markedly on solvent. To reduce the complexity of these highly approximate calculations, we have taken the value for acetamide (16.7 kcal/mol) as the correction value for substituted urea nitrogens and that for *N*-ethylacetamide (18.0 kcal/mol) as the corresponding value for unsubstituted nitrogens. The results are included in Table IV, and clearly the choice of correction values is hardly critical. Rotational barriers for **2a**–**e** appear to be much too low, and increasing the size of the N-alkyl substituent (**2a** → **2c** → **2f**) apparently increases E_a. In light of the relative constancy of the amide values, this result appears anomalous.

Thus, while ^{15}N chemical shifts may in fact be related to rotational barriers, quantitative evaluations are questionable at best. Direct determination still remains the most reliable method for evaluating rotational barriers.

Acknowledgment. This work was supported by the U.S. Public Health Service, Grant No. GM-21148, from the Division of General Medical Sciences. Additional support was derived from the Research Corporation., Eli Lilly and Co., and from Biomedical Science Support Grant No. RR-07109. We are grateful to Dr. S. Swaminathan and Ms. P. Furst for assistance with the multiple regression analyses used in this work and to Drs. G. Martin and F. Anet for providing preprints of ref 6 prior to publication. We also thank Dr. P. R. Srinivasan for obtaining the spectrum of 1,1-dimethylurea and Mr. K. Crimaldi and Dr. G. Furst for helpful discussions.

Registry No. 1a, 57-13-6; **1b**, 598-50-5; **1c**, 96-31-1; **1d**, 598-94-7; **1e**, 632-14-4; **1f**, 632-22-4; **2a**, 625-52-5; **2b**, 627-06-5; **2c**, 691-60-1; **2d**, 592-31-4; **2e**, 592-17-6; **2f**, 1118-12-3; **2g**, 64-10-8; **2h**, 557-11-9; **3a**, 623-76-7; **3b**, 1792-17-2; **3c**, 102-07-8.

Electrophilic Additions to Acetylenes. 7.[1] Relative Reactivity of Double and Triple Bonds toward Carbenium Ions

Franco Marcuzzi, Giovanni Melloni, and Giorgio Modena*

Centro Meccanismi di Reazioni Organiche del CNR, Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy

Received January 25, 1979

The relative reactivity of pairs of phenyl-substituted alkynes and alkenes toward diphenylmethyl- and 1-phenylethylcarbenium ions, generated in situ by the interaction of the corresponding chlorides with anhydrous zinc chloride in dichloromethane, has been determined by a competition method. Reactivity ratios alkyne/alkene ranging from 0.2 to 3.5 have been found, with the reactions involving *cis*-stilbene as the only exception. This behavior is similar to that previously found for alkyne–alkene pairs in hydration reactions but differs considerably from that of halogenation reactions, where alkenes are more reactive than alkynes by factors of 10^3–10^7. The results are discussed in terms of relative stability of saturated and unsaturated cationic intermediates with respect to the ground-state stability of substrates and, in a broader sense, in terms of relative ability of the various electrophiles to form open or bridged intermediates. The low reactivity of *cis*-stilbene is ascribed to steric factors.

In the previous papers of this series[1–5] we have shown that phenyl- and alkyl-substituted acetylenes may react with alkyl halides under Friedel–Crafts conditions to give 1:1 addition or cyclization products. These reactions were shown to occur via addition of a carbenium ion, generated by interaction of the alkyl halide with a Lewis acid, to the triple bond of the substrate to give a vinyl cation, which in a subsequent fast step is captured either by an external nucleophile present in the reaction medium, e.g., a halide ion, thus leading to the product of 1:1 addition, or by an internal nucleophile, e.g., a phenyl ring in an appropriate position, to give a product of cyclization by an intramolecular Friedel–Crafts reaction. Similar reactions are known or can easily be postulated to occur also with alkenes. We have decided therefore to use these reactions in order to obtain information on the relative reactivity of the two unsaturated systems toward the addition of carbenium ions.

