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STEREOCHEMISTRY AND MECHANISM OF ACYLATION OF ACETYLENES[1]

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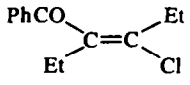
Abstract—The addition of acid chloride-$AlCl_3$ complexes and of acyl triflates to several acetylenes has been performed. Evidence is given that these additions occur at least partly through a vinyl cation intermediate. In the case of aroyl chlorides or aroyl triflates the intermediate vinyl cation can be attacked by the aromatic nucleus of the aroyl group, leading to the formation of indenones. The difference in behaviour between aroyl chloride-$AlCl_3$ complexes and aroyl triflates is explained by the hardness of the triflate anion as a nucleophile, compared to the tetrachloraluminate anion. Further evidence for the intermediate vinyl cation is found in the formation of rearranged products in the addition of 3,5 dimethoxybenzoyl chloride-$AlCl_3$ complex and benzoyl triflate to 4,4-dimethyl-2-pentyne.

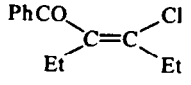
The addition of Friedel-Crafts acid chloride-$AlCl_3$ complexes to acetylenes leads to the formation of β-chlorovinyl ketones, which are very useful intermediates for the synthesis of quite a variety of compounds.[2,3] Though a lot of preparative information is given, very little work has been done on the mechanism of these additions.[4] The acylation of acetylenes with mixed anhydrides of carboxylic acids and trifluoromethane sulfonic acid, which leads to the formation of β-ketovinyl triflates has not been described as far as we know. In a recent study of Effenberger and Epple,[5] these acyl triflates were used in the acylation of aromatics and were reported to be very reactive acylation agents. We investigated these two modes of acylation of acetylenes, with acid chloride-$AlCl_3$ complexes and with acyl triflates, with respect to their stereochemistry and their mechanism of addition.

RESULTS AND DISCUSSION

Several studies have shown that β-chlorovinyl ketones prepared from acetylene have the *trans* configuration,[6] chlorine and carbonyl in *trans* to each other. This type of β-chlorovinyl ketones is extremely sensitive to *cis-trans* isomerisations.[7]† For the more stable β-chlorovinyl ketones, prepared from disubstituted acetylenes, the *cis-trans* proportion has not been determined as far as we know. The addition of equimolecular amounts of benzoyl chloride-$AlCl_3$ complex to 3-hexyne in dichloromethane solution was instantaneous and quantitative at room temperature. The GLC analysis of the reaction mixture revealed three components: **1b**: 80%; **2b**: 12% and 2,3-diethylindenone: 8%.



1b



2b

In view of new results,‡ we can no longer hold our first assignments[1] of *cis*- and *trans*-structures of the two β-chlorovinyl ketones: the principal product is the *trans*-β-chlorovinyl ketone **1b** instead of the *cis*-β-chlorovinyl ketone **2b**.

By lowering the reaction temperature to −40°, the reaction could be followed. Analysis of the initial rate data (10% reaction) showed approximately first order kinetics for both the 3-hexyne and the benzoylchloride-$AlCl_3$ complex. However, the reproducibility of the rate data was not very good. The pure *trans*- and *cis*-β-chlorovinylketones, in the presence of $AlCl_3$ at −40° in dichloromethane, did not lead to the formation of any indenone,§ neither to *cis-trans* isomerization. Thus the product distribution is kinetically controlled.

Performing the addition of *p*-methoxy-, *m*-bromo-, *m*-nitro- and *p*-nitrobenzoyl chloride to 2-butyne and 3-hexyne, decreasing amounts of *trans*-β-chlorovinyl ketones are formed (Table 1).

†Montanari *et al.* reported that a slight excess of HCl or a higher reaction temp (more than −40°) resulted in a rapid *cis*-to-*trans* inversion.

