much slower. trans- and cis-1-phenyl-1-butene (III) and trans- and cis-1-phenyl-2-butene (IV) were formed simultaneously (see Figure 2), but 1-phenyl-1,2-butadiene (V) and 1-phenyl-2-butyne (VI) were not observed (see Table I).

In n-Octane (Run 7). Finally, 1-phenyl-1-butyne (I) did not react with sodium at room temperature in n-octane, but did react slowly at 120°, and here again 1-phenyl-1-butene (cis- and trans-III) was the main product of the
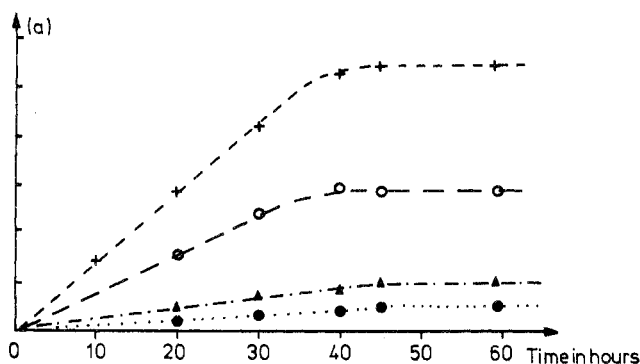
Figure 2. Formation of 1-phenyl-1-butenes (III) and 1-phenyl-2-butenes (IV) in the reaction of I with sodium in DEE: +, *trans*-III; O, *cis*-III; ▲, *trans*-IV; ●, *cis*-IV; (a), absolute yields referred to diisoamyl ether as a standard.

reaction, whereas the concentration of 1-phenyl-2-butene (*cis*- and *trans*-IV) was much smaller than in the reaction with the K/Na alloy. Compounds of higher molecular weight were formed only in small amounts (see Table I). In all the experiments with sodium (runs 4–7) hydrolysis with deuterium oxide led to undeuterated III, but deuterated IV, V, and VI.

Thus in the reaction of I with alkali metals we have to consider at least three competitive reactions (Scheme III): (a) reductive metalation at the triple bond of 1-phenyl-1-butyne (I) leading to the olefinic product III, which can rearrange to its positional isomer IV [this metalation process can in some cases (with K/Na alloy) proceed further, yielding 1-phenylbutane (II)]; (b) isomerization of I leading to the species V and VI; (c) formation of products of higher molecular weight (VII, VIII, and IX) arising from the addition of an anionic species derived from IV or V to ethylene, which is present in the medium as will be discussed below (Scheme III). We did not investigate a fourth competitive reaction which led to the formation of dimeric species.

Discussion

Metalation at the Triple Bond of 1-Phenyl-1-butyne. In the past several years more light has been shed upon the metalation process at the multiple bond of unsaturated compounds. Among others the work of Evans[3] and Szwarc[4,5] have provided a better understanding of the influences of the metal, the metal reagent, the solvent, and the temperature upon the character of the metal–carbon bond in the species formed during the process. In the case of the reaction of diphenylacetylene (DPA) with an alkali metal or sodium naphthalenide, for instance, evidence has been obtained for the initial formation of an anion radical, DPA·$^-$. This latter is stable in hexamethylphosphoramide[4b] but dimerizes very rapidly to a dianionic species in THF when the metalating agent is sodium naphthalenide. The anion radical reacts further with another metal atom to give a dianion DPA^{2-} when the reaction is carried out with the alkali metal itself.[3e] This dianion is in an equilibrium with the radical anion DPA·$^-$ when an excess of the starting material DPA is present in the medium (2DPA·$^-$ ⇌ DPA^{2-} + DPA). All these reactions and equilibria are dependent on the temperature, the nature of the solvent, and the nature of the alkali metal (Li *vs.* Na *vs.* K), since it is possible for the species to exist as loose ion pairs, solvent-separated ion pairs, or tight ion pairs depending on the solvent and the counterion used. Hirota[6] found actually that such different types of ion pairs exchange electrons at different rates with neutral

Scheme III
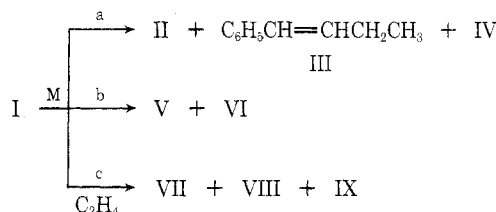
aromatic hydrocarbons in ether-like solvents. Quite similar pathways have been proposed for the metalation processes of olefins. In the case of tetrasubstituted alkenes [tetraphenylethylene (TPE)] the radical anion TPE·$^-$ which is formed in the first step[7] leads to the dianion TPE^{2-}, which is in equilibrium with the radical anion when an excess of olefin is present in the medium.[3a,4a]

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

For less highly substituted olefins [1,1-diphenylethylene (DPE)] the radical anion rapidly dimerizes to dianion $^-$DPE–DPE$^-$ [3e] in the absence of the steric hindrance which prevents dimerization of tetrasubstituted ethylenic anion radicals. Here again the behavior of these species (anions and radical anions) is actually somewhat more complex because of the influence of solvents and cations which affect the state of aggregation and the character of the metal–carbon bond in the reacting species. We feel quite confident that the metalation of 1-phenyl-1-butyne (I) with alkali metal occurs according to a process quite similar to those proposed in the literature for the reaction of other unsaturated compounds. Thus in the presence of sodium or potassium I may react with a metal atom to give initially the radical anion XII (see Scheme IV), which is expected either (1) to dimerize (step b); (2) to further react with another metal atom to form the dianion XIII (step c); (3) to undergo radical or charge transfers to other species (step d); or (4) to rearrange as will be discussed below (step f).

Formation of a radical anion species XII is supported by the fact that by esr measurement[8] we observed a signal very early in the reaction of I with either Na or a K/Na alloy in THF. However, this signal collapsed after a short time (5–10 min at −20°), although a considerable amount of starting material was still present. These results are entirely consistent with the observations made by Szwarc, who reported that·in the metalation of diphenylacetylene (DPA) and tetraphenylethylene (TPE) a large excess of the starting material (about 1000-fold in the case of TPE in THF at room temperature[4b]) must be present to maintain an appreciable concentration of the respective radical anions DPA·$^-$ and TPE·$^-$.

