Journal of Organometallic Chemistry, 376 (1989) 31–40
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20029

The aldol-type condensation of methyl diazoacetate with 3-organyl-silyl and -germyl propynals and their carbon analogues

O.I. Margorskaya, A.S. Medvedeva *, M.M. Demina, I.D. Kalikhman,
M.G. Voronkov
Irkutsk Institute of Organic Chemistry, Siberian Division, U.S.S.R. Academy of Sciences, Irkutsk (U.S.S.R.)

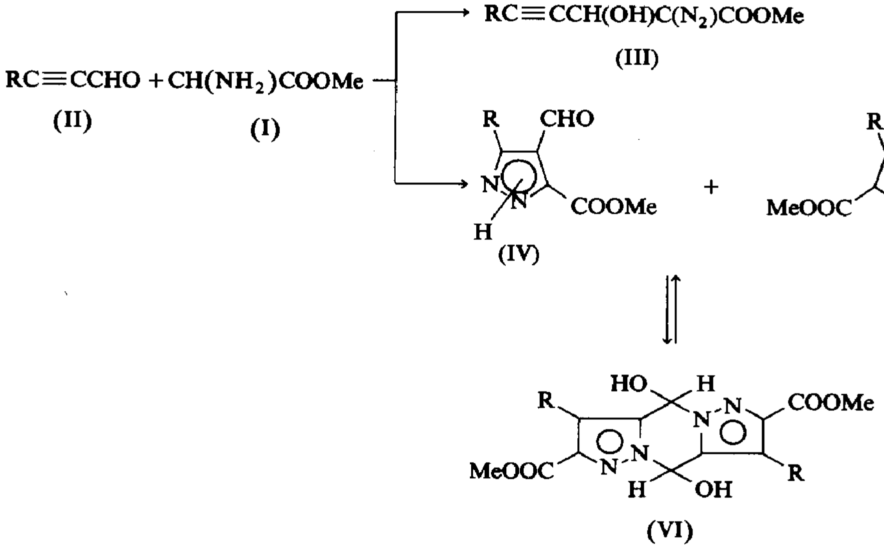
(Received March 15th, 1989)

Abstract

The optimal conditions for the uncatalyzed, selective addition of methyl diazoacetate (I) to the carbonyl group of the substituted propyn-1-als $RC{\equiv}C{-}CHO$ (II) (R = alkyl, Alk_3Si, Et_3Ge) to give the corresponding methyl esters of 2-diazo-3-hydroxy-4-pentyn carboxylic acid $RC{\equiv}CCH(OH)C(N_2)COOMe$ (III) have been found. Shielding of the triple bond in II by the bulky R group or complexation with dicobalt octacarbonyl, the presence of strong electron acceptor ($4\text{-}NO_2C_6H_4$) in the 3-position of II, and the low polarity of the solvent result in the selective aldol type condensation. The reaction of γ-hydroxy-propynals $R^1R^2C(OH){\equiv}CCHO$ with methyl diazoacetate also proceeds by the aldol-type addition and involves two molecules of the propynal with the formation of diacetylenic diazotetraoles $R^1R^2C(OH)\text{-}\underset{\substack{| \\ C(N_2)COOMe}}{C}{\equiv}C(OH)CH(OH)C{\equiv}CC(OH)R^1R^2$ (VIII). The β-addition of methyl diazoacetate to the triple bond in trialkylsilyl or -germyl propynals leads to the isomeric formyl pyrazoles, IV and V. The presence of the Si- or Ge-containing substituents in the 4-position of IV promotes their dimerization into the tricyclic hemiaminals, VI.

Introduction

Propyn-1-al and its derivatives are known as active dipolarophiles towards diazo group-containing compounds [1,2]. In earlier work, the addition of the 1,1-dimethyl diazomethylphosphonate anion to the C=O bond of phenyl propynal was reported [3]. We have shown that in the absence of catalyst the methyl diazoacetate reacts selectively with the aldehyde group of 4,4-dimethyl-2-pentyn-1-als [4]. The linear isomer (II, R = n-Bu) as well as triorganylsilyl and -germyl propynals act as ambident electrophiles towards methyl diazoacetate; both reactive sites are involved in the reaction. The isomeric 4- and 3(5)-formyl pyrazoles, IV and V, as well as the dimers of IV viz. VI are the products of dipolar cycloaddition, whereas the aldol-type addition gives the acetylenic diazocarbinoles (III) (Scheme 1).



