

Alkali salts of 1,3,3-trisubstituted propynes and use of these organometallic compounds in syntheses

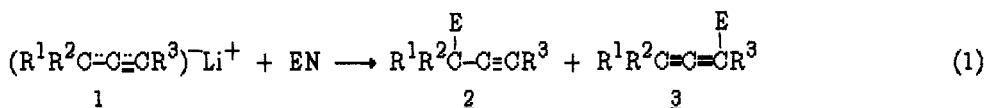
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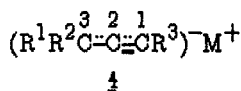
Abstract — With the decrease of delocalizing ability of substituents in salts **4** of 1,3,3-trisubstituted propynes the structure of carbanions shifts from propargylic towards allenyl type. Such a changeover of structure — from propargylic to purely allenyl — is particularly developed for CIP of salts **4**. Variation in both structure of carbanions in **4**, and ionic association in solutions of **4** exerts a marked effect on regioselectivity of their alkylation, leading to mixtures of acetylenic and allenic products. Influence of the nature of alkylating agent on regioselectivity of alkylation of **4** is essential. Protonation and trimethylsilylation of salts **4** lead exclusively to allenic products.

INTRODUCTION

Propargylic and/or allenyl organometallic compounds are extensively used in preparations of acetylenes and allenes (ref. 1-5), lithium derivatives **1** of propynes and allenes being the most useful. In reactions with electrophilic agents EN these derivatives generally yield mixtures of products of acetylenic **2** and allenic **3** structure. The structure of **1**, which is a typical example of ambident system, is studied rather weakly (ref. 1, 4, 6, 7), that presents obstacles for conscious control over the direction of the reactions (1)



with electrophilic agents towards preferential formation of either acetylenes or allenes. In the present work we investigate a scope of factors, which exert influence on the ratio **2/3** of products forming in reactions (1) of salts **4**. Salts **4** have been obtained as purified crystalline solids by metallation of the corresponding acetylenic hydrocarbons by n-butyl lithium (ref. 8-10), triethylgermyl sodium or triphenylmethyl cesium in solutions of pentane/diethyl ether (DE) (ref. 9, 11).



4a $\text{R}^1 + \text{R}^2 = 2,2'$ -biphenylene;

$\text{R}^3 = \text{Ph}$; $\text{M} = \text{Li}$

4b $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$; $\text{M} = \text{Li}$

4c $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$; $\text{M} = \text{Na}$

4d $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$; $\text{M} = \text{K}$

4e $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$; $\text{M} = \text{Cs}$

4f $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$; $\text{M} = \text{Ph}_4\text{As}$

4g $\text{R}^1 = \text{R}^3 = \text{Ph}$; $\text{R}^2 = 4\text{-MeOC}_6\text{H}_4$; $\text{M} = \text{Li}$

4h $\text{R}^1 = \text{R}^3 = \text{Ph}$; $\text{R}^2 = 2\text{-MeOC}_6\text{H}_4$; $\text{M} = \text{Li}$

4i $\text{R}^1 = \text{R}^2 = 2\text{-MeOC}_6\text{H}_4$; $\text{R}^3 = \text{Ph}$; $\text{M} = \text{Li}$

4j $\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{R}^3 = 2\text{-MeOC}_6\text{H}_4$; $\text{M} = \text{Li}$

4k $\text{R}^1 = \text{R}^3 = \text{Ph}$; $\text{R}^2 = \text{Me}$; $\text{M} = \text{Li}$

4l $\text{R}^1 = \text{R}^3 = \text{Ph}$; $\text{R}^2 = \text{H}$; $\text{M} = \text{Li}$

4m $\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{R}^3 = \text{Ph}$; $\text{M} = \text{Li}$

The obtained solids have been used for preparation of solutions in the required solvent. Since salt 4m couldn't be obtained in crystalline state, it was generated in solutions by metallation of 1-phenyl-2-isopropylacetylene by *n*-butyl lithium (ref. 10). Salt 4d has also been obtained in solution by metallation of 1,3,3-triphenylpropyne (TPP) by suspension of phenylethynyl potassium in THF. Occasionally, salt 4c has been similarly generated in solution using the suspension of phenylethynyl sodium in THF (ref. 9, 11). The solutions of salt 4f have been prepared from 4b, 4c, or 4e by ion exchange with tetraphenylarsonium chloride.

