Organometallic Chemistry

State in solution, structure, and regioselectivity of reactions of the lithium 1-(2-methoxyphenyl)-3,3-diphenylpropyne derivative

*P. I. Dem'yanov, D. P. Krut'ko, M. V. Borzov, E. V. Luk'yanov, and V. S. Petrosyan**

M. V. Lomonosov Moscow State University, Department of Chemistry, Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: 007 (095) 939 5546. E-mail: pdem@organic.chem.msu.su

According to the spectrophotometric data, the lithium 1-(2-methoxyphenyl)-3,3-diphenylpropyne derivative in diethyl ether exists as contact ion pairs, while in THF, according to the spectrophotometric and ^{13}C NMR data, solvent-separated ion pairs are predominantly formed. According to the ^{13}C NMR data, the carbanion in the solvent-separated ion pairs has a structure close to the propargylic type. The regioselectivity of reactions of the lithium derivative with ethyl halides in diethyl ether, THF, and hexamethyphosphoramide, with benzyl chloride in the first two solvents, and with methanol in THF were studied. The protonation with methanol proceeds exclusively at the allenylic center (C-1) while the ethylation and especially benzylation proceed predominantly at the propargylic center (C-3). The selectivity of ethylation of the propargylic center of both solvent-separated ion pairs in THF and contact ion pairs in diethyl ether increases as the hardness of the ethylating agent increases, and in the case of the same ethyl halide, the selectivity increases from the solvent-separated ion pairs to the contact ion pairs. The spectral data obtained and the data on changes in the regioselectivity do not allow one to believe that the contact ion pairs of the lithium derivative in ether exhibit the intramolecular coordination of the lithium cation to the methoxy group, which might lead to the allenylic structure of contact ion pairs of this derivative.

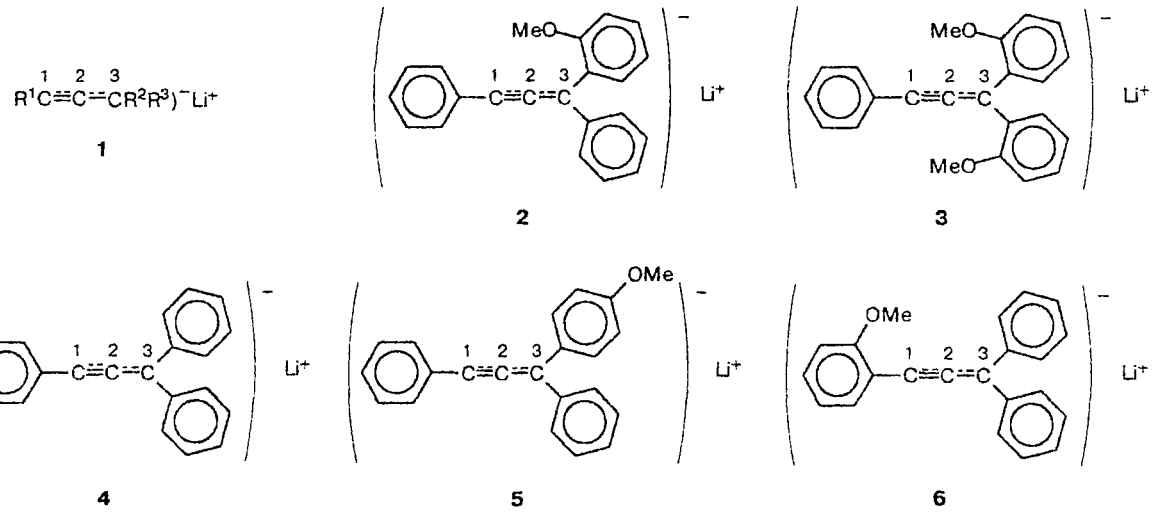
Key words: lithium derivative of 1-(2-methoxyphenyl)-3,3-diphenylpropyne, contact ion pairs, solvent-separated ion pairs, structure, ethylation, benzylation, protonation, regioselectivity.

The regioselectivity of reactions of electrophilic reagents at the "allenylic" (C-1) and "propargylic" (C-3) centers of lithium (**1**) and other metallated derivatives of propyne and allene depends on many factors.[1—5] This regioselectivity is determined mainly by the state of derivative **1** or analogous alkali metal derivative in solution (contact ion pairs (IP's), solvent-separated ion pairs, and/or free ions) and by the structure (propargylic, allenylic, or intermediate between these forms) of the ambident carbanion in the reacting ionic particle (contact IP, solvent-separated IP, or cation-free carbanion).[6,7]

In solvent-separated IP's of lithium and other alkali derivatives of CH-acids, the cation almost does not affect the electron density distribution in the carbanion. Therefore, the spectral behavior[8] and reactivity[9,10] of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2043—2051, November, 1997.

1066-5285/97/4611-1939 $18.00



solvent-separated IP's are very close to those of cation-free carbanions. This is valid for alkali metal derivatives of propynes and allenes.[6,7,11] In contact IP's of lithium derivatives **1**, the structure of mesomeric carbanions is determined by the position of the lithium cation, which polarizes the carbanion,[12,13] rather than by the nature of the R^1, R^2, and R^3 substituents. For example, in contact IP's **2** and **3**, the cation can be localized closer to the propargylic C-3 center due to the intramolecular coordination with the methoxy groups and thus favor the shift of the electron density to this center. That is why the carbanions in contact IP's **2** and **3** have a more pronounced propargylic structure than those in contact IP's **4** and **5**, where the position of the cation is determined only by the electron density distribution in the carbanions.[12,13]

In contact IP's **6** of the lithium 1-(2-methoxyphenyl)-3,3-diphenylpropyne derivative (**7**), the cation can form an intramolecular coordination with the methoxy group localized at the allenylic C-1 center and thus confer the pronounced allenylic structure to the carbanion in compound **6**. It is precisely this pattern which is observed by X-ray diffraction analysis for contact IP's **6** in the crystalline state.[14]

Based on the aforesaid, we can expect the carbanion in contact IP's **6**, *e.g.*, in diethyl ether, to possess also a pronounced allenylic structure. At the same time, when in THF in which compound **6** should exist in the form of solvent-separated IP's (the interaction of the cation with the methoxy group and carbanion is almost absent), the carbanion of this derivative, according to the ^{13}C NMR data, has a structure close to the propargylic type (δ(C-2) 114.2),[14] as in solvent-separated IP's **2** (δ(C-2) 114.3),[13] **3** (δ(C-2) 117.0),[13] **4** (δ(C-2) 110.9),[13] and **5** (δ(C-2) 112.7)[13] in THF.

Thus, unlike compounds **2**—**5** and other similar derivatives,[6,13] compound **6** makes it possible, in principle, to elucidate how the change in the carbanion structure from the almost propargylic type in solvent-separated IP's (in THF) to the substantially allenylic type in contact IP's (in diethyl ether) can affect the regioselectivity of the attack of electrophilic reagents at the C-1 and C-3 centers of the mesomeric carbanion derived from propyne. This work is devoted to revealing the structures of contact and solvent-separated IP's **6** and studying the regioselectivity of their ethylation, benzylation, and protonation.