Scheme 1. R = 4-$NO_2C_6H_4$ (a); Ph (b), Ph_3Ge (c); MeEt(OH)C (d); MePr(OH)C (e); EtAm(OH)C (f); n-Bu (g); Et_3Ge (h); Me_3Si (i); Et_3Si (j).

Aldol condensation is useful for making molecules that have several asymmetric centres [5].

In order to find the optimal conditions for the selective aldol-type addition of methyl diazoacetate to the substituted propynals II we investigated the effects of the electron-acceptor substituents at the sp-carbon (II, R = 4-$NO_2C_6H_4$; $R^1R^2C(OH)$), the protection of the triple bond by complexation with dicobalt octacarbonyl, and the polarity of the medium on the direction of the nucleophilic attack.

Results and discussion

Saturated aldehydes (n-butanal, iso-butanal) do not react with methyl diazoacetate in the absence of catalyst (i.e. under the conditions of diazocarbinol (III) formation). The rather facile addition of a relatively weak nucleophile, such as I, to the propynals II can be explained in terms of the steric accessibility of the carbonyl group as well as by the acceptor effect of the ethynyl group which enhances the electrophilicity of the carbon atom in the C=O group [6]. When bases such as triethylamine or potassium ethoxide in ethanol are used in this reaction, resinification results.

The reactions of the propynals (IIa–IIc) with methyl diazoacetate (I) in ether proceed at ambient temperature in the dark. Only with 4-nitrophenyl propynal (IIa) does the addition of the nucleophile take place selectively at the carbonyl group (Table 1). Phenyl propynal (IIb) under the same conditions forms adducts both with the C≡C and the C=O groups. The introduction of the strongly accepting 4-nitrophenyl group seems to increase the electrophilicity of the carbonyl carbon

Table 1

Ratio of the products of methyl diazoacetate addition to the C≡C or C=O bond in propynals RC≡CCHO in diethyl ether (determined by ^{1}H NMR in $CDCl_3$)

R	Addition to C≡C	Addition to C=O
$4\text{-}NO_2C_6H_4$ (a)	0	100
Ph (b)	35	65
Ph_3Ge (c)	100	0
$Alk_2(OH)C$ (d–f)	0	100

atom, to result in the selective formation of methyl 2-diazo-3-hydroxy-5-(4-nitrophenyl)pentynoate (IIIa). The selective addition of methyl diazoacetate to the triple bond is observed in case of triphenylgermylpropynal (IIc). As in the case of the trimethylsilyl group [1], the triphenylgermyl group probably does not significantly hinder attack by the dipole I on the triple bond in the propynals II. The 1,3-dipolar cycloaddition is known to be very sensitive to steric hindrance [7–9].

In Table 2 are listed the analytical and other data, and in Table 3 are listed the ^{1}H NMR and IR data for compounds III–VI, VIII.

In order to study the reactivity of the triple bond under the influence of the two acceptor substituents — carbonyl group and hydroxy-containing group — we have examined the reaction of the acetylenic γ-hydroxyaldehydes (IId–IIf) with methyl diazoacetate. Like the propynals that have their triple bond shielded by the bulky t-butyl substituent or activated by a strong acceptor, such as 4-nitrophenyl, the compounds IId–IIf add methyl diazoacetate only to the aldehyde group. However, the expected diazoglycols VII react with a second molecule of the initial γ-hydroxypropynal along the lines of an aldol condensation with the participation of the hydrogen atom attached to the secondary carbon atom to give the hitherto unknown diacetylenic diazotetraoles (VIII) (Scheme 2). The ease of the subsequent condensation of diazoglycols (VII) which is in sharp contrast to diazocarbinols (III) is probably accounted for by the effect of the hydroxy group in IId–IIf which activates the carbonyl group towards nucleophile and catalyzes addition of the carbonyl by general acid-catalysis.

The structures of the tetraoles VIII have been confirmed by elemental analysis (Table 2) and by IR and ^{1}H NMR spectroscopy (Table 3).