IONIC ASSOCIATION IN SOLUTIONS AND THE STRUCTURE OF ALKALI SALTS OF 1,3,3-TRISUBSTITUTED PROPYNES

Like other analogous derivatives of OH-acids (ref. 12) alkali metal derivatives 4, exist in ethereal solutions as contact (CIP) or solvent separated (SSIP) ion pairs, that has been established (ref. 13, 14) by UV/Vis spectrophotometry (Table 1) and NMR spectroscopy.

TABLE 1. Absorbance maxima (nm) for CIP, SSIP, and free carbanions of salts 4 (ref. 10).

| Salt | CIP | SSIP | Free carbanion |
|-----------------------|-----------------------|-----------------------|----------------|
| | in DE | in THF | in HMPA |
| <u>4a</u> | 401 | 452 | 452 |
| <u>4b</u> | 380, 438 ^a | 439, 512 ^b | 440, 513 |
| <u>4b^c</u> | 435, 508 | | |
| <u>4c</u> | 406, 466 | 438, 512 | d |
| <u>4c^c</u> | 438, 512 | | |
| <u>4e</u> | 418, 480 | e | d |
| <u>4g</u> | 380, 438 | 428, 522 | 431, 525 |
| <u>4h</u> | 438 | 450, 513 | 449, 517 |
| <u>4i</u> | 440 | 450, 513 | 450, 514 |
| <u>4k</u> | 380(sh.), 410 | 533 | 533 |
| <u>4m</u> | 340-350 ^f | 345-355 ^g | h |

^a $\epsilon(380) = 24,000$, $\epsilon(438) = 27,800$.

^b $\epsilon(439) = 31,000$, $\epsilon(512) = 50,300$.

^c In the presence of ca. 100-fold excess of 18-crown-6.

^d Not determined.

^e In THF 4e exists predominantly as CIP and a small amount of free ions.

^f Probably, the absorbance belongs to aggregates, the existence of which in concentrated solutions is established by ¹³C NMR (ref. 13-14).

^g Absorbance of CIP 4m in THF. In this solvent SSIP 4m could not be observed.

^h Not determined, since 4m decomposes rapidly not only in HMPA, but in the mixture HMPA-THF (1/5 v/v).

In dilute solutions of 4 in THF free carbanions might exist. Occurrence of free carbanions (4)⁻ for 4b, 4c, 4e, 4h, 4i, 4k in THF is confirmed by observation that the intensity of their UV-Vis absorption bands (Table 1) decreases or vanishes on addition of common cation in the form of the corresponding tetraphenylborates (ref. 9-11). Dissociation of 4b in THF has been also confirmed by conductance measurements (ref. 9). Free carbanions are likely to occur in dilute solutions of 4a, 4g in THF. In bipolar aprotic solvents, such as DMSO and HMPA, a majority of salts 4 would dissociate completely (ref. 9, 15, 16) like many of alkali salts with highly delocalized carbanions (ref. 17-21).

A possibility that alkali derivatives of propynes and allenes occur in solutions as different types of ionic species, and that this species might react with different regioselectivities in reactions (1), have only slightly been touched upon in literature. As a rule, alkali metal (most often lithium) cation was supposed to be bound to propargylic C3, or allenyl C1 centers of 1 (ref. 1, 2, 4-7). The information on structure of 1 has been often inferred (ref. 1, 4) from the structures of products formed in reactions (1). Only recently the first X-ray investigations were performed for several lithium (ref. 22, 23) and one sodium (ref. 24, 25) derivatives of some propynes, revealing

that this derivatives show preference for allenylic structure, though generally bridged by cation between C1 and C3. Such structural features of alkali derivatives of allenes and propynes are confirmed by some computational data (ref. 24). However, ^{13}C NMR (ref. 14, 26–28) and MNDO (ref. 14, 29) investigations demonstrated that with the decrease of delocalizing ability of substituents (DAS) R^1 and R^2 , (values of δC_3 in the starting acetylenic hydrocarbons (AH) have been taken (ref. 14, 27) to be the quantitative measure of DAS), the structure of not only free carbanions (Table 2), but also of CIP and SSIP of salts 4 (Fig. 1) shifts progressively from mostly propargylic towards allenylic.