‡An extensive NMR spectroscopic study of a number of β-chlorovinyl ketones and model compounds, including the observations of the aromatic solvent induced NMR shifts, lead us to the conclusion that in alkyl-β-chloro-α,*b*-dialkylvinyl ketones, the carbonyl function has a low deshielding effect on the β-*cis* alkyl group, whereas for the aryl ketones a shielding effect is observed.[8]

§At higher temperatures (reflux in dichloroethane) this internal ketovinylation goes on well and constitutes a new method of indenone formation.[9]

Table 1. Percentage *trans*-β-chlorovinyl ketone formed in the $AlCl_3$ catalyzed addition of the acid chloride A to the acetylene B; % *cis* + % *trans* = 100%

B \ A	$CHCl_2COCl$	$CH_2ClCOCl$	CH_3COCl	C_2H_5COCl	*p*-$NO_2C_6H_4COCl$	*m*-$NO_2C_6H_4COCl$	*m*-BrC_6H_4COCl	C_6H_5COCl	*p*-$MeOC_6H_4COCl$
Me—C≡C—Me	0[b]	10[b]	100[a,b]	100[a,b]	37[b]		80[a] 84[b]	95[a]	100[a,b]
Et—C≡C—Et		0[b]	75[a,b]	70[a]	30[c]	33[b]	55[b]	87[a]	100[a]
Ph—C≡C—Et		87[b]	88[a,b]	92[a,b]	80[b]			88[a] 86[b]	

[a] GLC analysis
[b] NMR analysis
[c] preparitive TLC and weighing of the fractions

In the aliphatic series propionyl chloride, acetyl chloride, monochloroacetyl chloride and dichloroacetyl chloride give also decreasing percentages of *trans*-β-chlorovinyl ketones in their addition to 2-butyne and 3-hexyne (Table 1).

The results of the acylations of 2-butyne and 3-hexyne with a series of aromatic and aliphatic acyl triflates are tabulated in Table 2. The product distributions have been proved to be kinetically controlled.

Comparing the results of Tables 1 and 2, one can observe a remarkable agreement: in both acylation modes, electron donating substituents favour *trans* addition, whereas electron withdrawing substituents favour *cis* addition. This can be explained if the *trans* addition occurs by an attack of the acylium ion on the acetylenic compound: in an equilibrium of ion pair and donor-acceptor complex, electron donating substituents increase the amount of ion pairs.

The formation of indenones without the intermediacy of β-chlorovinyl ketones of β-ketovinyl triflates can be explained by an electrophilic attack of an intermediate vinyl cation[10] on the aromatic nucleus of the aroyl group. A difference between the two modes of acylation is the higher percentage indenone formed in the acylation with acyl triflates (Table 3). An α-aryl substituent in the intermediate vinyl cation increases the amount of indenone in the acylation with benzoyl triflate and decreases it in the acylation with benzoyl chloride-$AlCl_3$ complex. On the other hand, by substituting the α-Me group in the intermediate vinyl cation for an α-Et group, the indenone formation is increased in both acylation modes.

We suggest the following explanation for these facts. The intermediate vinyl cation can react via two competitive paths: with the tetrachloroaluminate (or triflate) anion to form the *trans* addition product or with the aromatic nucleus of the aroyl group to form an indenone. So the relative reactivity of the vinyl cation with three nucleophiles has to be considered.

According to the theory of the "hard" and "soft"

Table 2. Product distribution for the acylation of the acetylenes B with the acyl triflates A. This distribution has been determined by a preparative TLC and weighing of the fractions; the average of three determinations was taken

Acetylene B	Me—C≡C—Me			Et—C≡C—Et		
Acyl triflate A (X = OSO_2CF_3)	% *trans*	% *cis*	% indenone	% *trans*	% *cis*	% indenone
p-$MeOC_6H_4COX$	82	1·5	16·5			
C_6H_5COX	71·5	6·5	22	50	24·5	25·5
p-$NO_2C_6H_4COX$	40	60	—			
C_2H_5COX	80	20	—			
CH_3COX	70	30				
CH_2ClCOX	15	85[a]				
$CHCl_2COX$	no reaction					

[a] These 85% contain 50% of the expected *cis*-β-ketovinyl triflate and 35% of a *cis*-β-ketovinyl triflate where the chlorine has been exchanged for a triflate group by reaction with excess silver triflate.