Additional support for the formation of a radical anion such as XII is the observation of a large amount of 1-phenylbutane (II) but no detectable amount of 1-phenyl-1-butene (III) after hydrolysis of the mixture at the very beginning of the reaction of I with K/Na alloy in THF, DEE, or *n*-octane[9] (see Figure 1). With increasing reaction time, hydrolysis produced decreasing amounts of II until its concentration fell to a constant value. This observation is in agreement with the explanation proposed by Szwarc[5] for the formation of dibenzyl during the hydrolysis of the corresponding radical anion DPA·$^-$ (or dianion DPA^{2-}) of diphenylacetylene (DPA) and a very similar mechanism could as well be responsible for the formation during hydrolysis of the 1-phenylbutane that we observed. We also found that the radical concentration (esr) is much higher in the case of the reaction of I with the K/Na alloy than with sodium, and this corresponds also to the far
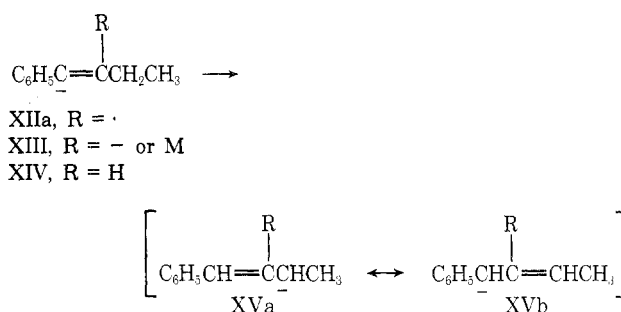
Scheme IV

$$C_6H_5C\!\equiv\!CCH_2CH_3$$

I

$$[C_6H_5C\!=\!CCH_2CH_3]\,2M^+$$

XIII

$$[C_6H_5C\!\equiv\!CCH_2CH_3]^{\cdot-},\,M^+$$

XII

rearranged products
(see XV, Scheme VI)

$$C_6H_5C\!=\!CHCH_2CH_3$$

or

XIV

$$C_6H_5CH\!=\!CHCH_2CH_3$$

III

greater amount of 1-phenylbutane that we observed at the beginning of the reaction with K/Na alloy than that observed in the reaction with sodium.

Although our experiments do not allow us a conclusion concerning the fine structure of radical anion XII,[10] it is very likely that it is resonance stabilized (Scheme V), and XIIa, in which the anion is stabilized by conjugation with the phenyl ring, is expected to be the more important contributor.

This conclusion is supported by results reported in the literature. In the metalation of 1,1-diphenylethylene (DPE)[3d] in cyclohexane with K/Na alloy, the presence of only 1,1,4,4-tetraphenylbutane after hydrolysis of the mixture corresponds to the dimerization of the radical anion of DPE in which the radical is located at the carbon β to the phenyl rings; this emphasizes the combined effect of the two phenyl rings in stabilizing a benzylic anion rather than the corresponding radical. This is also in agreement with the results presented by Wooster and Ryan[11] in the metallic reduction of DPE with sodium amide, except that in that case the authors reported not only the presence of the dianionic species of 1,1,4,4-tetraphenylbutane, but also the presence of 1,1-diphenylethyn-1-ylsodium, indicating that the radical anion DPE·⁻ has undergone partial electron transfer to the protic solvent (ammonia). It is interesting to note that under the same conditions phenylethylene leads to phenylethane but not to the expected 1-phenylethyn-1-ylsodium, indicating that the latter has undergone a further electron transfer to the solvent. This discrepancy in the reductions of 1,1-diphenylethylene and phenylethylene shows significantly the greater stabilization of an anion by two phenyl rings as compared with that by only one, in spite of the fact that the secondary benzylic anion formed in the metalation of phenylethylene should be more stable than the tertiary anion formed from 1,1-diphenylethylene.

The difference observed in the product distribution in the reactions of I with sodium and K/Na alloy, respectively, suggests that the fate of the radical anion XII might be largely influenced by the nature of the counterion used.

Reaction with Sodium. The small amount of 1-phenylbutane (II)[8] as well as the low intensity of the esr signal that we observed in the reaction of I with sodium, in contrast to the reaction with a K/Na alloy, suggest that when sodium is the counterion the radical anion XII leads rapidly to more stable species. Since the amount of rearranged products [1-phenyl-2-butene (IV)] formed is small in the reactions with sodium, in that case (see Table I, runs 4–7), it is very likely that step f in Scheme IV does not occur to a very large extent, and that either step c, which leads to the dianion XIII, is very fast, or that the

Scheme V

$$C_6H_5C\!=\!CCH_2CH_3 \quad\longleftrightarrow\quad [C_6H_5C\!\equiv\!CCH_2CH_3]^{\cdot-} \quad\longleftrightarrow$$

XIIa   XII

$$C_6H_5C\!=\!CCH_2CH_3$$

XIIb

radical anion XII undergoes a fast electron transfer to other species (step d). This latter possibility is consistent with (1) the absence of deuterium in the 1-phenyl-1-butene isolated when the mixture was hydrolyzed with deuterium oxide, and (2) the fact that the only 1.2 to 1.3 sodium atoms per mole of 1-phenyl-1-butyne (I) were necessary to effect complete reaction, whereas at least 2 atoms of sodium would have been used if the dianion XIII had been formed. The questions now to be answered are how those transfer reactions (steps d and e, Scheme IV) actually occur and between which species they take place. It is of course very possible that in the case of the reaction with sodium in THF or in DEE the solvent can play a significant role in the metal–hydrogen transfer due to the acidity of the hydrogens α to the oxygen atom.[12] However, such transfers with the solvent are known to be slow, and, since we find that the 1-phenyl-1-butene (III) isolated after hydrolysis with deuterium oxide of the reaction mixture of I with sodium in *n*-octane was free of deuterium, we must conclude that such metal–hydrogen transfers occurred with species present in the medium other than the solvent itself. Both the starting material and the 1-phenyl-1-butene (III) formed during the reaction contain acidic hydrogens at the propargylic[13] and the allylic carbon atoms, respectively, and also at the sp² carbon atoms of the phenyl ring and of the double bond of III. These hydrocarbons could indeed act as proton sources for metallic species. However, in that case hydrolysis with deuterium oxide would have afforded the corresponding deuterated hydrocarbons (I and/or III) and these were not observed. Another possibility is that a radical mechanism could be responsible for those metal transfers as well and that the radical species formed dimerize very rapidly. In the reactions with sodium (runs 4–7) we actually isolated 1-phenyl-1-butene (III) alone or together with 1-phenyl-2-butene (IV) in 30–50% yield, which indicated that 70–50% of the materials had either dimerized or polymerized (although of course one of the dimeric species might have been formed from the radical anion XII; see Scheme IV, step b).