Results and Discussion

Lithium derivative of 1-(2-methoxyphenyl)-3,3-diphenylpropyne (6) state in solutions. Like lithium derivatives of other propynes, in anions of which the negative charge is considerably delocalized, compound **6** should be greatly dissociated in HMPA, which is strongly polar and solvates alkali cations well.[7,11] Therefore, both absorption maxima of a solution of **6** in HMPA (Table 1) can be assigned to the absorption of the free 1-(2-methoxyphenyl)-3,3-diphenylpropyne carbanion.

The position of the absorption maxima of a solution of compound **6** in THF remains almost unchanged when the concentration of **6** changes by more than 600 times and is close to the position of the absorption maxima of a solution of this derivative in HMPA. At the same time, the spectral parameters of **6** in both THF and HMPA are very close to those for **4** in these solvents (see Table 1). These facts along with the arguments presented previously[7,11] allow us to conclude that at room temperature solvent-separated IP's and a certain number of free ions are present in dilute (10^{-3}—10^{-6} mol L^{-1}) solutions of **6** in THF and in dilute solutions of **4** in this solvent. Compound **6** exists predominantly in the form of the solvent-separated IP's also in much more concentrated THF solutions, which follows[13,15] from the weak temperature dependence of the positions of signals for different carbon atoms in the

Table 1. Comparison of spectral parameters in the visible and UV regions for solutions of lithium derivatives of 1-(2-methoxyphenyl)-3,3-diphenylpropyne (**6**) and 1,3,3-triphenylpropyne (**4**) at ~20 °C

Solvent	Solvating additive	**6**			**4**[a]		
		λ_{max1}/nm	λ_{max2}/nm	$\varepsilon_{max2}/\varepsilon_{max1}$[b]	λ_{max1}/nm	λ_{max2}/nm	$\varepsilon_{max2}/\varepsilon_{max1}$[b]
HMPA		444	518	1.50	440	513	1.60
THF		441	519	1.71[c]	439	512	1.62[d]
Ether		364	451	0.74	380	438	1.16
Ether	TMEDA[e]	391	455, 510 sh	1.06			
Ether	18-Crown-6[f]	435	510	1.61	435	508	1.43

[a] Data in Refs. 7 and 11. [b] The ratio between the absorption intensities in the second and third maxima. [c] ε_{max1} = 21300, ε_{max2} = 36400. [d] ε_{max1} = 31000, ε_{max2} = 50300. [e] A 175-fold molar excess of TMEDA with respect to **6**. [f] A 12-fold molar excess with respect to **6** and a ~100-fold excess with respect to **4**.

^{13}C NMR spectra measured in THF-d_8 (Table 2) with the concentration of **6** of ~0.25 mol L^{-1}. Since δ(C-2) is slightly greater (Table 2), the number of contact IP's **6** in THF slightly increases as the temperature increases from −100 to 60 °C.

This behavior of derivative **6** in THF differs sharply from that of derivative **2**, which exists in this solvent at normal temperature (20—27 °C) in the form of contact IP's for both low (~10^{-3} mol L^{-1} and lower)[11] and high (0.1—0.25 mol L^{-1})[13,16] concentrations. This allows one to conclude that, first, in THF the interaction of the lithium cation with the methoxy group in derivative **6** is considerably weaker than that with the same group in **2**. Second, the great similarity in spectral parameters and behavior of derivatives **6** and **4** in THF testifies that in this solvent the interaction between the cation and methoxy group in **6** is very weak.

The absorption maxima of solutions of **6** in diethyl ether lie in a considerably shorter-wave region than those in THF (see Table 1). This is evidence[8,11] for the fact that solvent-separated IP's of compound **6** are absent in ether, and this derivative exists in a dilute ether solution in the form of contact IP's, like lithium derivatives of many other 1,3,3-trisubstituted propynes in this solvent.[7,11] The addition of excess *N,N,N',N'*-tetramethylethylenediamine (TMEDA) or macrocyclic 18-crown-6 polyether to an ether solution of **6** results in the bathochromic shift of the absorption bands, which is especially pronounced in the case of 18-crown-6 (see Table 1). These changes can be explained[11,17] by the transformation of contact IP's **6** that are externally solvated with ether into the contact IP's in which the cation (located externally respective to the carbanion) is solvated by TMEDA or 18-crown-6. The lithium cation is solvated by TMEDA better than by ether, but worse than by 18-crown-6,[17] which explains the different positions of the absorption bands of ether solutions of **6** in the absence and presence of TMEDA and 18-crown-6. The sufficiently great (6—9 nm) differences in positions of solvent-separated IP's **6** in THF and ion pairs **6** solvated by 18-crown-6 in ether show[11,17] that even the solvating ability of this macrocyclic polyether is not enough to transform contact IP's **6** in ether into ion pairs **6** separated by the crown ether.

Table 2. Temperature dependence of chemical shifts ($\delta^{13}C$) for some carbon atoms of compound **6** in THF-d_8

Temperature/°C	δ(^{13}C)			
	C(1)	C(2)	C(3)	OCH_3
60	90.9	119.7	73.3	56.4
25	90.6	116.5	73.3	56.0
−20	90.3	115.3	73.3	55.5
−60	90.2	114.6	73.2	55.2
−100	90.1	114.0	73.2	55.1

The very low solubility of **6** in diethyl ether (not higher than 0.01 mol L^{-1}) and broadening of the signals due to the spin-spin interaction, especially that of $^{13}C(1)$, $^{13}C(2)$, and $^{13}C(3)$ with ^{7}Li[13,18,19] in contact IP's **6**, did not allow us to measure signals of the $^{13}C(1)$ and $^{13}C(2)$ nuclei of this contact IP in ether even on a highly sensitive AMX-500 NMR spectrometer. The structure of contact IP **6** in diethyl ether cannot be exactly determined when the value of the chemical shift for C(2) is unknown. However, even under the drastic conditions mentioned, we succeeded in detecting signals of C(3) (74.0 ppm) and $C_p(3)$ (120.6 ppm, *para*-carbon atoms in the phenyl rings linked to C(3)) in the ^{13}C NMR spectrum of **6** in ether. Since δC(3) and $\delta C_p(3)$ for solvent-separated IP's **6** in THF (73.2 and 114.0 ppm) are known,[14] we can determine the difference in the values of the chemical shifts (ΔδC) for these atoms in contact and solvent-separated IR's **6** (ΔδC(3), 0.8 ppm; $\Delta\delta C_p(3)$, 6.6 ppm). The ΔδC(2) value for contact IP's **6** can be estimated from the dependences of ΔδC(2) on ΔδC(3) and on $\Delta\delta C_p(3)$ for the contact IP's of lithium derivatives of 1,3,3-trisubstituted propynes.[13] According to these estimations, this value is not greater than 25 ppm. For solvent-separated IP's **6** in THF, δC(2) is 114.0 ppm (see Table 2). Therefore, for contact IP's **6** in diethyl ether, the δC(2) value should not exceed 139 ppm. The δC(2) values for allenyllithium compounds are equal to 174—196 ppm,[13,18] and vary from 90 to 120 ppm for propargyllithium compounds.[13,18] Therefore, it can be considered that contact IP **6** in diethyl ether does not possess the allenylic structure, but an intermediate structure between the allenylic and

propargylic types, *i.e.*, similar to that of contact IP **5** (δC(2), 133.2 ppm)[13] or the contact IP of the lithium derivative of 1,3-diphenylbutyne (δC(2), 148.8 ppm)[13] in the same solvent at 27 °C.