Table 2

Data for the compounds obtained from the reaction of propynals (II) with methyl diazoacetate

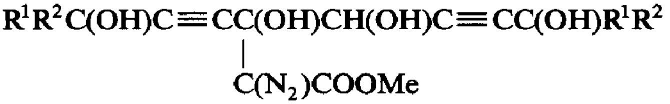
Compound	R	Yield (%)	m.p. (°C)	Analysis (found (calcd.) %)			
				C	N	H	Si/Ge
IIIa	$4\text{-}NO_2C_6H_4$	76	oil	52.54 (52.38)	14.99 (15.27)	3.11 (3.27)	–
IIIb	Ph	64	oil	62.28 (62.63)	12.61 (12.17)	4.85 (4.35)	–
Vb	Ph	14	131	62.39 (62.63)	12.09 (12.17)	4.65 (4.35)	–
Vc	Ph_3Ge	10	149.5	63.37 (63.11)	6.61 (6.13)	4.21 (4.38)	15.55 (15.87)
VIc	Ph_3Ge	60	161	63.01 (63.11)	6.25 (6.13)	4.42 (4.38)	15.12 (15.87)
VIIId	MeEt(OH)C	70	oil	57.28 (57.95)	7.21 (7.95)	6.74 (6.82)	–
VIIIe	MePr(OH)C	68	oil	60.05 (59.97)	6.62 (7.36)	7.23 (7.43)	–
VIIIf	EtAm(OH)C	65	oil	64.13 (64.62)	6.81 (6.03)	8.42 (8.69)	–

$$R^1R^2C(OH)C{\equiv}CCHO + CH(N_2)COOMe \longrightarrow$$

(II)

$$R^1R^2C(OH)C{\equiv}CCH(OH)C(N_2)COOMe \xrightarrow{II}$$

(VII)



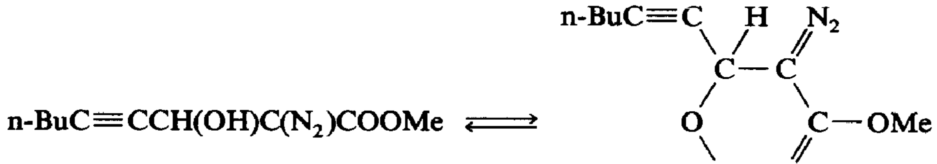
$$R^1R^2C(OH)C{\equiv}CC(OH)(C(N_2)COOMe)CH(OH)C{\equiv}CC(OH)R^1R^2$$

(VIII)

Scheme 2. $R^1 = Me$, $R^2 = Et$ (IId); $R^1 = Me$, $R^2 = Pr$ (IIe); $R^1 = Et$, $R^2 = Am$ (IIf).

The IR spectra of compounds III and VIII are typical and show intense bands for all the functional moieties in the molecule, viz., 2210–2250 [ν(C≡C)], 1705–1725 [ν(COOMe)], 2105–2115 [ν(N≡N)], and 3350–3440 cm^{-1} [ν(OH)]. Aliphatic diazocarbinols are usually unstable and readily eliminate nitrogen [10]. In contrast, the α-diazo-β-hydroxyacetates (III) and diazotetraoles (VIII) are rather stable and can be stored in absence of solvent without decomposition at ambient temperature in the dark during 5–6 months. Their relative stability is attributable to the intramolecular hydrogen bond and to the electron acceptor effects because the ethynyl, ester, and hydroxy groups enhance the positive charge on the diazo group-bearing carbon atom.

The IR spectrum of the solution of methyl 2-diazo-3-hydroxy-4-nonynoate (VIg) in CCl_4 shows stretching vibrations of the free OH group at 3585 cm^{-1} and a H-bonded hydroxy band at 3430 cm^{-1} which does not disappear with a fall in the concentration to $5 \cdot 10^{-5}$ mol l^{-1} and the intensity ratio remains constant. The presence of two absorption bands points to the equilibrium between non-bonded and H-bonded conformations, as shown below (Scheme 3).