The much faster transfer process that we observed in the reactions with sodium compared to those with the K/Na alloy could be a quite good indication of a mechanism in which electron or atom transfers rather than charge or ion transfers are involved, since sodium–carbon bonds are known to be less ionic than potassium–carbon bonds. This also agrees with the work of Weissmann,[14] who reported that in the metal-transfer reaction between the sodium ketyl of benzophenone and benzophenone itself "the electron carries its sodium nucleus with it"[14b] and that, in the oxidation–reduction transfer reaction of the naphthalene–naphthalenide system, "the alkali metal and spin are transferred together."[14c] Although it could be advanced that a very similar process is responsible for the sodium transfer that we observed, our results are more consistent with a metal-atom transfer than with a metal-cation transfer. In all of the experiments of I with sodium, the 1-phenyl-1-butene (III) formed was a mixture of cis and trans isomers (see Table I), whereas only the trans olefin could be detected in the reaction with the K/Na alloy. Another peculiar difference was the absence of deuterium in the *cis*- and *trans*-1-phenyl-1-butene (III) isolat-

ed in the reaction with sodium, whereas the trans isomer isolated from the reaction with the K/Na alloy was polydeuterated when the reaction mixtures were hydrolyzed with D_2O. It seems therefore that the geometric isomerization of *trans*-1-phenyl-1-butene to its cis isomer is not due to the isomerization of its metalated species but occurs rather during the metal–hydrogen transfer process which gives rise to the corresponding olefins. A control experiment showed that isomerization of *trans*-III to *cis*-III is extremely slow under such conditions and cannot alone account for the simultaneous formation of both isomers during the reaction of I with sodium (see Figure 2).

Reaction with K/Na Alloy. When potassium was used instead of sodium a drastic change was observed in the product distribution of the reaction of 1-phenyl-1-butyne (I). Initially greater amounts of 1-phenylbutane (II) (see Figure 1) were formed, and then only II and *trans*- and *cis*-1-phenyl-2-butene (IV) were present at the end of the reaction (see Table I), although kinetic measurements indicated that *trans*-1-phenyl-1-butene (*trans*-III) was present in the medium during the course of the reaction. Hydrolysis with deuterium oxide at 1 half-life and at the end of the reaction (5 half-lives) gave mixtures of polydeuterated 1-phenylbutane (II) and 1-phenyl-2-butene (IV) which indicates the presence in the reaction mixture of the polymetalated species corresponding to those hydrocarbons. We found that the *trans*-1-phenyl-1-butene (III) isolated by hydrolysis with D_2O at 1 half-life was also polydeuterated. The decrease of deuterium content of IV with time shows that a slow metal transfer occurs also when the counterion is potassium.

We found that a large excess of alloy was necessary to carry the reaction to completion. In *n*-octane three to four atoms of metal per mole of starting material I were necessary for the disappearance of only 50% of I, although hydrolysis of the reaction mixture with deuterium oxide gave rise to deuterated products in which the average deuterium content corresponded to the use of only 2.1 atoms per mole. When I was mixed with the K/Na alloy, we observed a rapid tarnishing of the bright alloy particles and then formation of a purple-red colored slurry. Therefore it is very likely that the metalation process of I occurs at the surface of the metal particles, forming a protective shell around them,[15] preventing further reaction with the metal. This could explain the high degree of metalation of the species formed in the reaction of I with the K/Na alloy due to their intimate contact with the metal. It is interesting to observe that in the case of I with sodium we did observe a tarnishing of the metal particles at the very beginning of the reaction but then the sodium rapidly recovered its original brightness. This indicates that the shell of the first-formed metallic compounds has been removed because of the metal–hydrogen exchange with other species present in the medium (see above). Concerning the differences observed in the product distributions in runs 4–7, we found that with sodium in THF at 0° *trans*- and *cis*-1-phenyl-1-butene (III), but no *trans*- or *cis*-1-phenyl-2-butene (IV), were formed (Table I, run 5), but that, in either THF or DEE at room temperature (or in *n*-octane at 120°), *trans*- and *cis*-IV were also present, whereas III was not present at the end of the reaction with the K/Na alloy.

Although it could be argued that IV could have been formed by metalation of the 1-phenyl-2-butyne (VI), which was found to be present in some cases (see below), we rejected this possibility for several reasons: (1) formation of 1-phenyl-2-butene (IV) was found to occur prior to the appearance of 1-phenyl-2-butyne (VI); (2) IV was found to be present also in reactions in which no 1-phe-

Scheme VI

$$C_6H_5C \overset{\overset{\displaystyle R}{\displaystyle |}}{=\!=\!=} CCH_2CH_3 \longrightarrow$$

XIIa, R = ·
XIII, R = – or M
XIV, R = H

$$\left[C_6H_5CH \overset{\overset{\displaystyle R}{\displaystyle |}}{=\!=\!=} \underset{\displaystyle XVa}{CCHCH_3} \quad \longleftrightarrow \quad C_6H_5CH \overset{\overset{\displaystyle R}{\displaystyle |}}{C} \overset{}{=\!=\!=} \underset{\displaystyle XVb}{CHCH_3} \right]$$

nyl-2-butyne (VI) could be detected; (3) it is very unlikely that metalation of the unactivated triple bond of VI occurs faster than at the activated one in 1-phenyl-1-butyne (I). Gurfinkel and Klein[16] reported that metalation of unactivated triple bonds occurred to a very small extent in *n*-heptane.