These arguments indicate a low probability for the intramolecular coordination of lithium with the methoxy group in contact IP **6** in an ether solution, although this coordination could be expected from the X-ray diffraction analysis data[14] and semiempirical quantum-chemical calculations.[15] Probably, in solutions of **6** the intramolecular interaction of the cation with the methoxy group is weak, which is also confirmed by the comparison of the behavior of **6** and **2** in THF presented above.

Regioselectivity of ethylation, benzylation, and protonation. In general, the reactions of compound **6** with electrophilic reagents (EN) lead to products with the acetylenic (**8**) and allenic (**9**) structures (Tables 3 and 4). The reactions of **6** with ethyl halides in THF, diethyl ether, and HMPA result mainly in the formation of compounds **8** and **9** (E = Et) (Table 3), *i.e.*, in the products of ethylation of **6** of both the propargylic and allenylic centers, respectively. The structures of these products were confirmed by ^1H and ^{13}C NMR spectroscopies and GLC-mass spectrometry. The ^1H NMR study of the reaction mixtures obtained by the ethylation of **6** in THF indicates that only compounds **8** and **9** are formed. At the same time, capillary GLC, which separates efficiently all compounds formed during the ethylation of **6** in both THF and ether or HMPA, also detected and determined quantitatively compounds **10**—**12** in the reaction mixtures.

$(2\text{-MeOC}_6H_4C{\equiv}C{=}CPh_2)^-Li^+ + EN \longrightarrow$

6

$\longrightarrow$ $2\text{-MeOC}_6H_4C{\equiv}C{-}\underset{\displaystyle E}{\underset{|}{C}}Ph_2$ + $2\text{-MeOC}_6H_4\underset{\displaystyle E}{\underset{|}{C}}{=}C{=}CPh_2$

8 **9**

$2\text{-HOC}_6H_4C{\equiv}C{-}\underset{\displaystyle Et}{\underset{|}{C}}Ph_2$ $2\text{-HOC}_6H_4\underset{\displaystyle Et}{\underset{|}{C}}{=}C{=}CPh_2$

10 **11**

$2\text{-MeOC}_6H_4\underset{\displaystyle H}{\underset{|}{C}}{=}C{=}CPh_2$ $(2\text{-LiOC}_6H_4C{\equiv}C{=}CPh_2)^-Li^+$

12 **13**

The reaction of **6** with methanol gives only 1-(2-methoxyphenyl)-3,3-diphenylallene (**12**). The protonation of lithium derivatives of the other 1,3,3-trisubstituted propynes occurs similarly, and their regioselectivity is determined by the thermodynamic stability of the final product.[20] The formation of **12** in the ethylation reactions can be explained by both the proto-

Table 3. Products of ethylation, benzylation, and protonation of lithium derivative **6** in different solvents

$c(\mathbf{6})\cdot10^2$ /mol L^{-1}	EN	$c(EN)\cdot10^2$ /mol L^{-1}	Additive[a]	Yield (%)[b]				
				8	**9**	**10**	**11**	**12**
				THF				
2	EtI	11		72.0(1.4)	25.4(1.2)	0.5(0.08)	0.9(0.06)	1.2(0.2)
2	EtBr	8.0		76.6(1.2)	21.6(1.1)	0.4(0.06)	0.4(0.06)	0.9(0.2)
2	EtBr	24	18-Crown-6(3)	75.8(1.4)	21.7(0.8)	0.3(0.02)	0.4(0.06)	2.1(0.4)
2	EtCl	23		85.7(0.5)	14.3(0.5)	HO[c]	HO[c]	Traces
1.5	$C_6H_5CH_2Cl$	5.1		[d]	[d]	[d]	[d]	[d]
2	MeOH	20						100
				HMPA				
2.6	EtI	55		73.0(0.6)	25.0(0.3)	1.2(0.3)	0.9(0.2)	Traces
2.1	EtCl	44		62.9(0.6)	19.7(0.2)	0.2(0.1)	0.3(0.2)	16.9(0.5)
				Diethyl ether				
1	EtI	43		84.2(0.7)	15.3(0.2)	HO[c]	HO[c]	0.8(0.03)
1	EtI[e]	29	TMEDA(11)	81.1(0.4)	16.6(0.2)	HO[c]	HO[c]	2.2(0.3)
1	EtI[e]	25	18-Crown-6(5)	81.7(1.1)	17.4(0.3)	HO[c]	HO[c]	1.6(0.3)
1	EtBr	42		73.9(0.4)	10.1(0.4)	Traces	0.9(0.01)	15.0(0.01)
1	EtCl	67		87.9(0.7)	10.6(0.5)	0.2(0.04)	0.2(0.07)	1.3(0.2)
1	EtCl[e]	41	18-Crown-6(4)	68.3(0.3)	15.1(1.4)	0.3(0.03)	0.3(0.03)	13.9(2.1)
1	EtOTs	11		85.1(1.0)	13.3(1.0)	0.2(0.1)	0.2(0.1)	1.3(0.1)
1	$C_6H_5CH_2Cl$	18		[d]	[d]	[d]	[d]	[d]
1	$C_6H_5CH_2Cl$[e]	24	18-Crown-6(2)	[d]	[d]	[d]	[d]	[d]

[a] The molar excess of the solvating additive with respect to the lithium derivative is presented in parentheses. [b] According to the capillary GLC data, with the assumption that the responses of the flame-ionization detector for all reaction products are equal. The values of the standard σ_{n-1} deviations (n = 2—11) are presented in parentheses. [c] No OH groups were observed. [d] Gas-chromatographic analysis was not performed due to the low volatility of the benzylation products. [e] The reaction mass is heterogeneous due to the very low solubility of the complex of the lithium derivative with the solvating additive.

nation of **6** by traces of water in the reagents and the β-elimination of a proton from the molecules of ethylating agents by the anion of compound **6**.

The formation of compounds **10** and **11**, which is testified by the mass spectroscopic study of the reaction mixtures, is evidently associated with the cleavage of the C—O bond of the methoxyphenyl group by *n*-butyllithium[22] during the metallation of the starting propyne **7**. This cleavage should result in the formation of dilithium derivative **13**, which most likely remains in the crystalline residue of compound **6** even after thorough washing with a pentane—ether mixture, because the solubility of **13** in this mixture is even lower than that of **6**. The dilithium derivative is evidently ethylated, first of all, on the more reactive C(3) and C(1) reaction centers rather than on the oxygen atom. After the decomposition of the reaction mixture by a saturated solution of NH_4Cl, the products of the monoethylation of **13** give **10** and **11**, respectively. The overall yield of these two compounds is not greater than 2.5% (see Table 3).