As a matter of fact, the question of the relative reactivity of double and triple bonds toward electrophilic reagents is still open,[6–13] for with electrophiles like the halogens, alkenes are 10^3–10^7 times more reactive than alkynes bearing the same substituents,[9,10,13–17] whereas in hydration (or acid addition) reactions rate ratios close to unity were observed for the two systems.[8,9,18] This clearly indicates

---

(1) F. Marcuzzi and G. Melloni, *J. Chem. Soc., Perkin Trans. 2*, 1517 (1976).

(2) R. Maroni, G. Melloni, and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 2491 (1973).

(3) R. Maroni, G. Melloni, and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 353 (1974).

(4) F. Marcuzzi and G. Melloni, *Gazz. Chim. Ital.*, **105**, 495 (1975).

(5) F. Marcuzzi and G. Melloni, *J. Am. Chem. Soc.*, **98**, 3295 (1976).

(6) P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973). See also: P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, "Vinyl Cations", Academic Press, New York, N.Y., 1979.

(7) (a) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); (b) G. Modena and U. Tonellato, *Chim. Ind. (Milan)*, **56**, 207 (1974).

(8) G. Modena, F. Rivetti, G. Scorrano, and U. Tonellato, *J. Am. Chem. Soc.*, **99**, 3392 (1977).

(9) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H. W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973).

(10) G. Olah and T. R. Hockswender, Jr., *J. Am. Chem. Soc.*, **96**, 3574 (1974).

(11) G. H. Schmid, A. Modro, and K. Yates, *J. Org. Chem.*, **42**, 2021 (1977).

(12) M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **42**, 2689 (1977).

(13) G. Modena, F. Rivetti, and U. Tonellato, *J. Org. Chem.*, **43**, 1521 (1978).

(14) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

(15) J. M. Kornprobst and J. E. Dubois, *Tetrahedron Lett.*, 2203 (1974).

(16) J. M. Kornprobst, X. Q. Huynh, and J. E. Dubois, *J. Chim. Phys. Phys.-Chim. Biol.*, 71, 1126 (1974).

(17) M. F. Ruasse and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 1977 (1975); *Tetrahedron Lett.*, 4555 (1975).

Table I. Results of the Competition Reactions

substrates	no.	phenylalkyl chloride	reagent ratio[a]	reactivity ratio[b]
PhC≡CH/PhCH=CH_2	**1/4**	7	1:1:1[c]	0.26
			1:5:5[c]	0.21
PhC≡CMe/*trans*-PhCH=CHMe	**2/5a**	7	1:5:5	0.5
			1:9:4.5	0.4
PhC≡CMe/*cis*-PhCH=CHMe	**2/5b**	7	1:2:2	3.5
			1:3.7:5.5	3.4
PhC≡CPh/*trans*-PhCH=CHPh	**3/6a**	7	1:5:5	3.2
			1:5:10	3.0
PhC≡CPh/*cis*-PhCH=CHPh	**3/6b**	7	1:5:5	*d*
			1:1.2:11.3	$\geqslant 300$[e]
PhC≡CH/PhC≡CMe	**1/2**	7	1:4.9:4.9	ca. 6
			1:15.4:3.5	5.0
PhC≡CMe/PhC≡CPh	**2/3**	7	1:3.75:3.75	ca. 10
			1:3:9	10.8
PhC≡CH/*trans*-PhCH=CHPh	**1/6a**	8	1:4:8	2.2
PhC≡CH/*cis*-PhCH=CHPh	**1/6b**	8	1:2:8	8.3
PhC≡CH/PhC≡CPh	**1/3**	8	1:2.5:5	0.9

[a] Ratio alkyl chloride/alkyne/alkene (approximate figures). [b] Ratio alkyne/alkene. [c] In the presence of *n*-$Bu_4N^+Cl^-$. [d] Products of addition to alkene not detectable. [e] Products of addition to alkene formed at the estimated limit of detection in the ^{1}H NMR spectrum of the mixture (ca. 3%).

that the reactivity ratio depends very much upon the nature of the electrophile; also, different transition states or different intermediates are possibly involved in apparently similar reactions. It follows that the evaluation of reactivity ratios for an electrophile completely different from those investigated so far to this purpose may shed light on the problem.

Direct measurements of reaction rates, however, are quite difficult and scarcely reliable in reacting systems like the one described here, as they are generally difficult for Friedel–Crafts reactions. We decided therefore to carry on this work by measuring the reactivity ratios with a competition method. Although the precision of this method may not be very high in principle, the first results obtained[19] proved to be well reproducible. We give here a full report of our results, which indicate that phenyl-substituted alkynes and alkenes are roughly equally reactive toward the addition of carbenium ions.