The isomerization of olefins in the presence of alkali metals or alkali compounds in protic solvents, aprotic solvents, or without solvent is a well-known process. In aprotic solvents Benkeser[17] showed that the metalation of the benzylic position of toluene, for instance, is due to a rearrangement of ring-metalated species, and Broaddus[18] demonstrated that in the allylic rearrangement of α olefins to their β isomers, a vinylic metalated species may be formed first in a kinetically controlled step, but it then rearranges to a thermodynamically more stable allylic metalated system.

It is therefore to be assumed that vinylic metalated species such as the radical anion XIIa, the dianion XIII, or the anion XIV (see Scheme IV) are very likely to rearrange to a thermodynamically more stable allylic system such as XVa (where R is either an electron, an electron pair, a metal atom, or a hydrogen) (see Scheme VI). The resonance form XVb must be a more important contributor than XVa, since the negative charge of XVb is stabilized by delocalization into the phenyl ring. Protonation of XVb thus could account for the formation of the *cis*- and *trans*-1-phenyl-2-butene (IV) after hydrolysis of the reaction mixture with water.[19]

In the case of the reactions with K/Na alloy the rearrangement from XIII (or XIIa, or XIV) to XV is complete owing to the stability of the metallic species formed with the potassium, but in the case of the reactions with sodium this rearrangement is only partial, because of a competitive metal–hydrogen transfer reaction (Scheme IV, steps d and e), which affords the thermodynamically more stable olefin III; moreover, when the temperature is low enough (see Table I, run 5), it is only the metal-transfer reaction which takes place, and thus it corresponds to a lower activation energy process than the one leading to the rearrangement. When the reaction with sodium was carried out at higher temperature followed by hydrolysis with deuterium oxide, the 1-phenyl-2-butene (IV) which was formed was found to be monodeuterated, although the III formed contained no deuterium. This result emphasizes the difference in basicities and stabilities of the corresponding metalated species.

Proposed Mechanism. These results lead us to propose the following mechanism for the formation of the phenylbutene isomers in the reaction of 1-phenyl-1-butyne (I) with alkali metals. In the first step a radical anion XII (Scheme IV) is formed. When potassium is the counterion this latter radical anion partially dimerizes but also reacts with another metal atom to give rise to the dianion XIII. Species XII or XIII, or both, then rearranges to the reso-
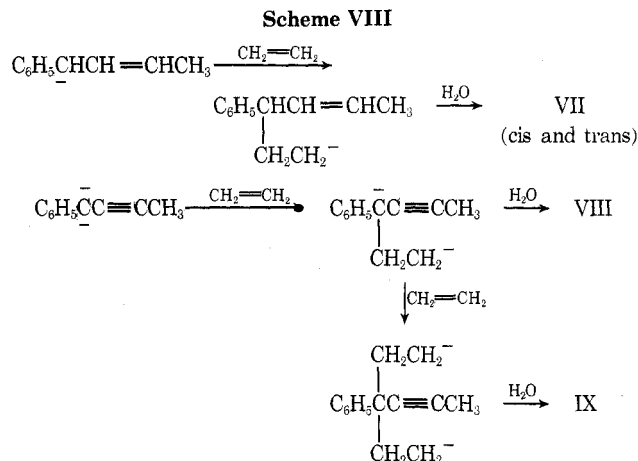
Scheme VII

$$I \xrightarrow[a]{RM}$$

$$C_6H_5C\equiv CCHCH_3 \xrightarrow[b]{RM} [C_6H_5C\equiv C-CCH_3 \longleftrightarrow C_6H_5C=C=CCH_3]$$

$$\text{XVI} \qquad\qquad \text{XVII} \qquad\qquad \text{XVIII}$$

$$C_6H_5CH=C=CCH_3 \qquad C_6H_5CC\equiv CCH_3]$$

$$\text{XX} \qquad\qquad\qquad \text{XIX}$$

(f and RM / d paths indicated between structures)

Scheme VIII

$$C_6H_5CHCH=CHCH_3 \xrightarrow{CH_2=CH_2}$$

$$C_6H_5CHCH=CHCH_3 \xrightarrow{H_2O} \text{VII (cis and trans)}$$
$$\quad|\quad CH_2CH_2^-$$

$$C_6H_5CC\equiv CCH_3 \xrightarrow{CH_2=CH_2} C_6H_5CC\equiv CCH_3 \xrightarrow{H_2O} \text{VIII}$$
$$\qquad\qquad\qquad\qquad\qquad |\quad CH_2CH_2^-$$

$$\downarrow CH_2=CH_2$$

$$CH_2CH_2^-$$
$$\quad|$$
$$C_6H_5CC\equiv CCH_3 \xrightarrow{H_2O} \text{IX}$$
$$\quad|$$
$$CH_2CH_2^-$$
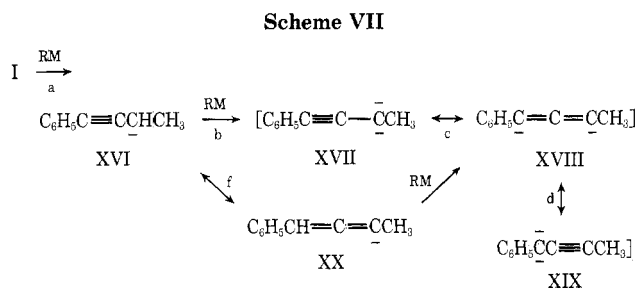
nance-stabilized metalated allylic system XV (Scheme VI), of which XVb represents the more important contributor. Thus the equilibrium is shifted far to the right and hydrolysis leads exclusively to the formation of *cis-* and *trans-*1-phenyl-2-butene (IV). In all of the reactions with potassium, which occur at the surface of the metal, the intimate contact with that metal leads to the formation of polymetalated species.

When sodium is the counterion a fast electron transfer leads to the anion XIV (Scheme IV, step d), which then partitions between (1) rearrangement to the allylic system XV (R = H) and (2) competitive metal-hydrogen transfer (Scheme IV, step e) which leads to the thermodynamically more stable olefin III.