The reaction of **6** with ethyl bromide in THF in both the absence and presence of 18-crown-6 results, according to capillary GLC, in equal ratios of the products with the acetylenic (**8**) and allenic (**9**) structures (see Table 4). This, along with the spectral data (see above), is an additional argument in favor of the fact that contact IP's **6** are almost absent in THF, and predominantly solvent-separated IP's **6** and, perhaps, a small number of free anions of this compounds participate in the reactions in this solvent.

The regioselectivity of the ethylation of solvent-separated IP's **6** in THF, which is quantitatively characterized by the **8**/**9** ratio (see Table 4), increases on going from ethyl iodide to ethyl chloride, *i.e.*, as the hardness of the ethylating agent increases. This tendency coincides with that observed for the ethylation of **4**,[7,22,23] **2**, **3**, **5**, and lithium derivatives of some other propynes in THF.[6] As in the case of **4**, the selectivity of the reactions on the propargylic center of compound **6** in THF also noticeably increases on going from ethylation to benzylation.

The reactivity of the solvent-separated IP's is very close, as a rule, to that of cation-free carbanions[9,10] (under conditions where the organometallic compound is dissociated in solution). However, as the data in Table 4 show, the regioselectivities of the ethylation of solvent-separated IP's in THF and the free carbanion of derivative **6** in HMPA differ sufficiently strongly, and the last solvent demonstrates the inverse (compared to that in THF) dependence of the regioselectivity on the hardness of the ethylating agent. As in the case of the differences in the regioselectivity of the ethylation of compound **4** in THF, on the one hand, and in HMPA and DMSO, on the other hand, this is most likely related to the fact that ethyl halide with HMPA and some other dipolar protic solvents can form onium compounds, which are harder alkylating agents than the starting ethyl halides.[23]

The data in Table 4 show that the ratios between products **8** and **9** formed in the reactions of **6** with ethyl halides are 1.5-fold higher than the ratios between the compounds with the acetylenic and allenic structures formed in similar reactions of the lithium derivative **4**. The same situation is observed for benzylation (see Table 4).

When the structures of the anions in solvent-separated IP's **4** and **6** are very close (see above), the fact that the regioselectivity of the ethylation and benzylation on the allenylic center of solvent-separated IP's **6** is substantially lower than that for solvent-separated IP's **4** can be related most likely to the existence of the methoxy group in the phenyl substituent at this center in **6**, which sterically prevents the accessibility of an electrophilic reagent to the p-orbital of the C(1) atom. This assumption is confirmed by the fact that steric hindrances

Table 4. Ratios between products **8** and **9** of ethylation and benzylation of compound **6** and products with the acetylenic (Acet) and allenic (Allen) structures formed in similar reactions of compound **4**

Reagent	Additive	8/9[a]			Acet[b]
EN		GLC[c]	^{1}H NMR[d]	HPLC[e]	Allen
		THF			
EtI	—	2.84(0.18)	3.6(0.4)		2.3[f]
EtBr	—	3.59(0.23)	4.0(0.3)		2.7
EtBr	18-Crown-6	3.60(0.3)			
EtCl	—	5.99(0.2)	6.1(0.3)		4.0
$PhCH_2Cl$	—	[g]	10.8(0.1)	9.4(0.5)	6.2[h]
		HMPA			
EtI	—	2.92(0.06)			3.1(0.2)[i]
EtCl	—	3.20(0.03)			2.2(0.1)[i]
		Diethyl ether			
EtI	—	5.52(0.11)			6.0
EtI	TMEDA	4.87(0.06)			4.8
EtI	18-Crown-6	4.68(0.06)			2.9
EtBr	—	7.48(0.22)			6.3
EtCl	—	8.32(0.49)			7.2
EtCl	18-Crown-6	4.56(0.42)			
EtOTs	—	6.44(0.58)			6.8
$PhCH_2Cl$	—	[g]	9.1(0.4)	8.2(0.3)	
$PhCH_2Cl$	18-Crown-6	[g]	12(1)	9.6(0.4)	

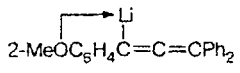
[a] The values of standard σ_{n-1} deviations (n = 2—11) are presented in parentheses. [b] Data in Refs. 7 and 23. [c] Determined from the capillary GLC data by the division of the height of the chromatographic peak of **8** into the height of the chromatographic peak of **9**. [d] The average magnitude of the values obtained by the division of the integral intensity of the signal of protons (IISP) of the CH_2 group in compound **8** into IISP of the CH_2 group in compound **9** and by the division of IISP of the MeO group in compound **8** into IISP of the MeO group in compound **9**. [e] Determined by HPLC by the division of the height of the chromatographic peak of compound **8** into the height of the chromatographic peak of compound **9**. [f] See also Ref. 24.[24] [g] Not determined due to the low volatility of the benzylation products. [h] In dimethoxyethane.[25] [i] Data in Ref. 24.[24]

created by the methoxy groups in the phenyl rings at the C(3) atoms of the lithium derivatives considered lead to an increase in the regioselectivity of the ethylation on the allenylic center.[6,7,20]

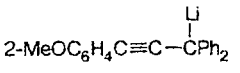
The tendency for the values of the ratios of products **8** and **9** to increase as the hardness of the ethylating agent increases, which is typical of the reactions of derivative **6** in THF and compound **4** in THF and diethyl ether (see Table 4), is retained in diethyl ether. However, the reactions of derivative **6** with ethyl bromide and ethyl tosylate in ether exhibit the reverse order of regioselectivity as compared to the similar reactions of compound **4** in this solvent.

For the same ethylating agent, the regioselectivity of the ethylation of compound **6** on the propargylic center in diethyl ether is higher than in THF (see Table 4). The addition of TMEDA or 18-crown-6 to an ether solution of compound **6** decreases considerably the regioselectivity of the interaction of ethyl iodide with this center, and this decrease occurs to a somewhat greater extent in the presence of the macrocyclic polyether. When 18-crown-6 is added to an ether solution, a decrease in the regioselectivity of the alkylation on the C(3) atom also occurs in the reaction of **6** with ethyl chloride. The data presented agree well with the spectrophotometric data that derivative **6** in diethyl ether exists in the form of contact IP's, which are transformed into contact IP's externally solvated by TMEDA or macrocyclic polyether when the latter are added to the ether solution.

The data on the ratios of the products of the benzylation of **6** in THF, ether, or ether with an additive of 18-crown-6 (see Table 4) do not allow one to draw the same conclusions as in the case of the ethylation of this derivative. Probably, this is related not to the specific character of benzylation, but to the fact that benzylation products are analyzed by ^{1}H NMR and HPLC methods that are less exact than capillary GLC used for analysis of ethylation products. However, this assumption should be studied in more detail.



14



15

If contact IP's of compound **6** in diethyl ether had the allenylic structure of type **14**, in these contact IP's the cation would polarize the electron density to the allenylic C(1) center, decreasing it on the propargylic C(3) center. In this case, for the same ethylating agent, we could expect the regioselectivity of the ethylation on the allenylic center of derivative **6** in diethyl ether to be higher than that in THF. What actually happens is that the regioselectivity of the ethylation reactions on the allenylic center decreases on going from THF to ether, as evidenced by the increase in the experimental **8/9** values (see Table 4). Thus, the replacement of THF with ether in the ethylation of **6** results in the same change in the regioselectivity of ethylation as in the case of **4**. However, this tendency in the ethylation of **6** is less pronounced than that in the ethylation of **4**.