Table 3. Percentage of indenone formed in the acylation of different acetylenes with benzoyl triflate (A) and with benzoyl chloride-$AlCl_3$ complex (B); % indenone + % *trans* adduct = 100%

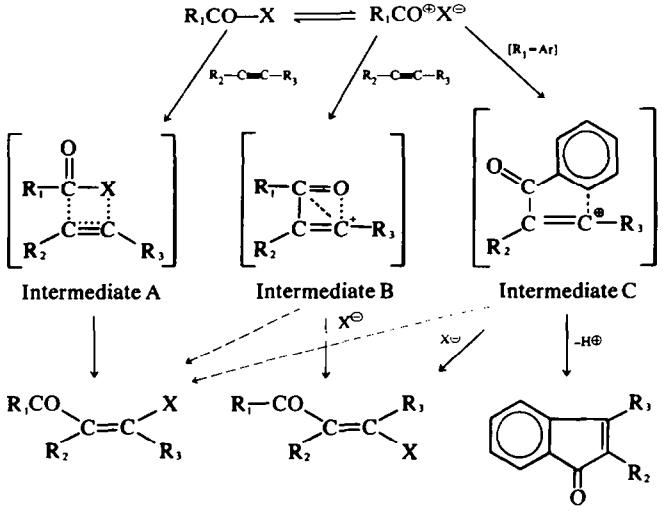
R_1—C≡C—R_2		% Indenone in the acylation with	
R_1	R_2	A	B
Me	H	—	0
Me	tBu	36	—
Me	Me	24	2
Et	Et	34	9
tBu	Me	41	—
Ph	Et	100	0
Ph	Ph	100	—

behaviour of electrophiles and nucleophiles,[11] the reactivity order of different nucleophiles is dependent on the nature of the electrophile. Classifying the three nucleophiles with respect to their softness,[11a] the triflate anion would be the least soft nucleophile, followed by the aromatic nucleus, while the softest nucleophile could be the tetrachloroaluminate anion.

The other partner in the reaction, the vinyl cation, will show a softer electrophilic behaviour, the more the empty *p*-orbital will be stabilized by the α-substituent. This softer behaviour will result in an enhanced reactivity towards the softest of the two competitive nucleophiles: the tetrachloroaluminate anion in the case of the $AlCl_3$ catalyzed acylation, the aromatic nucleus in the case of the acylation with benzoyl triflate.

A second factor which influences the proportion of indenone to *trans*-adduct is the β-substituent of the vinyl cation (R_2 in intermediate B and C in Scheme 1). The stabilizing effect of this β-substituent being small,[10b,c] this substituent will effect the *trans* addition only by steric hindrance: the larger this substituent the less *trans* adduct will be formed. Comparing the addition of benzoyl chloride to 2-butyne and to 3-hexyne, the vinyl cation formed in the addition to 3-hexyne would be more stabilized (by the inductive effect of an ethyl instead of a methyl), favouring attack of the tetrachloroaluminate anion. However, this *trans* attack is opposed to by the steric hindrance of the β-Et group. If the steric factor would be preponderate, more indenone can be expected with 3-hexyne than with 2-butyne.

On the basis of these observations, the following reaction scheme can be proposed (Scheme 1). Reaction of the donor-acceptor complex between the acid chloride and $AlCl_3$, or reaction of the undissociated mixed anhydride with the acetylene, leads via a transition state A to the *cis*-β-chlorovinyl ketone, respectively the *cis*-β-ketovinyl triflate. Attack of the acylium ion on the triple bond leads to the formation of a vinyl cation. This vinyl cation can effect an aromatic substitution, leading to the observed indenone via intermediate C. The tetrachloroaluminate anion or the triflate anion can also attack the vinyl cation. Which side of the empty *p*-orbital will be attacked, will depend on the "freedom" of the two sides, i.e. on



X = OSO_2CF_3 in the acylation with acyl triflates
X = Cl . . . $AlCl_3$ in the acylation with acyl chlorides
$X^{\ominus}$ = $AlCl_4^{\ominus}$ or $^{\ominus}OSO_2CF_3$