The presence of 1-phenylbutane (II) at the end of the reaction with the K/Na alloy (see Table I, runs 1–3) can be explained by a further metalation of the 1-phenyl-1-butene (III) rather than of the 1-phenyl-2-butene (IV) because of the activation of the double bond by a phenyl ring in III. In a separate experiment, treatment of 1-phenyl-1-butene (III) with K/Na alloy in THF or n-octane afforded a significant amount of 1-phenylbutane (II), while formation of II from 1-phenyl-2-butene (IV) under the same conditions was much slower (see Experimental Section).

Formation of Species Isomeric to I. We found that 1-phenyl-1,2-butadiene (V) and 1-phenyl-2-butyne (VI) or its derivatives (VIII and IX) (see the reaction with K/Na alloy in THF) were formed in significant amounts[20] in the reaction of I with K/Na alloy in THF or ether (see Table I, runs 1 and 2) and with sodium in THF (see Table I, runs 4 and 5). No detectable amounts of those compounds were formed in the other cases (sodium in DEE or n-octane, K/Na in n-octane), although derivatives of VI were formed in small amounts.

The base-catalyzed isomerization of alkynes to allenes and positional isomers first observed by Favorskii[21] has recently been further examined. West[22] and Mulvaney[23] reported that, in studies of the rearrangement of 1-phenylpropyne to 3-phenylpropyne in the presence of n-butyllithium, evidence has been observed for the formation of trimetalated species when an excess of the metalating reagent was used. Klein and Brenner[24] have recently investigated the formation and properties of the propargylic anions derived from 1- and 3-phenylpropyne as well as that from phenylallene, which was found to be an intermediate in the rearrangement of 1-phenylpropyne to 3-phenylpropyne. Because 1-phenylpropyne and 1-phenyl-1-butyne (I) are quite analogous and because we observed deuterium incorporation by 1-phenyl-1,2-butadiene (V) and by 1-phenyl-2-butyne (VI) when the reaction mixtures were hydrolyzed with deuterium oxide, it seems quite reasonable that the mechanism proposed by Mulvaney and Klein can be invoked to explain the formation of V and VI from 1-phenyl-1-butyne (I). Thus metalated compounds present in the medium can generate the propargylic anion XVI (see Scheme VII), which, according to the observa-

tions of Klein and Brenner,[25] is expected to be readily converted to dianion XVII. Two resonance forms of XVII are the allenic species XVIII and the propargylic dianion XIX, and XIX should be the most important contributor owing to the stabilization of the dianion at a propargylic position α to a phenyl ring. The importance of the dianion XIX is indicated by the formation of 3-phenyl-3-ethyl-4-hexyne (IX) (see Scheme I) in the reaction of I with the K/Na alloy in THF. However, it is not impossible that the alkyne–allene isomerization occurs, at least partially, at the stage of the monopropargylic anion XVI to afford the allenic anion XX[26] (Scheme VII, step f). The acidic hydrogen at the other sp² carbon atom of the allenic system of XX could easily be abstracted by a metalated species to yield the dianionic allene XVIII.

Isomerization of 1-phenyl-1-butyne (I) to 1-phenyl-1,2-butadiene (V) and to 1-phenyl-2-butyne (VI) occurs under conditions which favor the polarization of the carbon–metal bond (*i.e.*, with sodium in THF or with K/Na in THF or DEE), whereas it does not occur to a large extent under conditions favoring a more covalent carbon–metal bond (*i.e.*, sodium in DEE or n-octane, or K/Na in n-octane). This fact suggests to us that the metal–hydrogen transfer process which leads to the formation of those anions is one in which anions or polarized species rather than radicals or metal atoms are involved. It is noteworthy that in the reaction of I with sodium in THF the species corresponding to 1-phenyl-1,2-butadiene (V) and to 1-phenyl-2-butyne (VI) were metalated, although those corresponding to *cis-* and *trans-*1-phenyl-1-butene (III) were not, as shown by hydrolyzing the reaction mixture with deuterium oxide.

Formation of Higher Molecular Weight Products in the Reaction of 1-Phenyl-1-butyne (I) with K/Na Alloy in THF (See Table I, Run 1). In the reaction of I with K/Na alloy in THF we observed formation of large amounts (49%) of products of higher molecular weight (see Scheme I, compounds VII, VIII, and IX). It has been reported that ether-like solvents can fragment in the presence of alkali metals or alkali compounds and that in the case of THF and DEE ethylene can be formed.[27]

Since addition of anions to olefins is a well-known process, the formation of 4-phenyl-2-hexene (VII), 4-phenyl-2-hexyne (VIII), and 3-phenyl-3-ethyl-4-hexyne (IX) can be easily explained by the addition of the anion of 1-phenyl-2-butene (IV) or the dianion (XIX) of 1-phenyl-2-butyne (VI) to ethylene generated under the reaction conditions (see Scheme VIII). The much smaller percentage of products of ethylene addition such as VII, VIII, and IX when the reaction was run in DEE (compare runs 1 and 2, Table I) is compatible with the significantly slower cleav-

age of diethyl ether by alkali metal compounds[27,28] as compared with the cleavage of THF. However, it seems that the solvents are not the only substances responsible for the formation of ethylene. We found that, in the reaction of I with K/Na alloy also in *n*-octane at room temperature or with sodium at 120°, there were formed small amounts of compounds containing additional ethylenic units (mol wt 160, 162, 186, and 188). This would mean that ethylene was formed, at least partially, by fragmentation of I or some species derived from it. This analysis is supported by the presence of small amounts of ethylbenzene, which could be detected by mass spectrometric analysis, in these reactions.

We do not intend to propose any mechanism for such fragmentations, but there is some precedent for such base-catalyzed reactions. Wooster and Morse[29] reported formation of triphenylmethane in the reaction of the 1,1,1-triphenylprop-3-yl iodide with sodium amide; Roberts[30] observed formation of diphenylmethane in the reaction of the diphenylcyclopropylmethane with dimsylsodium in DMSO; and Evans[3a] noted the presence of a small amount of 1,1-diphenylethane in the reaction of 1,1,3,3-tetraphenyl-1-butene with sodium–naphthalenide. The formation of the unidentified products X and XI with an odd number of carbon atoms ($C_{13}H_{18}$) might also arise by such fragmentations.