TABLE 2. MNDO data (ref. 14) on bond lengths (pm), bond orders, and charges (a.u.) at carbon atoms in free carbanions of salts 4.

| | (<u>4a</u>) ⁻ | (<u>4b</u>) ⁻ | (<u>4k</u>) ⁻ | (<u>4l</u>) ⁻ | (<u>4m</u>) ⁻ |
|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Bond length C1–C2 | 121.3 | 121.6 | 122.0 | 122.2 | 123.4 |
| Bond order C1–C2 | 2.620 | 2.556 | 2.519 | 2.487 | 2.337 |
| Bond length C2–C3 | 138.8 | 138.6 | 138.3 | 137.0 | 135.4 |
| Bond order C2–C3 | 1.157 | 1.217 | 1.252 | 1.289 | 1.463 |

While, e.g. for CIP 4a δC_2 is equal to 94.1, for CIP 4b 126.3 ($\Delta\delta\text{C}_2 = \delta\text{C}_2(\text{CIP}) - \delta\text{C}_2(\text{AH})$ for 4a and 4b is equal to 6.4 and 35.5 ppm, respectively), in the case of CIP 4m this value amounts to 183.3 ppm ($\Delta\delta\text{C}_2 = 87.7$ ppm) being close to δC_2 for allenyl lithium (196.4 ppm (ref. 30)).

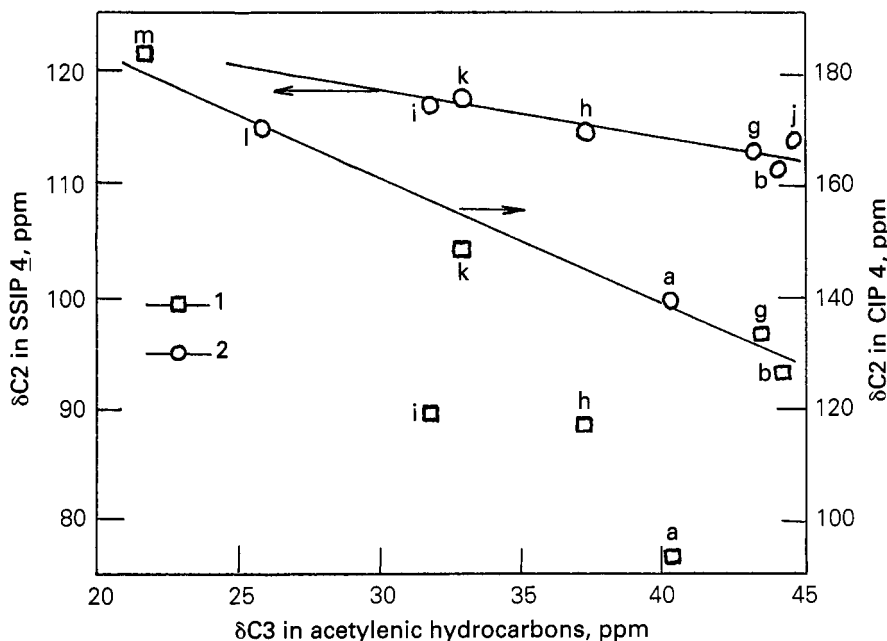


Fig. 1. Relationship of carbanion structure (δC_2) in CIP (1) and SSIP (2) of 4 vs. delocalizing ability of substituents R^1 and R^2 ($\delta\text{C}_3_{\text{AH}}$).

Usage of the values of δC_2 for distinguishing between propargylic and allenylic structures of carbanions in 4 is justified since the ^{13}C shielding is probably determined mainly by bond orders C2 – C1, and C2 – C3 (ref. 14, 27). Thus, in the case of SSIP 4 (in which the effect of counteraction is negligibly small), with the decrease of C1–C2 bond order and the growth of C2–C3 bond order (Table 2), i.e. with the increase of allenylic character of carbanion, $^{13}\text{C}_2$

resonance linearly shifts downfield (Fig. 2).

Fig. 1 shows that carbanions in CIP **4b**, **4g**, **4k**, **4m** are more propargylic than those in SSIP, that must have been associated with the bridging character of cation in the CIP under consideration, more strongly interacting with C1 to polarize electron density mostly towards this atom. This assumption is supported by X-ray data on CIP **4b** (ref. 29). In solid state in CIP **4b**

the cation hangs exactly over C2, being closer to C1, than to C3. The decrease of DAS of R¹ and R² at C3 results in such a change in electron density distribution in carbanion that causes a shift of the energy minimum of electrostatic interaction between countercation and carbanion from C3 towards C1, that is shown by drawing an electrostatic potential map taking into account the interactions of a charged particle q⁺ not only with C1 and C3, but also with all other carbons in carbanion (ref. 14). (It proved unreasonable to use MNDO for computations of CIP of salts **4**, since the method greatly overestimates covalent binding of lithium with C3, as well as with ortho- and ipso-carbons of phenyl rings at C3 (ref. 14, 29)). Thus, with the