SCHEME 1

the size and the electronic character of the β-groups.[12] Vinyl cations are known as intermediates with a very high energy content,[10] and they will look for stabilisation of the positive charge. In Scheme 1 we propose several types of stabilisation. Interaction of the positive center with the CO group could lead to an oxetenelike[13] intermediate B (Scheme 1), which could rearrange in the case of strong interaction.[13d] This can be excluded as for both additions of C_6H_5COCl + Et–C≡C–Et and of EtCOCl + C_6H_5C≡C–Et, which should lead to the same oxetene intermediate, only the normal addition products are observed instead of a mixture of products arising from the two different modes of attack of the tetrachloroaluminate anion on the common oxetene intermediate. However, also a weak interaction between the vinyl cation and the carbonyl group can block the empty p-orbital at one side, leading to preferential formation of *trans* addition products as is proposed in the intramolecular acylation of *cis* - cyclohept - 4 - ene - 1 - carbonyl chloride.[14]

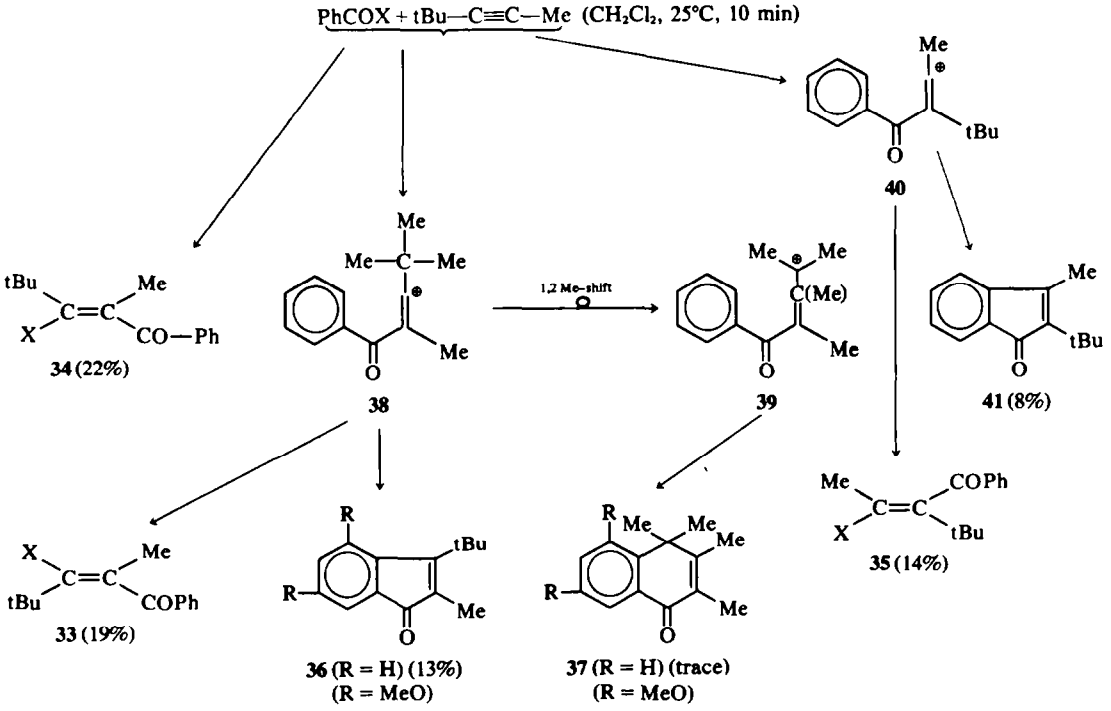
By the formation of indenone, strong evidence exists for the second type of stabilization: interaction of the vinyl cation with the π-electrons of the aromatic nucleus (intermediate C, Scheme 1). Aryl participation to stabilize ordinary carbonium ions[15] but also vinyl cations[16] has been studied, mostly in solvolytic reactions. Several reports about the rearrangement of aromatic substituents in cyclialkylation reactions, by arylparticipation, have been published.[17] In the indenone formation no rearrangement of aromatic substituents has been observed.[9]

A third type of stabilization of the vinyl cation can occur by interaction with the α-substituent. In cases where there is no competitive indenone formation, stabilizing substituents on the acetylene are expected to increase the percentage of *trans* addition. This is clearly demonstrated in Table 1, comparing the percentage of *trans* addition of *p*-nitrobenzoyl chloride and monochloroacetyl chloride to 2-butyne and to 1-phenyl-1-butyne.