However, if contact IP's **6** in diethyl ether had a propargylic structure similar to that of, *e.g.*, **15**, based on the arguments presented above, we could expect[20] a decrease in the regioselectivity of the ethylation of **6** of the allenylic center, *i.e.*, an increase in the **8/9** ratio on going from THF to diethyl ether, which is observed in fact (see Table 4). This is one more evidence for the fact that contact IP's **6** in diethyl ether have a structure closer to the propargylic type rather than the allenylic structure.

Thus, the spectral studies and data on the regioselectivity of ethylation show that contact IP's **6** in diethyl ether have a structure intermediate between the propargylic and allenylic types and, unlike the solid[14] or gas phase,[15] these contact IP's in solutions exhibit no coordination of the lithium cation to the methoxy group. This can be related to the fact that the energy of the interaction between the lithium cation and the MeO group is not very high and in the solution is compensated by the energy of the stronger solvation of the cation by ether molecules.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300, Bruker AM-400, Bruker AMX-500, and Varian VXR-400 spectrometers. Mass spectra were obtained on a Varian MAT 44S GLC-MS spectrometer. Absorption spectra in the visible and UV regions were recorded on a Varian DMS-100S spectrophotometer.

Gas-chromatographic analysis was carried out on a Varian 3400 chromatograph with a flame-ionization detector and a capillary column of melted silica (length 30 m, inner diameter 0.22 mm) with the cross-linked SE-54 stationary phase ("Khromatografist" Scientific Industrial Co., Moscow). Helium was used as the carrier gas, the helium flow rate was 30 cm s^{-1}, and the flow division of the carrier gas was 1 : 50. The temperatures of the injector and the detector were 310 °C. The temperature in the thermostat of the column was programmed from 200 °C (2 min) to 300 °C with a rate of 5 deg min^{-1}. High-performance reversed-phase liquid chromatography was carried out on a Varian 5020 liquid chromatograph with a spectrophotometric detector (254 nm) using a column (length 25 cm, inner diameter 4 mm) filled with Diasorb-130 C16T (7 μm) ("Biokhimmak" Co., Moscow) and gradient elution with a water—acetonitrile (A) mixture: 0 min, 60% A; 20 min, 100% A. In both cases (GLC and HPLC), the chromatographic data were collected and processed using a Varian Vista 402 chromatographic system.

Purification of solvents, ethyl halides, benzyl chloride, and methanol, their storage in evacuated tubes, reactions of **6** with electrophilic reagents in evacuated vessels using breaking ampules and barriers[25] have been described previously.[22,26]

2-Methoxystyrene was synthesized according to the modified Neumann and Kochi procedure.[27] Tris(acetylacetonato)-iron(III) (3.53 g, 10 mmol) was added at 0—5 °C to an ether solution of 2-methoxyphenylmagnesium bromide prepared from 2-bromomethoxybenzene (187 g, 1 mol) and magnesium chips (25 g, 1.03 mol) in diethyl ether. The reaction mixture was

stirred for 10 min, and vinyl bromide (91.6 mL, 139 g, 1.3 mol) in an equal volume of diethyl ether was carefully (the temperature was not allowed to increase much) added for 1 h. After all the vinyl bromide was added, stirring and cooling of the mixture was continued for 20 min. The temperature of the reaction mixture was gradually brought to ~20 °C, and stirring was continued for 30 min. The syrup-like dark-brown reaction mixture obtained was cooled again to 0—5 °C, and water was slowly added (the addition of the first water droplets results in the crystallization of $MgBr_2$ and considerable warming, which can lead to boiling of the mixture). Water was added until the precipitation of $MgBr_2$ ceased. The ether layer was separated from the precipitate, which was washed with ether (2×100 mL). The combined ether extracts were washed with a dilute solution of NH_4Cl and water until the washings became neutral and dried with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator, and the residue was distilled *in vacuo*. The second distillation gave the target product (97 g, 72%), b.p. 83 °C (9 Torr). The pure product was stabilized by the addition of 1% hydroquinone and stored at −18 °C.

(2-Methoxyphenyl)acetylene. *Method A.* A solution of freshly distilled 2-methoxystyrene (78.05 g, 0.582 mol) in carbon tetrachloride (200 mL) was cooled to −40 °C, and a solution of bromine (29.7 mL, 0.582 mol) in carbon tetrachloride (200 mL) was slowly added dropwise, monitoring the state of the reaction mixture (it should remain almost colorless, and its temperature should not rise over −30 °C). The mixture was allowed to warm to ~20 °C. The solvent was removed on a rotary evaporator, and the residue was distilled *in vacuo* accompanied by the release of HBr. The fraction boiling at 139—170 °C (10 Torr) was collected. The distillate (~105 g) containing, according to the ^1H and ^{13}C NMR and GLC-MS data, 1- and 2-bromo-1-(2-methoxyphenyl)ethylenes and 1,2-dibromo-1-(2-methoxyphenyl)ethane was added to KOH (120 g) in ethanol (400 mL), and the reaction mixture was refluxed for 6 h with stirring and gas-chromatographic monitoring of the completeness of dehydrobromination. After the reaction mixture was cooled to ~20 °C, twice the amount (in volume) of water was added. Ethanol was distilled off on a rotary evaporator. Diethyl ether (100 mL) was added to the residue. The organic phase was separated, and the aqueous phase was extracted with ether (2×50 mL). The combined ether extracts were dried with anhydrous magnesium sulfate, the solvent was distilled off on a rotary evaporator, and the residue was distilled *in vacuo*. The second distillation gave the target product (34.8 g, 41%) with b.p. 90—92 °C (8 Torr).

Method B. A three-necked flask with a mechanical stirrer, a reflux condenser, and a dropping funnel was heated with the flame of a gas burner in a strong nitrogen flow. The flask in the nitrogen flow was cooled first in air and then by immersing in a pasty chloroform—liquid nitrogen mixture (−65 °C). (Bromomethyl)triphenylphosphonium bromide (Aldrich, Germany) (65 g, 0.149 mol) and purified THF (200 mL) were placed in the cooled flask through which nitrogen was passed. Potassium *tert*-butylate (Merck, Germany) (17 g, 0.151 mol) was added to the intensely stirred and cooled mixture. Forty minutes later, the next portion of potassium *tert*-butylate (17 g, 0.151 mol) was added to the lemon-yellow reaction mixture, and then a solution of 2-methoxybenzaldehyde (Merck, Germany) (20 g, 0.147 mol) in THF (50 mL) was added dropwise for 40 min. After the aldehyde was introduced, the third portion of potassium *tert*-butylate (17 g, 0.151 mol) was added, and stirring and cooling were continued for 4 h. The reaction mixture was let to stand in a nitrogen atmosphere for 12 h with gradual warming to room temperature. The mixture was poured onto ice (1 kg), acidified with dilute sulfuric acid to pH 1.5—2, saturated with sodium chloride, and triply extracted with pentane. The oily product obtained after evaporation of the combined extracts was purified on a column with alumina using a petroleum ether—diethyl ether (10 : 1 vol/vol) mixture as the eluent, and the first fraction was collected. The yield of the chromatographically pure (capillary GLC) product with b.p. 68 °C (1 Torr) was 13.9 g (72%). MS (EI, 70 eV), m/z (I_{rel} (%)): 132 $[M]^+$ (27), 131 $[M-H]^+$ (27), 103 $[M-H-CO]^+$ (19). ^1H NMR ($CDCl_3$), δ: 3.37 (s, 1 H, ≡CH); 3.72 (s, 3 H, OMe); 6.74 (d, 1 H, H-3); 6.83 (t, 1 H, H-5); 7.20 (t, 1 H, H-4); 7.43 (d, 1 H, H-6). ^{13}C NMR ($CDCl_3$), δ: 55.5 (OMe); 80.3 (—C≡); 81.7 (≡CH); 110.8 (C-3, 2-$MeOC_6H_4$); 111.2 (C-1, 2-$MeOC_6H_4$); 120.4 (C-5, 2-$MeOC_6H_4$); 130.3 (C-4, 2-$MeOC_6H_4$); 134.0 (C-6, 2-$MeOC_6H_4$); 160.6 (C-2, 2-$MeOC_6H_4$).