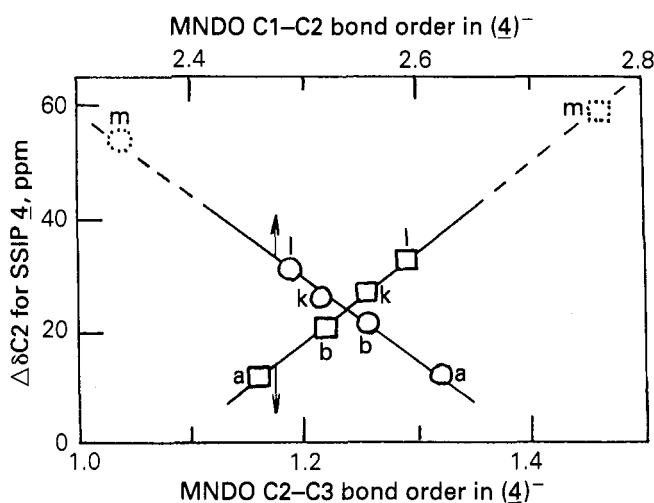


Fig. 2. Downfield shift ($\Delta\delta C2$) of C2 resonance in SSIP of **4** relative to resonance of the same nuclei in the starting AH vs. the variation of C1-C2 and C2-C3 bond orders.

C1, so the cation would more strongly polarize a carbanion from C3 to C1, leading to a growth of allenylic character of carbanion in CIP, both compared to SSIP, and within the series of salts **4**. The values of $dC2 = \delta C2(CIP) - \delta C2(SSIP)$ might be used as a measure of the degree of electron density polarization from C3 towards C1. Basing on these values: **4a** (-5.1 ppm), **4i** (1.6), **4h** (2.4), **4b** (15.4), **4g** (20.5), **4k** (31.2), **4m** (ca.56 ppm, cf. Fig.2), the following sequence by Li-C1 distance in CIP of **4** might be drawn: **4m** < **4k** < **4g** < **4b** < **4h** < **4i** < **4a**.

Carbanions in CIP **4h**, **4i** are more propargylic than in CIP **4b** and **4g** in spite of higher or comparable DAS at C3, most probably because the cation in CIP **4h**, **4i** locates closer to C3 owing to coordination with ortho-methoxy groups. Such coordination is well known for organo-lithium compounds in literature (ref. 31-37). Similar interaction of lithium with ortho-methoxy group in salt **4j** might result in allenylic character of carbanion, that is indeed the case in solid state (ref. 38). Carbanion **4a** in CIP is more propargylic than that in SSIP, most likely due to that in CIP **4a** the cation, according to MNDO calculations, lies closer to C3 (C-9 of fluorenyl), ipso- and ortho-carbons of one of phenyl rings of fluorenyl moiety. Occupying such a location the cation polarizes carbanion of CIP **4a** towards C3, rendering it more propargylic character, than in SSIP.

Thus, investigation of salts **4** using electron absorption spectroscopy, ¹³C NMR, and MNDO calculations of free carbanions of these salts has established that the structure of carbanions, either free or ion paired (CIP or SSIP) in alkali salts of propynes and allenes may vary between allenylic and propargylic depending on substituent effects and specific interactions of countercation with these substituents. Variations in carbanion structure would undoubtedly change electron density distribution in them, that would alter regioselectivity of the reactions of **4** with electrophiles. The data on alkylation of salts **4** presented below confirm this conclusion.

REACTIONS OF ALKALI SALTS OF 1,3,3-TRISUBSTITUTED PROPYNES

Alkylation of **4** have been run at their concentration in the range from 10⁻¹ to 10⁻⁴ mol/l with excess (often huge one) of alkylating agent. GC yields of alkylation products have usually been quantitative.

Regioselectivity of alkylation of 1,3,3-triphenylpropyne salts

Salts **4b–4f** exist in DE as CIP, which are alkylated to give essentially higher yields of acetylenic product, than of allenic one (Table 3), in spite of larger steric hindrance to attack of ethylating agent at C3. The increase of cation radius on going from lithium to cesium, and especially to bulky tetraphenylarsonium leads to the decrease of $2/3$ ratio. The effect of addition of agents (TMEDA, 18-crown-6) solvating alkali cations is similar. Moreover, the effects of both factors is followed by the variation of the magnitude of red shift of absorption maxima in spectra of **4** (Table 1).