Scheme 3

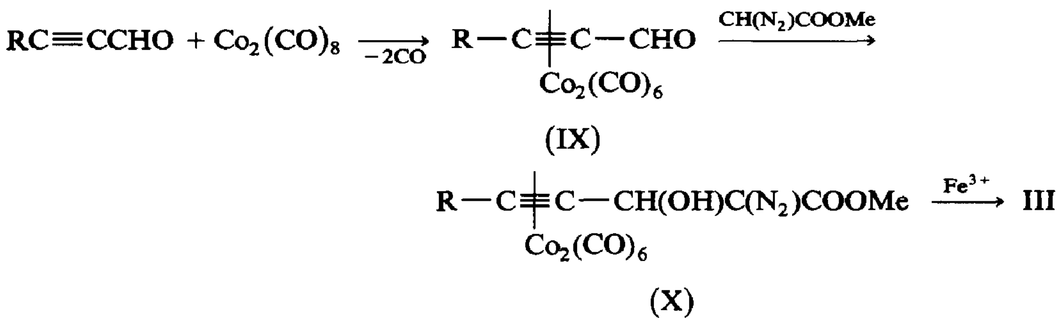
The existence of two conformers is confirmed by the doublet shape of the band in the carbonyl stretching vibration region with maxima at 1700 and 1682 cm^{-1} attributable to the free [ν(C=O)] and the associated [ν(C=O···H)] carbonyl groups, respectively.

In the course of our studies on optimizing the conditions for the selective aldol type addition of methyl diazoacetate (I) to II we protected the triple bond by complexation with dicobalt octacarbonyl $Co_2(CO)_8$ (Scheme 4).

Table 3

^{1}H NMR data and IR frequencies of the compounds obtained

Compound	^{1}H NMR (deuterochloroform), ppm from TMS)						IR (cm^{-1})					
	R	MeOCO	OH	CH	CHO	NH	C≡N	C=O	OC=O	C≡C	OH(NH)	N≡N
IIIa	7.83m	3.80s	–	5.78s	–	–	–	–	1700	2160	3350	2110
IIIb	7.10m	3.65s	4.62s	5.70s	–	–	–	–	1700	2235	3400 (3100)	2115
IVb	7.22m	3.70s	–	–	9.83s	9.47s	–	–	–	–	–	–
Vb	7.22m	3.75s	–	–	10.40s	9.65s	1530	1650	1745	–	3080	–
Vc	7.44m	3.91s	–	–	10.38s	–	1540	1680	1730	–	3100	–
VIc	7.17m	3.65s	2.48s	5.43s	–	–	1530	–	1740	–	3200	–
VIIId	1.36s, 0.90t, 1.61q	3.71s	3.86s	5.44s	–	–	–	–	1725	2250	3440	2115
VIIIe	1.77s, 0.87t, 2.18t, 1.49m	3.78s	4.62s	5.74s	–	–	–	–	1705	2210	3350	2105
VIIIf	0.99t, 1.51m, 1.73m	3.73s	4.70s	5.44s	–	–	–	–	1710	2215	3430	2110



Scheme 4. R = n-Bu (g); Et_3Ge (h); Me_3Si (i).

These complexes are the first examples of the π-complexes of triorganylsilyl and -germyl propynals. Their formation is confirmed by the fact that the C≡C stretching vibrations in the IR spectrum are decreased by about 600 cm^{-1} with respect to the initial propynal as well as by the appearance of a series of bands in the region 2000–2100 cm^{-1} which pertain to the stretching vibrations of Co-associated carbonyl groups. The absorption band of the aldehyde group remains unchanged (Table 4).

The ^1H NMR spectrum of complex IXh in $CDCl_3$ when compared with that of the free propynal IIh shows broadening and a downfield shift of the aldehyde proton signal from 9.07 ppm to 10.31 ppm. The IR spectra are in good agreement with the parameters previously described for the propynal π-complexes [11] (Table 4).

The protection of the triple bond of the propynals II by complexation with dicobalt octacarbonyl allows the selective attack of methyl diazoacetate on the carbonyl group even for the trimethylsilylpropynal (IIi) which under conventional conditions reacts exclusively by 1,3-cycloaddition [4]. The results of the reaction of methyldiazoacetate with propynals (IIg–IIk) performed without the complexing agent and in the presence of dicobalt octacarbonyl are listed in Table 3. The reaction in the presence of $Co_2(CO)_8$ is accompanied by resinification, probably, owing to oligomerization of the starting propynals; cobalt complexes of acetylenic compounds are known to promote the oligomerization of ethynylcarbinols [12].