1-(2-Methoxyphenyl)-3,3-diphenylpropyn-3-ol. A solution of (2-methoxyphenyl)acetylene (2.4 g, 18 mmol) was added from a dropping funnel for 15 min to a solution of ethylmagnesium bromide prepared from ethyl bromide (1.5 mL, 20 mmol) and magnesium (0.44 g, 18 mmol) in diethyl ether (60 mL). Then the reaction mixture was refluxed for 30 min. A solution of benzophenone (3.3 g, 18 mmol) in ether (30 mL) was added dropwise for 20 min to the white precipitate of the magnesium (2-methoxyphenyl)acetylene derivative that formed with refluxing and stirring. After the all benzophenone was added, the reaction mixture was stirred and refluxed for 30 min, let to stand in an argon atmosphere for 12 h, and decomposed by a saturated solution of NH_4Cl. After extraction with diethyl ether and evaporation, the product obtained was purified on a column with silica gel using first petroleum ether—diethyl ether (2 : 3 vol/vol) as the eluent to remove unreacted benzophenone, and then diethyl ether removed the alcohol formed. The recrystallization from hexane gave white needles of the target product in 40% yield (2.25 g). MS (EI, 70 eV)), m/z (I_{rel} (%)): 314 $[M]^+$ (69), 299 $[M-Me]^+$ (10), 283 $[M-H-CO]^+$ (46), 237 $[M-Ph]^+$ (17), 206 $[M-C_6H_5OMe]^+$ (50), 194 $[Ph_2C=C=O]^+$ (18), 108 $[C_6H_5OMe]^+$ (60), 105 $[PhC=O]^+$ (100), 91 $[C_7H_7]^+$ (30), 77 $[Ph]^+$ (64). ^1H NMR ($CDCl_3$), δ: 3.22 (s, 1 H, OH); 3.82 (s, 3 H, OMe), 6.83 (d, 1 H, H-3, 2-$MeOC_6H_4$); 6.87 (t, 1 H, H-5, 2-$MeOC_6H_4$); 7.22 (t, 2 H, H-4, C_6H_5); 7.26 (t, 1 H, H-4, 2-$MeOC_6H_4$); 7.30 (t, 4 H, H-3, C_6H_5); 7.40 (d, 1 H, H-6, 2-$MeOC_6H_4$); 7.72 (d, 4 H, H-2, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 55.7 (OMe); 75.0 (Ph_2C(OH)—), 83.7 (2-$MeOC_6H_4$—C≡), 95.9 (—C≡); 110.7 (C-3, 2-$MeOC_6H_4$); 111.8 (C-1, 2-$MeOC_6H_4$); 120.4 (C-5, 2-$MeOC_6H_4$); 126.2 (C-2, C_6H_5); 127.5 (C-4, C_6H_5); 128.2 (C-3, C_6H_5); 130.0 (C-4, 2-$MeOC_6H_4$); 133.4 (C-6, 2-$MeOC_6H_4$); 145.3 (C-1, C_6H_5); 160.4 (C-2, 2-$MeOC_6H_4$).

1-(2-Methoxyphenyl)-3,3-diphenylpropyne (7) was obtained by the reduction of 1-(2-methoxyphenyl)-3,3-diphenylpropyn-3-ol (3.14 g, 10 mmol) by a 1.45 *M* solution of the borane—THF complex* (13.7 mL, 19.9 mmol) at −5 to −10 °C in THF in the presence of trifluoroacetic acid (10 mL, 135 mmol).[30] After the decomposition of the reaction mixture and extraction with diethyl ether, the required hydrocarbon was isolated by column chromatography (silica gel; pentane—ether, 5 : 1 vol/vol). The recrystallization from ethanol gave the chromatographically pure target propyne in 55.6% yield (1.66 g), which is substantially higher than the yield of this hydrocarbon synthesized by the reduction of a complex of 1-(2-methoxyphenyl)-3,3-diphenylpropyn-3-ol with octacarbonyldicobalt.[14] The mass spectrum of propyne 7 synthesized in this work

* A solution of the $BH_3 \cdot THF$ complex (1.45 *M*) was prepared by passing diborane[28] obtained by the Becher procedure[29] through THF.

coincides completely with the previously described mass spectrum of this hydrocarbon.[14] ^{1}H NMR (THF-d_8), δ: 3.81 (s, 3 H, OMe); 5.24 (s, 1 H, $Ph_2C\underline{H}$—); 6.82 (t, 1 H, H-5, 2-$MeOC_6H_4$); 6.90 (d, 1 H, H-3, 2-$MeOC_6H_4$); 7.14 (t, 2 H, H-4, C_6H_5); 7.21 (t, 1 H, H-4, 2-$MeOC_6H_4$); 7.24 (t, 4 H, H-3, C_6H_5); 7.35 (d, 1 H, H-6, 2-$MeOC_6H_4$);.7.48 (d, 4 H, H-2, C_6H_5). ^{13}C NMR (THF-d_8), δ: 44.6 ($Ph_2\underline{C}H$—); 55.9 (OMe); 82.2 (2-$MeOC_6H_4\underline{C}$≡; 94.9 (—C≡); 111.5 (C-3, 2-$MeOC_6H_4$); 113.8 (C-1, 2-$MeOC_6H_4$); 120.8 (C-5, 2-$MeOC_6H_4$); 127.3 (C-4, C_6H_5); 128.7 (C-2, C_6H_5); 129.1 (C-3, C_6H_5); 130.0 (C-4, 2-$MeOC_6H_4$); 133.8 (C-6, 2-$MeOC_6H_4$); 143.3 (C-1, C_6H_5); 161.5 (C-2, 2-$MeOC_6H_4$). UV (MeCN), λ_{max}/nm: 242, 252, 290, 298.