There remains still a problem in explaining why the addition of benzoyl chloride and acetyl chloride to 1 - phenyl - 1 - butyne does not lead to 100% *trans* adduct, as there is already 87 and 75% *trans* addition with 3-hexyne.

This can be interpreted by assuming that the vinyl cation stabilized by an α-phenyl group will be more free of interaction with the β-carbonyl group so that *cis*-attack on the empty p-orbital could be possible. This bears some resemblance to the different percentages of *cis* and *trans* adducts in the bromination of phenyl acetylene (42% *trans*) and 3-hexyne (72% *trans*), where linear vinyl cation and cyclic bromonium ion intermediates[18] have been assumed.

Additional proof for the intermediacy of a vinyl cation is obtained by the occurence of a 1,2-methyl shift[19] in the addition of 3,5-dimethoxybenzoyl chloride to 4,4-dimethyl-2-pentyne (Scheme 2); the



SCHEME 2. (X = OSO_2CF_3).

yield of **37** (R = MeO) was 5 to 10% of that of **36** (R = MeO). In the addition of benzoyl triflate to 4,4 - dimethyl - 2 - pentyne, three β-ketovinyl triflates have been obtained: **33** (19%), **34** (22%) and **35** (14%). The relative positions of the t-butyl and the methyl in **34** could be determined by the trifluoromethane sulfonic acid catalyzed cyclization to the compound **17** (R = H), by refluxing in dichloroethane.

The *cis* and *trans* structure of the β-ketovinyl triflates was assigned on the basis of the observed solvent shifts in the NMR spectrum[8] (Table 4).

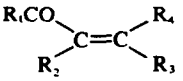
Apart from the β-ketovinyl triflates, three cyclization products have been obtained: the indenones **36** (R = H) (13%) and **41** (8%), and trace amounts of the compound **37** (R = H). The relative positions of the methyl and the t-butyl in the indenones **36** (R = H) and **41** have been secured by the NMR solvent shifts.

It must be mentioned that apart from the triflates and indenones still other unidentifiable products are formed probably through the intermediate carbocations.

EXPERIMENTAL

All acetylenic compounds used in this study were commercial products except for 1 - phenyl - 1 - butyne, 1 -