Dicobalt octacarbonyl also possesses a catalytic effect. Whereas the reaction of the free propynals (IIg–IIi) with methyl diazoacetate in diethyl ether at ambient temperature proceeds during 50 days, in the presence of $Co_2(CO)_8$ it is complete within 3 days. This implies that the increased acceptor character of the Co-coordi-

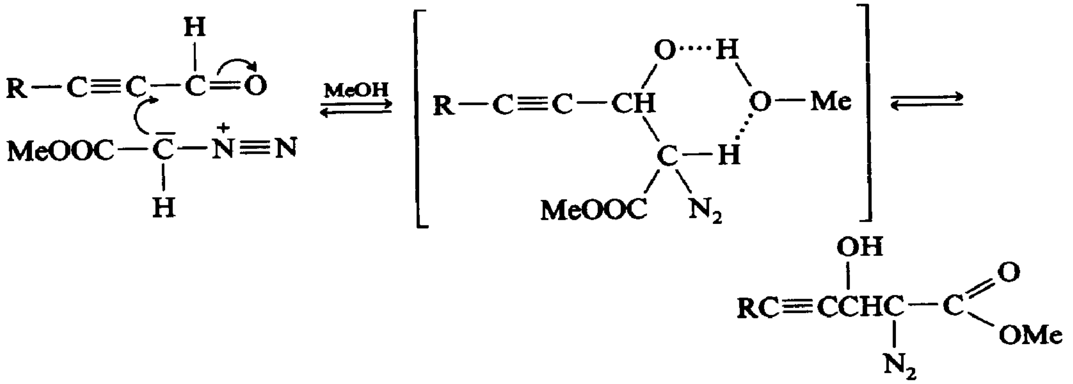
Table 4

Influence of protection by complexation of the triple bond in propynals (II) on the course of methyl diazoacetate addition (%)

R	Without $Co_2(CO)_8$		Complexing with $Co_2(CO)_8$	
	C≡C	C=O	C≡C	C=O
n-Bu (IIg)	47	53	–	100
Et_3Ge (IIh)	65	35	–	100
Me_3Si (IIi)	100	–	–	100

nated triple bond in the π-complexes (IXg–IXi) causes significant enhancement of the electrophilicity of the carbonyl carbon atom. The improved acceptor properties of the triple bond in cobalt complexes of disubstituted alkynes in their reactions with nucleophiles have been observed previously [13].

A study of polarity effects of the media on the course of the nucleophilic attack on the –C≡C–C=O system in various solvents(hexane, diethyl ether, tetrahydrofuran, dimethoxyethane, methanol) showed that the rate of reaction almost doubles on going from hexane to methanol. The reaction of triethylgermylpropynal (IIh) with methyl diazoacetate is complete in hexane within 60 days, in diethyl ether in 50, in tetrahydrofuran and dimethoxyethane in 40, and in methanol within 25 days. The increased rate in methanol is attributable to the enhanced electrophilicity both of the triple bond and the carbonyl group in II be cause of the general acid-catalysis. Owing to its dual solvating ability, methanol can both activate the nucleophile and decrease the energy of the transition state by the formation of the six-membered H-bonded cycle, which facilitates proton transfer (Scheme 5).



Scheme 5

Aprotic solvents seem to enhance proton abstraction from the negatively charged carbon atom in I owing to the formation of a donor–acceptor complex. Hence, the proton transfer should be facilitated by the increased polarity of the solvent, in the order as follows: diethyl ether, tetrahydrofuran, and dimethoxyethane. Table 5 reveals that the yield of the diazocarbinols (III) falls with rise in polarity of the medium: hexane, diethyl ether, tetrahydrofuran, dimethoxyethane, and methanol. The yields of the 1,3-dipolar cycloaddition products increase in the same order. This behaviour is akin to that for the nucleophilic 1,4-addition to the unsaturated aldehydes and ketones, in which rate-increasing effect of polar solvents is well documented [14].

The composition of the reaction mixture was monitored with time and showed: (a) initial growth of the diazocarbinol concentration and its subsequent gradual decrease (Table 6), (b) the simultaneous increase in the concentration of pyrazoles (IV, V) and in that of the dimer (VI). This is indicative of a kinetically controlled aldol-type addition of methyl diazoacetate to propynals (II), whereas the 1,3-cycloaddition results in thermodynamically stable products, the formation of which promotes the decomposition of diazocarbinols (III) by a retro-aldol reaction. This

Table 5

Influence of the solvent on the 1,3-cycloaddition : aldol condensation ratio in the reaction of methyl diazoacetate with propynals (II)