Conclusion

In this study it was found that in the presence of alkali metals 1-phenyl-1-butyne (I) may undergo three types of reactions: (1) reductive metalation at the activated triple bond leading to the formation of metalated derivatives of *trans*-1-phenyl-1-butene (*trans*-III), allylic rearrangement of which yields derivatives of *cis*- and *trans*-1-phenyl-2-butene (IV); (2) propargylic rearrangement promoted by metalated species present in the medium leading to the migration of the multiple bond in I; (3) addition of the metalated species formed from I to ethylene generated under the conditions by fragmentation of the solvent (or other species) induced by alkali metals to yield products of higher molecular weight.

The relative importance of these three processes depends largely on the nature of the alkali metal (Na *vs.* K). With potassium the three reactions are competitive, whereas with sodium it is the reductive metalation at the triple bond of I which predominates owing to a rapid metal–hydrogen transfer which prevents further reactions and leads to the formation of *cis*- and *trans*-1-phenyl-1-butene (III). The reaction leading to migration of the double bond in 1-phenyl-1-butene (III) can be regarded as good evidence for the vinyl to allyl anion rearrangement observed by Benkeser[17] and Broaddus[18] in the base-catalyzed isomerization of olefins in aprotic solvents.

The formation of initially large amounts and subsequently smaller amounts of 1-phenylbutane (II) upon hydrolysis of the reaction mixture of 1-phenyl-1-butyne with K/Na alloy, together with the observation of an esr signal, which disappeared after 5–10 min at −20°, suggests the formation of a radical anion such as XII. Initially, when the concentration of XII is high, II is formed during the hydrolysis by analogy to a mechanism proposed by Szwarc[5] for the reaction of diphenylacetylene (DPA) with sodium naphthalenide.

The formation of hydrocarbons resulting from the addition of ethylene units to metalated species formed from I is consistent with observations made by Maercker,[27] except that in our case species other than the solvents are also responsible for the generation of ethylene in the medium.

Experimental Section

Preparation of 1-Phenyl-1-butyne (I). A mixture of 20 g of phenylacetylene, NaH (from 10 g of a 50% NaH dispersion), and 31 g of diethyl sulfate was refluxed for 24 hr in absolute THF. The mixture was then cooled to room temperature, and water and ether were added. The organic layer was decanted, stirred for 1 hr with a 10% NaOH solution, washed with water, and dried ($CaCl_2$). The solvent was distilled at atmospheric pressure, and 1-phenyl-1-butyne (I) was distilled at reduced pressure, bp 81–83° (15 Torr), yield 75–85%. The product was redistilled until no more starting material (phenylacetylene) was detectable by vpc: nmr δ 1.22 (t, J = 7 Hz, 3 H), 2.38 (q, J = 7 Hz, 2 H), 7.23 (m, 5 H); mass spectrum m/e (rel intensity) 130 (68, molecular peak), 129 (55), 128 (40), 115 (100, $M^+ - CH_3$); ir 2200 cm^{-1} ($C\equiv C$ stretching).

General Procedure. Solvents were dried and purified by repeated distillation over sodium, and for THF over $LiAlH_4$. All the reactions were carried out under dry nitrogen. Suspensions of metal or alloy were prepared as follows.[31] Small pieces of freshly cut sodium, or potassium and sodium in a proportion of 5:1, respectively, in the case of the alloy, were introduced into the reaction flask previously filled with *n*-octane, and the mixture was heated with rapid stirring at 120–130° to liquefy the metal. The stirrer was then stopped and the mixture was allowed to cool to room temperature; when *n*-octane was not the solvent for the reaction it was pipetted out and the metal was washed several times with the desired solvent to remove traces of *n*-octane; finally, a quantity of the desired solvent was added to afford a final concentration of 0.3–0.5 mol/l. of the starting material 1-phenyl-1-butyne (I). A solution of I and the standard (diisoamyl ether) in the desired solvent was added to the preceding metal suspension all at once in the case of runs 2, 3, 6, and 7, and dropwise in the case of runs 1, 4, and 5. In runs 1, 2, 4, and 5 a brown slurry appeared after a few minutes, but in runs 3, 6, and 7 its formation required additional time (30 min to 1 hr). We attribute these colorations to the formation of metallic species. Samples were then withdrawn from time to time, quenched with a methanol–water mixture, and analyzed by vpc. In the reaction with K/Na alloy a large excess of metal (six- to eightfold) was necessary for the complete disappearance of the starting material 1-phenylbutyne (I), whereas in the reaction with sodium only 1.2–1.3 atoms per mole of I were sufficient for complete consumption of I. At the end of the reaction the bulk of the mixture was decomposed by carefully adding it either to a mixture of methanol–water or to D_2O stirred under a strong stream of dry nitrogen. The resulting mixture was decanted and the aqueous layer was extracted four times with *n*-heptane. The combined solutions were washed several times with saturated NaCl solution until neutral and dried ($CaCl_2$), and the solvent was slowly distilled on a steam bath. The residue was then distilled under increasing vacuum (from 10 to 0.05 mm), first at room temperature (the receiver being cooled in Dry Ice–methanol) and then at higher temperature. The fractions obtained by distillation at room temperature (0.05 mm) contained products II, III, IV, V, and remaining starting material I; the fraction distilling at 30–50° (0.05 mm) contained products VI, VII, VIII, IX, X, and XI. At 120° (0.05 mm) a constant-boiling fraction distilled corresponding to the dimers formed during the reaction (mol wt 258–262).

Structure Determination of the Products Formed in the Reaction of 1-Phenyl-1-butyne (I) with Alkali Metals. 1-Phenylbutane (II). Its mass and nmr spectra were identical with those of an authentic sample prepared by catalytic hydrogenation over Pd/C of 1-phenyl-1-butyne (I).