Table 4. NMR data of β-chlorovinyl ketones and β-ketovinyl triflates



X = OSO_2CF_3

No	R_1	R_2	R_3	R_4	Isomer	δ-Values[b] R_1	R_2	R_3	R_4	Δ-Values[c] R_2	R_3	R_4	J[d]
1[a]	Ph	Et	Cl	Et	*trans*		2·52	—	2·20	0·10	—	0·04	
2b[a]	Ph	Et	Et	Cl	*cis*		2·40	2·55	—	0·27	0·38	—	
3	Et	Et	Cl	Et	*trans*	2·56	2·40	—	2·47				
4	Et	Et	Et	Cl	*cis*	2·67	2·28	2·42	—				
5	Me	Et	Cl	Et	*trans*	2·22	2·45	—	2·45	0·15	—	0·07	
6	Me	Et	Et	Cl	*cis*	2·32	2·27	2·44	—	0·41	0·47	—	
7	CH_2Cl	Et	Et	Cl	*cis*	4·43	2·35	2·47	—				
8b[a]	Ph	Me	Cl	Me	*trans*		2·05	—	2·05	0·21	—	0·11	1·5
9b[a]	Ph	Me	Me	Cl	*cis*		1·98	2·25	—	0·39	0·50		1·1
10	Et	Me	Cl	Me	*trans*	2·59	2·02	—	2·25	0·16	—	0·06	1·6
11	Me	Me	Cl	Me	*trans*	2·33	2·04	—	2·33	0·28	—	0·15	1·6
12	CH_2Cl	Me	Cl	Me	*trans*	4·36	2·11	—	2·33	0·31	—	0·17	1·5
13	CH_2Cl	Me	Me	Cl	*cis*	4·50	1·93	2·22	—	0·34	0·41	—	1·1
14	$CHCl_2$	Me	Me	Cl	*cis*		1·82	1·95	—	0·23	0·31	—	1·2
15b[a]	Ph	Et	Cl	Ph	*trans*		2·76						
16b[a]	Ph	Et	Ph	Cl	*cis*		2·42						
17	Et	Et	Cl	Ph	*trans*	1·92	2·60						
18	Et	Et	Ph	Cl	*cis*	2·78	2·25						
19	Me	Et	Cl	Ph	*trans*	1·78	2·65						
20	Me	Et	Ph	Cl	*cis*	2·52	2·30						
21	CH_2Cl	Et	Cl	Ph	*trans*	3·60	2·65						
22	CH_2Cl	Et	Ph	Cl	*cis*	4·06	2·55						
23b[a]	Ph	Me	X	Me	*trans*		1·98	—	2·08	0·37	—	0·26	1·5
24b[a]	Ph	Me	Me	X	*cis*		2·02	2·25	—	0·50	0·47	—	1·1
25	Et	Me	X	Me	*trans*	2·62	2·03	—	2·22	0·38	—	0·25	1·6
26	Et	Me	Me	X	*cis*	2·65	1·90	2·15	—				1·2
27	Me	Me	X	Me	*trans*	2·34	2·05	—	2·28	0·45	—	0·28	1·5
28	Me	Me	Me	X	*cis*	2·37	1·90	2·17	—	0·60	0·57	—	1·1
29	CH_2Cl	Me	X	Me	*trans*	4·30	2·10	—	2·25	0·52	—	0·29	1·6
30	CH_2Cl	Me	Me	X	*cis*	4·34	1·98	—	2·22	0·64	0·60	—	1·1
31	Ph	Et	X	Et	*trans*		2·22	—	2·56				
32	Ph	Et	Et	X	*cis*		2·46	2·61					
33	Ph	Me	X	tBu	*trans*		1·94	—	1·28	0·41	—	0·07	
34	Ph	Me	tBu	X	*cis*		2·38	1·28	—	0·43	0·27	—	
35	Ph	tBu	X	Me	*trans*		1·16	—	2·08	0·14	—	0·21	

[a] The other aryl ketones (a, R_1 = *p*-$MeOC_6H_4$; c, R_1 = *m*-BrC_6H_4; d, R_1 = *m*-$NO_2C_6H_4$; e, R_1 = *p*-$NO_2C_6H_4$) gave nearly the same NMR data.

[b] δ values in ppm relative to TMS in $CDCl_3$ as solvent.

[c] $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$.

[d] Homoallylic coupling constant in cps.

phenyl - 3,3 - dimethyl - 1 - butyne and 4,4 - dimethyl - 2 - pentyne which were synthesized according standard procedures.

The NMR spectra were taken on a Varian A-60 (60 MHz) and on a Varian XL-100 (100 MHz) spectrometer. The gas chromatographic separations were performed on a 6 ft 10% OV-17 column and on a 6 ft carbowax 20 M/TFA 20% column. Preparative TLC separations were performed on silica gel with CCl_4–C_6H_6 (1/1) as eluens.