TABLE 3. Ethylation of alkali salts of 1,3,3-triphenylpropyne in DE at room temperature (ref. 8, 9, 39).

| Exp. No | Cation | $c(4) \cdot 10^4$ mol/l | EtX | $(2/3)^a$ | Exp. No | Cation | $c(4) \cdot 10^4$ mol/l | EtX | $(2/3)^a$ |
|---------|---------------------------------|-------------------------|-----|-----------|---------|-----------------|-------------------------|-------|-----------|
| 1 | Li ⁺ | 120 | EtI | 6.0 | 8 | Li ⁺ | 120 | EtBr | 6.3 |
| 2 | Li ⁺ ^b | 120 | EtI | 4.8 | 9 | Li ⁺ | 120 | EtCl | 7.2 |
| 3 | Li ⁺ ^c | 120 | EtI | 2.9 | 10 | Na ⁺ | 2 | EtBr | 6.7 |
| 4 | Na ⁺ | 2 | EtI | 5.8 | 11 | Na ⁺ | 2 | EtCl | 6.9 |
| 5 | Cs ⁺ | 1 | EtI | 5.6 | 12 | Cs ⁺ | 1 | EtCl | 6.0 |
| 6 | Cs ⁺ ^c | 1 | EtI | 2.2 | 13 | Li ⁺ | 120 | EtOTs | 6.8 |
| 7 | Ph ₄ As ⁺ | 52 | EtI | 2.1 | 14 | Li ⁺ | 120 | EtOTf | 8.5 |

^a Capillary gas chromatography data.

^b In the presence of 0.02 mol TMEDA.

^c In the presence of 0.04 mol 18-crown-6.

THF more efficiently solvates alkali metal cations, and therefore, the ethylation in this solvent is accompanied by a substantial decrease of $2/3$ ratios (Table 4) compared to the similar reactions in DE. The spectral evidence (see above) reveals that in THF 1,3,3-triphenylpropyne salts exist as mixtures of CIP,SSIP, and free ions. The data on ethylation in DE leads to a conclusion that SSIP **4a–4e** and free anion of TPP (TPPA) should give higher yields of allenic product, i.e. to the decrease of $2/3$ ratio. Thus, the data of Table 4 confirm spectral data that both ion pairs and free TPPA exist in THF. In fact, lowering the concentration of **4e** leads to a decrease of $2/3$ ratio in the reaction with ethyl iodide (exp. 33, 34). Still larger decrease of $2/3$ ratio is observed for ethylation of **4e** in the presence of 18-crown-6 (exp. 35, 36); effect of 18-crown-6 being more pronounced than that of dibenzo-24-crown-8. This fact is most likely due to the formation of sandwich complex between 18-crown-6 and cesium cation with stoichiometry of 2:1, in which crown ether molecule fits between the fragments of ion pair. In the case of dibenzo-24-crown-8 such a separation can not take place, though the apparent size of cation increases. Ethylation of **4e** in dilute solution in the presence of an excess of cesium tetraphenylborate, suppressing the dissociation of **4e**, leads to the same ratio $2/3$, as the reaction with more concentrated solution (exp. 33, 37). Such behavior of crown ethers was also demonstrated for other salts in THF. Here, the magnitude of above-mentioned variation of the ratio $2/3$ in the presence of 18-crown-6 increases along the series $Na^+ < K^+ < Cs^+$, despite of lower concentrations of **4d** and **4e** used for ethylation. The observed influence of crown ether on the $2/3$ ratio in the presented series of cations might be accounted for by the increase of CIP content from **4c** to **4e** in THF (ref. 9, 11).

Addition of 18-crown-6 and tetramethylethylenediamine (TMEDA) to solutions of **4b** exerts no effect on the regioselectivity of ethylation (exp. 15–18), that might be considered as evidence, that CIP are not formed for **4b** in THF, in perfect agreement with spectral evidence. Estimates of dissociation degree of **4b** in the range of concentrations used for alkylation, varies around 6–18 percent, so, not only SSIP, but also free TPPA should be involved in the alkylation. Lack of dilution effect on the ratio $2/3$, even in the presence of 18-crown-6 (exp. 15–17, 20, 21), as well as very weak effect of lithium tetraphenylborate (exp. 15 and 19), both reveal that SSIP and TPPA of **4b** are alkylated with roughly the same regioselectivity. On the other hand, near to equal values of the $2/3$ ratio, observed in ethylations of **4b–4e** in the presence of 18-crown-6 enable us to conclude that the regioselectivities of alkylation of other ion pairs separated by THF or crown are also similar. The data of Table 4 demonstrate, that the effect of cation on the ratio of products of alkylation of TPP salts in THF differs from that in DE. This is accounted for by an increase of relative content of CIP in THF on going from **4b** to **4e**, that leads to higher $2/3$ ratios. In DE CIP are the only reactive species.