***cis*-1-Phenyl-1-butene (*cis*-III).** This compound was identified by its mass, nmr, and ir spectra, and its vpc retention time, with an authentic sample obtained by hydroboration of 1-phenyl-1-butyne (I). Its mass spectrum[32] showed a molecular peak at m/e 132 and the base peak at m/e 117 ($M^- - CH_3$); nmr δ 1.05 (t, J = 7.2 Hz, 3 H), 2.31 (10 lines, J = 7.2, 7, 1.7 Hz, 2 H), 5.55 (d of t, J = 7, 11.5 Hz, 1 H), 6.33 (d of t, J = 1.7, 11.5 Hz, 1 H), 7.18 (5 H).

trans-**1-Phenyl-1-butene** (*trans*-**III**). Its mass spectrum was identical with that of the cis isomer[32] and its nmr spectrum was very similar as well: δ 1.08 (t, J = 7.2 Hz, 3 H), 2.21 (m, J = 7.2, 4 Hz, 2 H), 6.20 (m, 2 H), 7.18 (5 H). This is consistent with the structure *trans*-1-phenyl-1-butene in which the vinylic proton β to the phenyl ring is shifted downfield relative to that of the cis isomer, owing to the deshielding effect of the phenyl ring. The trans isomer of 1-phenyl-1-butene (*trans*-III) has a longer vpc retention time than does the cis isomer (*cis*-III).

trans-**1-Phenyl-2-butene** (*trans*-**IV**). Its mass spectrum was very similar to those of *cis*- and *trans*-1-phenyl-1-butene (III).[32] It was identified by comparison of its mass and nmr spectra with those of an authentic sample (purchased from EGA): nmr δ 1.68 (d, J = 4 Hz, 3 H), 3.25 (d, J = 4 Hz, 2 H), 5.50 (m, 2 H), 7.11 (5 H). This compound had the same vpc retention time as *cis*-1-phenyl-1-butene (*cis*-III) on both polyethylene glycol and ethylene glycol succinate columns.

cis-**1-Phenyl-2-butene** (*cis*-**IV**). Its structure was determined by its mass[32] and nmr spectra, this latter being very similar to that of *trans*-IV: δ 1.71 (d, J = 4 Hz, 3 H), 3.34 (d, J = 4 Hz, 2 H), 5.54 (m, 2 H), 7.12 (5 H).

1-Phenyl-1,2-butadiene (**V**). Its mass spectrum showed a molecular ion peak at m/e 130 (88%) and a base peak at m/e 115 (M$^+$ − CH$_3$), and its ir spectrum displayed a band at 1940 cm^{-1} (allene); nmr δ 1.78 (d of d, J = 7, 3 Hz, 3 H), 5.44 (5 lines, d of q, J = 7, 7 Hz, 1 H), 5.97 (6 lines, d of q, J = 7, 3 Hz, 1 H), 7.16 (5 H). This is consistent with the structure 1-phenyl-1,2-butadiene in which the two allenic protons form an AB quartet (J = 7 Hz), each part of which is further split by the methyl group (J_{AX} = 7, J_{BX} = 3 Hz). In the reactions hydrolyzed with deuterium oxide the patterns were less distinct and the intensity of the allenic protons was much smaller.

1-Phenyl-2-butyne (**VI**). This compound could not be isolated pure and was contaminated by higher molecular weight products. However, analysis of those mixtures by vpc coupled with a mass spectrometer (LKB-9000) showed the presence of a compound of molecular weight 130, for which the base peak is the molecular ion peak. The next significant peak is at m/e 115 (80%, M$^+$ − CH$_3$). This is consistent with the fragmentation of the 1-phenyl-2-butyne molecule in which the loss of either the methyl or the benzyl group corresponds to the rupture of a high-energy sp bond (molecular ion peak 100%). The ir spectrum of the mixtures containing VI showed two C≡C stretching bands at 2200 and 2210 cm^{-1}; one of those[33] was attributed to 1-phenyl-2-butyne. The nmr spectrum of the mixtures containing VI showed a broad peak at δ 1.79 and a partially resolved signal at δ 3.63 which are assigned to the methyl and the benzyl protons, respectively, in VI. This fit quite well the values of the nmr spectrum recorded in CDCl$_3$ for 1-phenyl-2-butyne:[33] δ 1.70 (t, 3 H), 3.45 (q, 2 H, J = 2.7 Hz). In the reactions hydrolyzed with deuterium oxide these signals were broadened and less intense owing to the presence of deuterium at these positions.

4-Phenyl-2-hexene (**VII**). The fraction isolated by vpc corresponding to VII was a 1:1 mixture of two isomers inseparable on an ethylene glycol succinate column but separate on a polyethylene glycol succinate column. Mass spectrometric analysis of the mixture with a LKB-9000 spectrometer[2] showed that these two compounds have the same mass spectrum: a molecular peak at m/e 160 (16%) and a base peak at m/e 131 (M$^+$ − CH$_2$CH$_3$), corresponding to the facile loss of an ethyl group thus expected to be bound to a highly substituted carbon atom. The nmr spectrum of the mixture could reasonably be interpreted as being due to the patterns of two geometrical isomers: δ 0.83 (t, J = 6.5 Hz, 3 H), 0.86 (t, J = 6.5 Hz, 3 H), 1.66 (t, J = 7 Hz, 3 H), 1.69 (t, J = 7 Hz, 3 H), 1.05–1.83 (m, 4 H), 3.02 (m, 1 H), 3.40 (m, 1 H), 5.46 (m, 4 H), 7.15 (10 H). Vpc, mass, and nmr spectral data are consistent with a mixture (1:1) of *cis*- and *trans*- 4-phenyl-2-hexene (VII). The structure 4-phenyl-2-hexene (VII) is also in agreement with the formation of 3-phenylhexane (XXI) that we observed upon catalytic hydrogenation of the reaction mixture of 1-phenyl-1-butyne (I) with K/Na alloy in THF.