R	Solvent	1,3-Cycloaddition	Aldol-type addition
Ph (IIb)	hexane	20	80
	diethyl ether	35	65
	dimethoxyethane	60	40
	methanol	78	22
Ph_3Ge (IIc)	diethyl ether	100	–
	tetrahydrofuran	100	–
Et_3Ge (IIh)	hexane	10	90
	diethyl ether	70	30
	dimethoxyethane	77	23
	tetrahydrofuran	78	22
	methanol	86	14
Et_3Si (IIj)	hexane	40	60
	diethyl ether	55	45
	tetrahydrofuran	71	29
	methanol	80	20

reaction was monitored by ^1H NMR spectroscopy for methyl 2-diazo-3-hydroxy-4-nonynoate (IIIg) and for methyl 2-diazo-3-hydroxy-5-trimethylsilyl-4-pentynoate (IIIi). After two months in diethyl ether solution the proportions stabilized at about 20% of (IIIg) and 17% of (IIIi).

That the yields of diazocarbinols (III) fall with increase of the solvent polarity can be explained in terms of their diminished stability owing to the breaking of the intramolecular hydrogen bonds which favours the retro-aldol reaction.

We have previously reported on the effect of solvent polarity and of temperature on the "monomer ⇄ dimer" equilibrium in the dimerization of 3(5)-formylpyrazole (IV) into tricyclic bis-hemiaminals (VI) [4]. The ratios of (IV) : (VI) determined by ^1H NMR spectroscopy in $CDCl_3$ are presented in Table 7. The silicon- and germanium-containing pyrazoles exist predominantly as dimers. In contrast, 4-phenylpyrazol (IVb), under the same conditions exists exclusively as the monomer.

Table 6

Dynamics of the reaction of triethylgermylpropynal (IIh) with methyl diazoacetate in diethyl ether (determined by ^1H NMR in $CDCl_3$)

Reaction time (days)	Percentage of products		$C{=}O/C{\equiv}C$
	Aldol condensation ($C{=}O$), (II)	1,3-Cycloaddition ($C{\equiv}C$), (III + IV + V)	
7	43	57	0.75
21	43.5	56.5	0.77
35	41	59	0.69
50	38	62	0.61
60	35	65	0.54

Table 7

Influence of the substituent on the monomer (IV) ⇄ dimer (VI) equilibrium

R	Percentage of	
	IV	VI
Me_3Si (i)	30	70
Ph (b)	100	–
Ph_3Ge (c)	0	100
Et_3Ge (h)	28	72
Et_3Si (j)	0	100

Apparently, the π-acceptor effect of the R_3Si or the R_3Ge group, like that in the propynals, enhances the electrophilicity of the carbonyl carbon atom and the mobility of NH protons and so facilitates the dimerization.

Therefore, a study of the reactivity of the (I)–(II), dipole–dipolarophile pair as a function of the structure of the propynal (II) and the polarity of the solvent led us to elucidate the best conditions for the non-catalyzed selective aldol-type reaction to give acetylenic diazocarbinols.

Experimental

Substituted propynals (IIa–IIc, IIg–IIg) and acetylenic γ-hydroxyaldehydes (IId–IIf) were prepared by oxidation of the corresponding ethynyl carbinols and γ-glycols with neutral γ-MnO_2 described previously [4].

The ^1H NMR spectra were recorded on a 80 MHz Tesla BS 487 C spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Infrared spectra were recorded by use of a Specord 75 IR spectrometer (400–4000 cm^{-1}) in thin layers, in Nujol, in pellets with KBr, or as solutions in CCl_4, Et_2O, hexane, and ethanol with concentrations from 0.1 to $5 \cdot 10^{-5}$ mol/l.

All reagents and solvents were distilled immediately before use. The reactions were carried out at atmospheric pressure in dry argon in the dark by a published procedure [4].

General procedure for reactions of methyl diazoacetate (I) with propynals (II)

Solutions of propynal (II) (1 mmol) and methyl diazoacetate (I) (1 mmol) in dry solvent (5 ml, the solvents used are listed in Table 5) were kept in the dark at ambient temperature under argon. The extent of conversion was monitored by thin-layer chromatography (Silufol, eluent: diethyl ether). Once the reaction had gone completion, the solvent was removed in vacuum (1 mmHg), than residue was diluted with $CDCl_3$, and the ratio of the products was determined by ^1H NMR spectroscopy (Table 5).