TABLE 4. Alkylation of alkali salts of 1,3,3-triphenylpropyne in THF at room temperature (ref. 8, 9, 11).

| Exp. No | Cation | $c(\underline{4}) \cdot 10^4$ mol/l | RX | $(2/3)^a$ | Exp. No | Cation | $c(\underline{4}) \cdot 10^4$ mol/l | RX | $(2/3)^a$ |
|---------|------------------------------|--|-----------------------|-----------|---------|------------------------------|--|-----------------------|-------------------|
| 15 | Li ⁺ | 320, 200 | EtI | 2.3 | 28 | Na ⁺ | 50 | EtCl | 5.3 |
| 16 | Li ⁺ ^b | 50 | EtI | 2.2 | 29 | Na ⁺ | 50 | EtOTs | 6.7 |
| 17 | Li ⁺ ^c | 320, 22 | EtI | 2.4 | 30 | K ⁺ | 10 | EtI | 3.3 |
| 18 | Li ⁺ ^d | 200 | EtI | 2.4 | 31 | K ⁺ ^c | 10 | EtI | 2.4 |
| 19 | Li ⁺ ^e | 200 | EtI | 2.6 | 32 | K ⁺ | 10 | EtBr | 3.8 |
| 20 | Li ⁺ | 200 | EtBr | 2.7 | 33 | Cs ⁺ | 50 | EtI | 4.2 |
| 21 | Li ⁺ ^c | 22 | EtBr | 2.7 | 34 | Cs ⁺ | 2.5 | EtI | 3.4 |
| 22 | Li ⁺ | 200 | EtCl | 4.0 | 35 | Cs ⁺ ^c | 50 | EtI | 2.2 |
| 23 | Li ⁺ | 200 | EtOTs | 6.0 | 36 | Cs ⁺ ^f | 50 | EtI | 2.8 |
| 24 | Li ⁺ | 200 | MeOCH ₂ Cl | 14.2 | 37 | Cs ⁺ ^g | 2.6 | EtI | 4.3 |
| 25 | Na ⁺ | 100 | EtI | 3.0 | 38 | Cs ⁺ | 50 | EtBr | 5.1 |
| 26 | Na ⁺ ^c | 100 | EtI | 2.4 | 39 | Cs ⁺ | 50 | EtCl | 5.4 |
| 27 | Na ⁺ | 100 | EtCl | 5.2 | 40 | Cs ⁺ | 50 | MeOCH ₂ Cl | 100% ² |

^a Capillary gas chromatography data.

^b 4b was obtained from 1,3,3-triphenylallene.

^c In the presence of 2-3-fold excess of 18-crown-6.

^d In the presence of 2-3-fold excess of TMEDA.

^e In the presence of more than 10-fold excess of lithium tetrafluoroborate.

^f In the presence of 2-3-fold excess dibenzo-24-crown-8.

^g In the presence of more than 10-fold excess of cesium tetrafluoroborate.

Carbanion structure in propyne salts and the regioselectivity of their alkylation

Trends in regioselectivity variation between CIP in DE and SSIP in THF, observed for 4b-4e, remain unchanged for other salts 4 (Table 5). Although, it is noteworthy that 4m in DE exists as ion pair aggregates, while in THF - as monomeric CIP. At ambient temperatures a substantial amount of CIP occurs in the solutions of 4h, 4i, 4k in THF, as well (ref. 10, 13). Still more interesting is the change of regioselectivity of alkylation, which varies by more than two orders of magnitude on going from CIP of 4a with propargylic structure to CIP of 4m with allenylic structure. An increase of allenylic character in the structure of carbanions in SSIP of 4 also results in substantial decrease of the yield of acetylenic product in THF, i.e. to reduced ratio 2/3. The only exclusions are 4h and 4i; regioselectivity of their alkylation is probably influenced by methoxy-groups, sterically hindering the attack at C3.