General procedure for addition of an acid chloride to an acetylene. Acid chloride (0·01 mole) and $AlCl_3$ (0·01 mole) in 25 ml dry dichloromethane were stirred at room temp under N_2 until all the $AlCl_3$ has dissolved. This soln was cooled to −50° and 0·01 mole acetylene derivative, dissolved in 25 ml dry dichloromethane, was added slowly (0·5 h). When all the acetylene was added, the mixture was allowed to warm up to room temp and the $AlCl_3$-complex was decomposed with a mixture of ice-HCl (10%). The organic layer was washed successively with water, $NaHCO_3$ aq and water. After drying on anhy $MgSO_4$ the dichloromethane soln was concentrated under vacuum. If possible the product distribution was determined by an NMR spectrum of this residue, after the pure products had been obtained by chromatographic separations and characterized by NMR. In some cases it was necessary to perform a distillation under vacuum on a "Büchi-Kugelrohr" to eliminate polymeric materials. If the products were stable to gaschromatographic analyses, the product distribution has also been determined by a GLC analysis and checked with the distribution obtained from the NMR analysis. When a GLC analysis was not possible, a preparative TLC separation was performed and the product distribution was obtained through weighing of the fractions.

General procedure for addition of acyltriflates to acetylenes. Silver trifluoromethanesulfonate (3 mmole; 0·75 g) previously dried under vacuum at 60°, was put in a dry reaction vessel under N_2 equipped with a magnetic stirrer and a rubber cap. Through a hypodermic syringe, 2·8 mmole acid chloride and 4 mmole acetylene derivative, dissolved in 50 ml dichloromethane, were added. This suspension was stirred for 0·5 h.

After the AgCl had been filtered off, the soln was washed several times with water, dried ($NaSO_4$) and concentrated under vacuum. Most of the mixtures were purified by TLC on silica gel with benzene as eluent. Product distributions were obtained by weighing of the TLC fractions and by NMR analysis. GLC is not as suitable, as extensive decomposition took place. All β-ketovinyl triflates show the following IR absorptions (CCl_4): 1710 cm^{-1} (aliphatic ketones), 1670 cm^{-1} (aromatic ketones) ($\nu_{C=O}$), 1640 cm^{-1} ($\nu_{C=C}$), 1420 cm^{-1} ($\nu_{as\,SO_2}$), 1220 cm^{-1} ($\nu_{s\,SO_2}$). All indenones show an IR absorption (CCl_4) at 1710 cm^{-1} ($\nu_{C=O}$). Only minor amounts of β-diketones are formed.

Addition of 3,5-dimethoxybenzoyl chloride to 4,4-dimethyl-2-pentyne. $AlCl_3$ (5 mmoles; 0·66 g) was added to a stirred precooled (−30°) soln of acid chloride (5 mmoles; 1·00 g) in 40 ml dry dichloromethane. After 5 min acetylene (10 mmoles; 0·96 g), dissolved in 10 ml dichloromethane, was added. After stirring for 1 h at −30°, the mixture was worked up in the usual way. Apart from selfacylation products of the acid chloride, and polymerization products of the acetylene, **36**, R = MeO (400 mg) and **37**, R = MeO (36 mg) could be isolated after repeated TLC separation on silica gel with CCl_4–C_6H_6 (1/1).

Indenone **36** (R = CH_3O): m.p. 128°; IR (CCl_4): 1710 cm^{-1} ($\nu_{C=O}$), 1620 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$): 1·96 (3p, s, 2-Me), 1·42 (9p, s, 3-tBu), 3·82 and 3·86 (6p, 2xs, 4- and 6-MeO), 6·50 (1p, d, J = 2 cps, 5-H), 6·80 (1p, d, J = 2 cps, 7-H). (Found: C, 73·59; H, 7·71. Calc. for $C_{15}H_{20}O_3$: C, 73·82; H, 7·74%).

Compound **37**: (R = CH_3O); IR (CCl_4): 1645 cm^{-1} ($\nu_{C=O}$), 1630 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$): 2·03 (6p, 2 broadened s, 2- and 3-Me), 1·54 (6p, s, 4-diMe), 3·89 (6p, s, 5- and 7-MeO), 6·68 (1p, d, J = 2·5 cps, 6-H), 7·41 (1p, d, J = 2·5 cps, 8-H). (Found: C, 74·22; H, 7·64. Calc. for $C_{15}H_{20}O_3$: C, 73·82; H, 7·74%).

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