4-Phenyl-2-hexyne (**VIII**). This compound was not isolated pure, but mass spectrometric analysis of the mixture[2] which contained it showed a material (mass 158) the fragmentation of which was consistent with 4-phenyl-2-hexyne: a peak at m/e 129 (85%) corresponding to the loss of an ethyl group bonded to a highly substituted carbon atom and a base peak at m/e 128 for the simultaneous loss of two methyl groups. Although these data are also consistent with the fragmentation of either 4-phenyl-2,3-hexadiene or 1-phenyl-3-methyl-1-pentyne, we discarded the for-

mer because of the presence in the ir spectrum of a weak C≡C stretching absorption at 2320 cm^{-1} (and the absence of an allene band), and the latter because when the reaction mixture from I with K/Na alloy in THF was hydrogenated over Pd/C we found 3-phenylhexane (XXI) as the sole product of molecular weight 162. Moreover, the 20% of XXI in the hydrogenation product (see Scheme II) cannot be fully accounted for by the catalytic hydrogenation of only 4-phenyl-2-hexene (VII) also present in the mixture, since this would have afforded only 5% of 3-phenylhexane (XXI). Therefore the structure assigned for VIII can account for the additional 15% of XXI observed. We found no other compounds of molecular weight 158 (or 160) in the reaction mixture of 1-phenyl-1-butyne (I) with K/Na alloy in THF.

3-Phenyl-3-ethyl-4-hexyne (**IX**). Its mass spectrum showed a molecular ion peak at m/e 186 (6%) and a base peak at m/e 157 (M$^+$ − CH$_2$CH$_3$) corresponding to the facile lost of an ethyl group attached to a highly substituted carbon atom. Another relatively intense peak (76%) occurred at m/e 142 corresponding to the simultaneous loss of an ethyl and a methyl group from two different positions of the molecule: nmr δ 0.76 (t, J = 7.5 Hz, 6 H), 1.77 (q, J = 7.5 Hz, 4 H), 1.95 (s, 3 H), 7.25 (5 H).

Compounds X and XI. These compounds of molecular weight 174 were contaminated by impurities which made difficult the interpretation of their nmr spectra and little structural information could be obtained from their mass spectra.[2]

Catalytic Hydrogenation over Pd/C of the Reaction Mixture of 1-Phenyl-1-butyne (I) with K/Na Alloy in THF. The general procedure described above was applied to a mixture of 1-phenyl-1-butyne (I, 2.5 g) and K/Na alloy (2 g of potassium, 0.40 g of sodium) in THF, but after the solvent was removed, instead of distilling the mixture, it was taken up in methanol containing a catalytic amount of Pd/C. The solution was shaken under a hydrogen atmosphere until no more gas was absorbed. After filtration of the solution, the solid residue was washed with saturated CaCl$_2$ solution, then with water, and dried (CaCl$_2$). The mixture was analyzed by vpc and then concentrated and distilled under vacuum. Separation by preparative vpc afforded products II, XXI, XXII, and XXIII, the structures of which are discussed below.

1-Phenylbutane (**II**). This compound was identified by comparison of its mass and nmr spectra with those of an authentic sample (see above).

3-Phenylhexane (**XXI**). Its mass spectrum showed a molecular ion peak at m/e 162 (35%) and a peak at m/e 133 (42%) corresponding to the loss of a propyl group, the base peak being the tropylium ion at m/e 91: nmr δ 0.75 (t, 3 H), 0.83 (t, 3 H), 1.17–1.75 (m, 6 H), 2.32 (m, 1 H), 7.05 (5 H). The mass and nmr data are consistent with 3-phenylhexane. The fragmentation of its molecular ion by electron impact should occur at the highly substituted benzyl carbon by loss of either an ethyl or a propyl group (peak at m/e 133 or 119, respectively).

3-Phenyl-3-ethylhexane (**XXII**). The quantity of material isolated was too small to allow nmr analysis. The mass spectrum showed a molecular ion peak at m/e 190. It is thus very likely that product XXII arose from the catalytic hydrogenation of compound IX (mol wt 186), the structure of which was determined with sufficient certainty as described above. Therefore we assigned the structure 3-phenyl-3-ethylhexane, since the reaction of I with K/Na alloy in THF produced no other product which would give a saturated hydrocarbon of molecular weight 190 upon hydrogenation.

Compound XXIII had mass spectrum molecular ion peak at m/e 176 (26%) and peaks at m/e 92 (100%), 91 (77%), 85 (26%), and 43 (89%). This corresponds to a compound of formula C$_{13}$H$_{20}$ which has an unsubstituted benzyl group attached to a substituted carbon atom. Although the signal integration of the nmr spectrum of compound XXIII, based on five protons for the phenyl signal, is in agreement with a C$_{13}$H$_{20}$ formula for that compound, no more could be said about its structure.

Reaction of 1-Phenyl-1-butene (III) and 1-Phenyl-2-butene (IV) with K/Na Alloy in *n*-Octane. *trans*-III (100 mg) was stirred at room temperature with a suspension of K/Na alloy (100 mg) in *n*-octane for 30 hr. After hydrolysis of the reaction mixture with methanol–water, vpc analysis gave the following product distribution: 35% 1-phenylbutane (II), 13% *cis*-1-phenyl-1-butene (*cis*-III), and 52% *trans*-1-phenyl-1-butene (*trans*-III). When *trans*-1-phenyl-2-butene (*trans*-IV) was treated under exactly the same conditions, vpc analysis gave the following product distribution: 2% 1-phenylbutane (II) and 98% starting material (*trans*-IV).

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(8) We wish to thank Dozent Dr. H. Stegmann, Chemisches Institut der Universität Tübinge, for obtaining these measurements for us.

(9) Although a small amount of phenylbutane could have been formed by reduction of the starting material by the hydrogen formed with the metal during the hydrolysis process, this cannot be responsible for the large amount of II that we observed. Moreover, II was also present after hydrolysis of samples pipetted out carefully avoiding the presence of metal particles.

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Gaseous Chlorine Action on Solid-State Phenols

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During study of the chlorination of 26 alkylmonophenols in the solid state by gaseous chlorine, 13 new substances were prepared, isolated, and characterized: four chlorophenols, eight chlorocyclohexadienones, and one chlorocyclohexenone. The main characteristic of these gas–solid reactions is that they are very rapid and nearly always lead to the total transformation of the initial product in the absence of solvent and catalyst. Consideration of the steric and electronic effects of the groups attached to the phenolic nucleus leads to a consistent interpretation.

During the study of organic solid-state reactivity,[1] we became interested in the chlorination of a number of solid-state phenols by gaseous chlorine. Under the conditions of our reactions and varying with the alkylphenol