Relative variation of charges at C3 and C1 with the growth of allenylic character of carbanions in SSIP of 4, that is with the decrease of DAS at C3 is of little use for understanding trends in regioselectivity changes for alkylation of SSIP. This can be achieved only when the interactions of electrophilic particle with all the carbons of a carbanion are taken into consideration through the electrostatic potential maps showing the interactions of unit charge q^+ with carbanion. Analysis of such maps has shown, that at a distance of 2 Å from carbanion plane electrostatic potential well is located: for free carbanions of 4a, 4b - over C3, for 4m - over C1, for 4k - between C1 and C3. Energy difference $E_e = E_e(C1) - E_e(C3)$ of electrostatic interaction of q^+ with C1 and C3

amounts to 0.35; 1.01; -0.22; -1.02 eV for (4a)⁻, (4b)⁻, (4k)⁻, and (4m)⁻ correspondingly. These data demonstrate that with the decrease of DAS at C3, interaction of electrophilic species with this center should weaken, and with C1 - strengthen, that is indeed the case (Table 5). Different trends in variations of 2/3 and E_e on going from SSIP 4a to SSIP 4b might be connected with both enhanced steric hindrance to the attack at C3 in the case of 4b, and with inconsistencies of the used simple electrostatic model.

The discussed simple electrostatic approach also enables to account for i) the decrease of alkylation selectivity at C3 in the series of CIP of salts 4 occurring with the decrease of DAS at C3;

ii) on going from SSIP to CIP; iii) change of regioselectivity with the increase of cation size. To get a notion of it, it's sufficient to consider the variation of the ratio $r = q(C3)/q(C1)$, where $q(C3)$ is a total of net charges on C3 and carbon and hydrogen atoms of substituents adjacent to C3; $q(C1)$ - total of charges at C1, hydrogens and carbons of phenyl bound to C1. The charges $q(C1)$ and $q(C3)$ are negative. Their values are obtained as a sum of the corresponding MNDO

TABLE 5. Regioselectivity of alkylation of salts **4** at 25°C. Salt concentrations $3 \cdot 10^{-2}$ - $3 \cdot 10^{-1}$ mol/l (ref. 40).

| RX | $(2/3)^a$ | | | | | | |
|-----------------------|-----------|-----------|-----------|-----------|-----------|------------------|-----------|
| | 4a | 4b | 4g | 4h | 4i | 4k | 4m |
| | in DE | | | | | | |
| EtI | 100 | 6.0 | 3.9 | 1.0 | 0.12 | 3.7 ^b | 0.27 |
| EtI ^c | 30 | 2.9 | 1.9 | 0.90 | 0.62 | 3.3 ^b | 0.19 |
| EtCl | 120 | 7.2 | 5.2 | 3.0 | 1.8 | 4.6 | 0.12 |
| MeOCH ₂ Cl | 300 | d | 9.5 | 2.4 | 0.90 | 6.9 | 0.80 |
| | in THF | | | | | | |
| EtI | 21 | 2.3 | 1.7 | 0.78 | 0.75 | 3.4 ^b | 0.12 |
| EtI ^c | 21 | 2.4 | | 0.78 | 0.72 | 3.3 ^b | 0.12 |
| EtCl | 67 | 4.0 | 3.2 | 1.6 | 1.2 | 3.8 | 0.06 |
| MeOCH ₂ Cl | 40 | 14.2 | 8.5 | 8.3 | 3.1 | 6.5 | 0.16 |

^a Capillary gas chromatography data.

^b This data disagree with that reported in (ref. 41), in which the reactions of **4k** with MeI, EtI, and *i*-PrI were found to yield exclusively acetylenic products.

^c 5-10-fold excess of 18-crown-6 added to the solution of salt before the addition of alkylating agent.

^d 100 percent **2**.

net atomic charges in free carbanions (**4**)⁻, and in lithium derivatives **4**. The values of r are: 1.97 and 3.55 for (**4a**)⁻ and **4a**; 1.51 and 3.24 for (**4b**)⁻ and **4b**; 1.30 and 1.87 for (**4k**)⁻ and **4k**; 0.70 and 0.51 for (**4m**)⁻ and **4m**. This data show that growing allenyl character of not only SSIP, but also CIP should result in enhancement of electrostatic interaction of electrophilic center of alkylating agent with C1 and its neighborhood, i.e. in the decrease of the ratio $2/3$. This conclusion finds confirmation in the data on alkylation of **4a**, **4b**, **4k**, **4m**, and other salts under study, certainly, after making corrections for the effect of methoxy-groups in **4h**, **4i** (Table 5). The data on variation of r leads to a conclusion that in the case of salts **4a**, **4b**, **4k** the changeover from SSIP (for which the influence of counteraction is negligible) to CIP should be associated with relative enhancement of the interaction of electrophilic agent with the region around C3 atom compared to that around C1, thus leading to an increase of alkylation regioselectivity at C3. Probably, this conclusion is valid also for **4h**, **4i**. For **4m** opposite trend might be expected to realize, that has not been confirmed in experiment, since **4m** in HMPA or in the mixtures of this solvent with THF, where SSIP could be expected to occur, is not stable enough. The decrease of r on going from CIP to free carbanions account for the decrease of $2/3$ with the growth of cation size in CIP (Table 3).