Lithium derivative of 1-(2-methoxyphenyl)-3,3-diphenylpropyne (6) and its solutions were obtained in all-sealed evacuated glass devices similarly to the preparation of the lithium 1,3,3-triphenylpropyne derivative.[22,26] The solution obtained was placed in evacuated NMR tubes, optical cells, and reaction ampules containing the necessary additives and reagents in evacuated ball-like ampules and glass peg stakes for breaking the latter. A solution of lithium derivative **6** in HMPA was prepared by evaporation of a solution of this derivative in diethyl ether in an evacuated device followed by the addition of HMPA (from an evacuated tube sealed to this device) to the crystalline residue of compound **6**.

The extinction coefficients of the lithium derivative of 1-(2-methoxyphenyl)-3,3-diphenylpropyne (**6**) were determined in evacuated optical cells by metallation of excess quantities of 9-methoxycarbonylfluorene and 9-phenylfluorene, which were placed in optical cells in breaking ball-like glass ampules, by a solution of compound **6** in THF. The optical densities of 9-methoxycarbonylfluorenyllithium or 9-fluorenyllithium were measured. Knowing the optical densities of solutions of **6** in THF, which were used for the preparation of the two last derivatives, and extinction coefficients of these derivatives in dimethoxyethane,[31] the extinction coefficients of **6** in THF were calculated.

Reactions of lithium 1-(2-methoxyphenyl)-3,3-diphenylpropyne derivative (6). At ~20 °C an ampule with the reagent was broken using a glass peg stake in a glass evacuated sealed reaction ampule containing a solution (5—30 mL) of lithium derivative **6** in the necessary solvent. If the reaction in diethyl ether or THF must be carried out in the presence of the solvating agent (TMEDA, 18-crown-6), the tube with this reagent was broken first, and after thorough stirring of the content of the reaction ampule, the ampule with the reagent was broken with a peg stake. After the reaction mixture was decolorized (this required from several seconds to several days depending on solvent, presence or absence of the solvating agent, and types of the electrophilic reagent), the ampule was opened, and its contents were poured into an approximately equal volume of ice-cold water. The aqueous phase was saturated with sodium sulfate and extracted with ether (3×5 mL). The combined extracts were dried with anhydrous magnesium sulfate and filtered. A small portion of the obtained solutions of this or another reaction was immediately analyzed by chromatography and GLC-MS. The remaining main portion of the solution was evaporated in an egg-like flask on a rotary evaporator, the flask was attached to a vacuum setup, and the solvent was removed in a vacuum (10^{-3} Torr). The residue was dissolved in deuterochloroform (0.5 mL). Several drops of TMS were added to the resulting solution of the reaction products, and the NMR spectra were recorded. In HPLC analysis, fractions eluted from the column were collected in quartz optical cells (1 cm thick), and the UV spectra corresponding to particular components of the reaction mixtures were recorded.

1-(2-Methoxyphenyl)-3,3-diphenylallene. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 298 $[M]^+$ (100), 297 $[M-H]^+$ (38), 283 $[M-Me]^+$ (76), 267 [M−OMe] (31), 266 $[M-H-Me]^+$ (27), 265 $[M-2H-OMe]^+$ (51), 252 $[M-Me-OMe]^+$ (31). ^{1}H NMR ($CDCl_3$), δ: 3.81 (s, 3 H, OMe); 6.86 (d, 1 H, H-3, 2-$MeOC_6H_4$); 6.89 (t, 1 H, H-5, 2-$MeOC_6H_4$); 7.10 (s, 1 H, =CH—); 7.17 (t, 1 H, H-4, 2-$MeOC_6H_4$); 7.25 (t, 2 H, H-4, C_6H_5); 7.31 (t, 4 H, H-3, C_6H_5); 7.42 (d, 4 H, H-2, C_6H_5); 7.48 (d, 1 H, H-6, 2-$MeOC_6H_4$). ^{13}C NMR ($CDCl_3$), δ: 55.6 (OMe); 91.7 (=$\underline{C}$H—); 111.2 (C-3, 2-$MeOC_6H_4$); 112.8 ($Ph_2\underline{C}$—); 120.8 (C-5, 2-$MeOC_6H_4$); 122.2 (C-1, 2-$MeOC_6H_4$); 127.3 (C-4, C_6H_5); 127.9, 128.4 (C-2, C-3, C_6H_5 and C-4, C-6, 2-$MeOC_6H_4$); 136.5 (C-1, C_6H_5); 156.3 (C-2, 2-$MeOC_6H_4$); 208.9 (=$\underline{C}$=). UV (MeCN), λ_{max}/nm: 257, 299.

1-(2-Methoxyphenyl)-3,3-diphenyl-3-ethylpropyne. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 326 $[M]^+$ (23), 311 $[M-Me]^+$ (3), 297 [M−Et or M−H−CO]$^+$ (100), 281 $[M-H-Me-Et]^+$ (10), 265 [M−H−Et−MeO]$^+$ (7), 252 $[M-2H-Me-Et-CO]^+$ (22), 219 $[M-MeOC_6H_4]^+$ (12), 203 $[M-H-Me-MeOC_6H_4]^+$ (16). ^{1}H NMR ($CDCl_3$), δ: 1.06 (t, 3 H, $C\underline{H}_3CH_2$); 2.39 (q, 2 H, $C\underline{H}_2CH_3$); 3.89 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 10.1 ($\underline{C}H_3CH_2$); 34.5 ($\underline{C}H_2CH_3$); 51.0 ($Ph_2(Et)\underline{C}$—); 55.8 (OMe); 82.4 (2-$MeOC_6H_4\underline{C}$≡); 97.8 (—$\underline{C}$≡); 110.8 (C-3, 2-$MeOC_6H_4$); 113.3 (C-1, 2-$MeOC_6H_4$); 120.3 (C-5, 2-$MeOC_6H_4$); 126.3 (C-4, C_6H_5); 127.6 (C-2, C_6H_5); 128.1 (C-3, C_6H_5); 129.2 (C-4, 2-$MeOC_6H_4$); 133.2 (C-6, 2-$MeOC_6H_4$); 145.6 (C-1, C_6H_5); 160.5 (C-2, 2-$MeOC_6H_4$).

1-(2-Methoxyphenyl)-3,3-diphenyl-1-ethylallene. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 326 $[M]^+$ (37), 325 $[M-H]^+$ (11), 311 $[M-Me]^+$ (91), 297 [M−Et or M−H−CO]$^+$ (100), 281 $[M-H-Me-Et]^+$ (27), 265 [M−H−Et−MeO]$^+$ (22), 252 $[M-2H-Me-Et-CO]^+$ (41), 219 $[M-MeOC_6H_4]^+$ (28), 203 $[M-H-Me-MeOC_6H_4]^+$ (36). ^{1}H NMR ($CDCl_3$), δ: 1.17 (t, 3 H, $C\underline{H}_3CH_2$); 2.59 (q, 2 H, $C\underline{H}_2CH_3$); 3.71 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 12.7 ($\underline{C}H_3CH_2$); 26.1 ($\underline{C}H_2CH_3$); 55.5 (OMe); 104.2 (2-$MeOC_6H_4(Et)\underline{C}$=); 109.8 ($Ph_2\underline{C}$=); 206.1 (=$\underline{C}$=).