Preparation of π-complexes and their reactions with methyl diazoacetate (I)

(i) $Et_3GeC{\equiv}CCHO \cdot Co_2(CO)_8$ *(IXh).* A mixture of triethylgermylpropynal (IIh) (1.68 g, 10 mmol) and $Co_2(CO)_8$ (3.42 g, 10 mmol) in 20 ml of dry diethyl ether was stirred under argon at ambient temperature for 2 h. The reaction was monitored by thin-layer chromatography and by its evolution of CO which was bubbled through a separate vessel containing glycerol. The complex formed was purified by column

chromatography (Silicagel 40/100, eluent: 2 : 1 diethyl ether : chloroform) under argon and identified in solution. ^1H NMR (δ) in $CDCl_3$ with trimethylchlorosilane (as initial standard): 10.31 (broad(ens), 1H, s, CHO), 1.1 (9H, m, Et_3Ge). IR (Nujol) 1550 ($C \equiv C$); 1675 ($C=O$); 2010–2070, 2099 cm^{-1} $(C=O)_{Co}$.

(ii) Reaction of IXh with I. A solution of propynal (IIh) (0.64 g, 3 mmol) in 3 ml of the corresponding solvent was added to a solution of $Co_2(CO)_8$ (1.026 g, 3 mmol) in 6 ml of dry diethyl ether, the mixture was stirred under argon until no further gas bubbles were observed, and left to stand for one day. A solution of I (0.3 g, 3 mmol) in 2 ml of dry diethyl ether was then added, and the mixture was kept for one week, then treated with $Fe(NO_3)_3$ in 96% ethanol, washed with H_2O, and extracted with diethyl ether. The combined organic extracts were dried with Na_2SO_4. Methyl 2-diazo-3-hydroxy-5-triethylgermyl-4-pentynoate (IIIh) (0.22 g, 23%) was isolated by column chromatography (Silicagel 40/100, eluent: diethyl ether).

Similar procedures were used for the complexes of trimethylsilylpropynal (IIi) and n-butylpropynal (IIg) with $Co_2(CO)_8$. After workup as above methyl 2-diazo-3-hydroxy-5-trimethylsilyl-4-pentynoate (IIIi) and methyl 2-diazo-3-hydroxy-4-nonynoate (IIIg) were obtained in 20 and 25% yields, respectively.

Decomposition of acetylenic diazocarbinols (III) by retro-aldol reaction

In order to elucidate the retro-aldol decomposition of diazocarbinols (III) in ethereal solution for the duration of the reaction (50 days) a series of independent experiments was carried out.

A solution of diazocarbinol (III) (0.312 g, 1 mmol) in 5 ml of dry diethyl ether was kept in the dark under argon. Each week the composition of the solution was checked by ^1H NMR spectroscopy; the results are shown in Table 6.

References

1 R. Hüttel, Chem. Ber., 74 (1941) 1680.
2 A.F. Noels, J.N. Braham, A.I. Hubert and Ph. Teyssie, Tetrahedron Lett., 34 (1978) 3495.
3 W. Disteldorf and M. Regitz, Chem. Ber., 109 (1976) 546.
4 A.S. Medvedeva, M.M. Demina, A.I. Borisova, O.I. Margorskaya, I.D. Kalikhman, E.I. Brodskaya and N.S. Vyazankin, J. Organomet. Chem., 231 (1982) 109.
5 C.H. Heathcock, in: Current Trends in Organic Synthesis. Ed. H. Nozaki, Pergamon Press, Oxford e.a., 1983, pp. 27–43.
6 A.N. Egorochkin, O.I. Margorskaya, S.E. Skobeleva, Izv. Akad. Nauk SSSR, Ser. Khim., (1986) 1789.
7 R.A. Firestone, J. Organomet. Chem., 37 (1972) 2181.
8 R. Huisgen, Angew. Chem., 75 (1963) 742.
9 G. Guillerm, A. Honore, L. Veniard, G. Pourcelot and I. Benaim, Bull. Soc. Chim. Fr., (1973) 2739.
10 E. Wenkert and C.A. McPherson, J. Am. Chem. Soc., 94 (1972) 8084.
11 A. Meyer and M. Bigorgne, Organometallics, 3 (1984) 1112.
12 U. Krüerke and W. Hübel, Chem. Ber., 94 (1961) 2829.
13 S. Padmanabhan and K.M. Nicholas, J. Organomet. Chem., 212 (1981) 115.
14 L.A. Yanovskaya, G.V. Kryshtal and V.V. Kul'ganek, Usp. Khimii (Russ. Chem. Rev.) 53 (1984) 1280.