Hardness of alkylating agent and the regioselectivity of alkylation

Yield of product of acetylenic structure **2** generally grows with the increase of the hardness of alkylating agent (Tables 3, 4, 5). The only exception is the ethylation of **4m**, which both in DE and in THF results in lower ratios $2/3$ for harder ethyl chloride than for softer ethyl iodide, though in a reaction of **4m** with still more hard agent chloromethyl ether the ratio $2/3$ increases. One might draw a conclusion that in the studied salts **4** propargylic center is harder than allenyl one. Opposite is probably the case with **4m**. Such trend in relative hardness of C1 and C3 centers is associated, probably, with the variation of electron density at C1, C3 and on adjacent groups in CIP and SSIP of **4**.

Benylation of solvent-separated ion pairs of lithium salt of triphenylpropyne

Hardness of substituted benzyl halides should follow the electron withdrawing ability of their substituents. Since the propargylic center in **4b** is rather hard, regioselectivity of benzylation of **4b** at

C3 atom should increase in the order of benzyl halides: **5a** (4-MeOC₆H₄CH₂Cl), **5b** (4-MeC₆H₄CH₂Cl), **5c** (C₆H₅CH₂Cl), **5d** (4-ClC₆H₄CH₂Cl), **5e** (4-O₂NC₆H₄CH₂Cl), **5f** (C₆F₅CH₂Br). However, experiments on benzylation of **4b** in DME at ambient temperatures, where only SSIP and free ions of this salt occur, revealed that $2/3$ decreases in the order **5a** (7.2); **5b** (7.0); **5c** (6.2); **5d** (5.2); **5e** (2.3); **5f** (1.75), that might be accounted for by involvement of electron transfer pathway in the benzylation of **4b** in DME. The contribution of ET pathway should grow with the increase of electron-withdrawing ability of substituents in **5**, and consequently - of oxidative power of these agents. The involvement of ET pathway is confirmed by the formation besides **2** and **3** of 1,3,3-triphenyl-3-(1,3,3-triphenylallenyl)propyne, **6**, owing probably to dimerization of triphenylallenyl (triphenylpropargyl) radical (Ph₃C₃)[•] (ref. 42); and of substituted diphenylethanes - via dimerization of radicals formed from benzyl halides **5**. Preliminary data showed that the content of **6** grow from 0 in reactions of **4b** with **5a** and **5b** to 0.3; 9; 59; 84; 100 percent for reactions with **5c**, **5d**, **5e**, **5g** (4-O₂NC₆H₄CH₂Br) and **5h** (3-O₂NC₆H₄CH₂Cl). Suppression of ET, i.e. when the reaction of **4b** with **5g** was run in the presence of 0.1 and 1 mol of 2,4-dinitrobenzene, and also at -96°C the yields of **6** fall to 79, 76, and 25 percent respectively, while the ratio $2/3$ increases to 2.6, 3.5, and 5.6. The present data show that the regioselectivity of benzylation of **4b** via polar pathway is likely to be determined by the motion of electrophilic agent in the electrostatic field of a carbanion, as indeed is the case for other alkylation reactions of **4**. Alkylation via ET pathway occurs with the intermediacy of free radical particles (ref. 43). If the products **2** and **3** in the reaction of **4b** form via recombination of neutral radicals (Ph₃C₃)[•] and ArCH₂[•], the regioselectivity of alkylation should be accounted for mainly by steric factors, which favor the attack at allenyl center, and not by the differences in spin density distribution in (Ph₃C₃)[•]. Probably, this is the main reason for the decrease of $2/3$ with the growth of ET pathway contribution in benzylation of **4b** occurring within the series of **5**. The investigation aimed at this problem, as well as on other trends in the interaction of **4** with **5**, is currently under way.

Other reactions of alkali salts of 1,3,3-trisubstituted propynes

Protonation by acids, trimethylsilylation of all salts **4**, and trimethylstannylation of **4b** yield exclusively **3**, so these reactions might be used to obtain pure allenes free from isomers. High selectivity of kinetically controlled protonation of **4** is most likely accounted for by product stability control (ref. 44), that is with higher stability of trisubstituted allenes, compared to propynes. The formation of isomerically pure trimethylsilylated allenes proceeds obviously via the equilibrium formation of more stable pentacoordinate organosilicon intermediates (ref. 45, 46) possessing allenyl structure. Trimethylstannylation of **4b** is likely to involve the same mechanism.

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