3-Benzyl-1-(2-methoxyphenyl)-3,3-diphenylpropyne. ^{1}H NMR ($CDCl_3$), δ: 3.66 (s, 2 H, CH_2); 3.83 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 47.3 ($\underline{C}H_2$); 51.3 ($Ph_2(Bn)\underline{C}$—); 55.7 (OMe); 84.0 (2-$MeOC_6H_4\underline{C}$≡); 97.3 (—$\underline{C}$≡); 110.8 (C-3, 2-$MeOC_6H_4$); 113.1 (C-1, 2-$MeOC_6H_4$); 120.3 (C-5, 2-$MeOC_6H_4$); 129.2 (C-4, 2-$MeOC_6H_4$); 133.2 (C-6, 2-$MeOC_6H_4$); 160.4 (C-2, 2-$MeOC_6H_4$). UV (MeCN), λ_{max}/nm: 245, 254, 291, 298.

1-Benzyl-1-(2-methoxyphenyl)-3,3-diphenylallene. ^{1}H NMR ($CDCl_3$), δ: 3.73 (s, 3 H, OMe); 3.92 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 39.6 ($\underline{C}H_2$); 55.5 (OMe); 209.9 (=$\underline{C}$=).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-09266).

References

1. J. Klein, in *The Chemistry of The Carbon-Carbon Triple Bond*, Ed. S. Patai, Wiley, New York, 1978, Part 1, 343.
2. J.-L. Moreau, in *The Chemistry of Ketenes, Allenes and Related Compounds*, Ed. S. Patai, Wiley, New York, 1980, Part 1, 363.
3. J.F. Bielmann and J.-B. Ducep, *Org. React.*, 1982, **27**, 1.

4. R. Epsztein, in *Comprehensive Carbanion Chemistry*, Eds. E. Buncel, T. Durst, Elsevier, Amsterdam, 1984, Part B, 107.
5. H. Jamamoto, in *Comprehensive Organic Synthesis*, Eds. B. M. Trost, I. Fleming, Pergamon Press, Oxford, 1991, Vol. 2, 81.
6. P. I. Dem'yanov, I. M. Shtyrkov, V. S. Petrosyan, and O. A. Reutov, *Vestn. Mosk. Gos. Univ., Ser. Khim.* [*Bull. Moscow State Univ., Div. Chem. Sci.*], 1988, **29**, 384 (in Russian).
7. P. I. Dem'yanov, I. M. Shtyrkov, G. V. Fyodorova, and V. S. Petrosyan, *Pure Appl. Chem.*, 1990, **62**, 681.
8. I. Smid, in *Ion and Ion Pairs in Organic Reactions*, Ed. M. Szwarc, Wiley, New York, 1972, Vol. **1**.
9. *Ion and Ion Pairs in Organic Reactions*, Ed. M. Szwarc, Wiley, New York, 1974, Vol. **2**, 566 p.
10. A. A. Solov'yanov and I. P. Beletskaya, *Usp. Khim.*, 1978, **47**, 819 [*Russ. Chem. Rev.*, 1978, **47** (Engl. Transl.)].
11. P. I. Dem'yanov, I. M. Shtyrkov, V. S. Petrosyan, and O. A. Reutov, *Vestn. Mosk. Gos. Univ., Ser. Khim.* [*Bull. Moscow State Univ., Div. Chem. Sci.*], 1988, **29**, 203 (in Russian).
12. P. I. Dem'yanov, I. M. Shtyrkov, D. P. Krut'ko, V. S. Petrosyan, and O. A. Reutov, *Metalloorg. Khim.*, 1988, **1**, 1048 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
13. P. I. Dem'yanov, I. M. Shtyrkov, D. P. Krut'ko, M. V. Vener, and V. S. Petrosyan, *J. Organomet. Chem.*, 1992, **438**, 265.
14. P. Dem'yanov, G. Boche, M. Marsch, K. Harms, G. Fyodorova, and V. Petrosyan, *Liebigs Ann.*, 1995, 457.
15. D. H. O'Brien, in *Comprehensive Carbanion Chemistry*, Eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, Vol. 5, 271.
16. P. I. Dem'yanov, I. M. Shtyrkov, D. P. Krut'ko, V. S. Petrosyan, and O. A. Reutov, *Metalloorg. Khim.*, 1988, **1**, 1033 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
17. P. I. Dem'yanov, I. B. Fedot'eva, V. S. Petrosyan, and O. A. Reutov, *Vestn. Mosk. Gos. Univ., Ser. Khim.* [*Bull. Moscow State Univ., Div. Chem. Sci.*], 1984, **25**, 467 (in Russian).
18. H. J. Reich and J. E. Holladay, *J. Am. Chem. Soc.*, 1995, **117**, 8470.
19. C. Lambert, P. v. R. Schleyer, and E.-U. Würthwein, *J. Org. Chem.*, 1993, **58**, 6377.
20. I. M. Shtyrkov, P. I. Dem'yanov, and V. S. Petrosyan, *Metallorg. Khim.*, 1992, **5**, 1348 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
21. T. V. Talalaeva and K. A. Kocheshkov, *Metody elementoorgaicheskoi khimii. Litii, natrii, kalii, rubidii, tsezii* [*Methods of Organoelement Chemistry. Lithium, Sodium, Potassium, Rubidium, and Cesium*], Nauka, Moscow, 1971, Vol **2**, 724 (in Russian).
22. P. I. Dem'yanov, I. B. Fedot'eva, E. V. Babaev, V. S. Petrosyan, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1983, **268**, 1403 [*Dokl. Chem.*, 1983 (Engl. Transl.)].
23. P. I. Dem'yanov, I. B. Fedot'eva, V. S. Petrosyan, and O. A. Reutov, *Vestn. Mosk. Gos. Univ., Ser. Khim.* [*Bull. Moscow State Univ., Div. Chem. Sci.*], 1984, **25**, 297 (in Russian).
24. P. I. Dem'yanov, G. V. Fedorova, V. S. Petrosyan, and O. A. Reutov, *Metalloorg. Khim.*, 1989, **2**, 620 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
25. P. H. Plesch, *High Vacuum Techniques for Chemical Syntheses and Measurements*, Cambridge University Press, Cambridge, 1989, 167 pp.
26. I. B. Fedot'eva, *Ph. D.* (*Chem.*) *Thesis*, Moscow State University, Moscow, 1984, 184 pp. (in Russian).
27. S. M. Neumann and J. K. Kochi, *J. Org. Chem.*, 1975, **40**, 599.
28. H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, 1968, **90**, 2915.
29. H.-J. Becher, in *Handbuch der Preparativen Anorganischen Chemie*, Dritte Auflage, Herausgegeben von G. Brauer, Verdinand Enke Verlag, Stuttgart, 1978, Band **2**.
30. B. E. Maryanoff, D. F. McComsey, and S. O. Nortey, *J. Org. Chem.*, 1981, **46**, 355.
31. E. S. Petrov, *D. Sc.* (*Chem.*) *Thesis*, L. Ya. Karpov Physicochemical Institute, Moscow, 1977, 266 pp. (in Russian).

Received April 19, 1996;
in revised form July 19, 1997