Results

The relative reactivities of 1-phenylalkynes **1**–**3** and of

PhC≡CR_1
1, R_1 = H
2, R_1 = Me
3, R_1 = Ph

PhCH=CHR_1
4, R_1 = H
5a, R_1 = Me, trans
b, R_1 = Me, cis
6a, R_1 = Ph, trans
b, R_1 = Ph, cis

the corresponding 1-phenylalkenes **4**–**6** toward diphenylmethyl- and 1-phenylethylcarbenium ions were determined by allowing cognate pairs of substrates **1**–**6** to react with a deficiency of diphenylmethyl chloride (**7**) and 1-phenylethyl chloride (**8**), respectively, and then determining the ratio between the products formed from each substrate.

The conditions used for the competition experiments were those of our previous work,[1-5] i.e., boiling dichloromethane as a solvent and anhydrous zinc chloride as a catalyst; the latter was used in the molar ratio of ca. 1:10 with respect to the alkyl chloride. The ratio between the substrates was chosen, on the basis of preliminary experiments, in order to have a product ratio between 3:1 and 1:3 and, consequently, minimize errors in the measurements. Excess between three- and tenfold of unsaturated substrates with respect to the alkyl chloride was used in most cases. No significant variation of the reactivity ratio with the reagent ratio was noticed.

The progress of the reaction was qualitatively followed by TLC. The reaction was interrupted when most of the alkyl chloride was consumed. Workup consisted of removal of the catalyst by filtration, evaporation of the solvent, and chromatography of the residue on a silica gel column in order to separate the unreacted substrates from the products. Care was taken also to obtain the mixture of products free from decomposition or polymerization materials, which were, however, formed in very small amount except in the case of styrene (**4**) (see below). The mixture was then analyzed by ^{1}H NMR and the molar ratio of the products determined by integration. This ratio was then corrected for the initial ratio of substrates to give the actual reactivity ratio.

The competition reactions, wherever possible, were carried out with pairs of alkynes and alkenes bearing identical substituents. In some cases this was precluded by the almost complete superimposition of the signals of the products in the NMR spectrum, which made integration impossible. This was the case of the competitions of diphenylacetylene (**3**) and stilbenes (**6**) toward **8**, where phenylacetylene (**1**) had to be used as a reference. With both chlorides **7** and **8** cross experiments were also carried out with pairs of alkynes in order to correlate the reactivity of all the substrates taken into consideration. In no case were products of isomerization or interaction between the unsaturated substrates detected.

The results of the competition experiments are reported in Table I.

Identification of the Reaction Products. This study required careful characterization of all the products formed from each single substrate. This was done independently for all the substrates used and under the same conditions of the competition reactions. For simplicity a 1:1 ratio of reagents (alkyl chloride to alkyne or alkene) was used in most cases. Under these conditions the overall yields, ranging from 75 to 85% except in the case of styrene, were not as high as a quantitative study would require. However, on the basis of previous results and by some independent experiments it was ascertained that with an excess of the unsaturated substrate, i.e., under the conditions of the competition reactions, yields were increased up to 90–95%.

---

(18) D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, **90**, 1020, 1023 (1968).

(19) F. Marcuzzi and G. Melloni, *Tetrahedron Lett.*, 2771 (1975).

Table II. Addition of Phenylalkyl Chlorides 7 and 8 to Alkynes 1-3 (Eq 1)

alkyne (R_1)	phenylalkyl chloride (R_2)	time, h	products (yield, %): 1:1 addition	products (yield, %): indene	products (yield, %): alkyl-substituted indene
1 (H)	7 (Ph)	3^a	9 (76)	none	none
1 (H)	8 (Me)	10^a	10 (86)	none	none
2 (Me)	7 (Ph)	3^b	11 (56.5)	13 (27.5)	none
3 (Ph)	7 (Ph)	4^a	none	14 (15)	16 (32)
		2^b	none	14 (53)	16 (22)
3 (Ph)	8 (Me)	12^a	12 (trace)	15 (60)	17 (15)

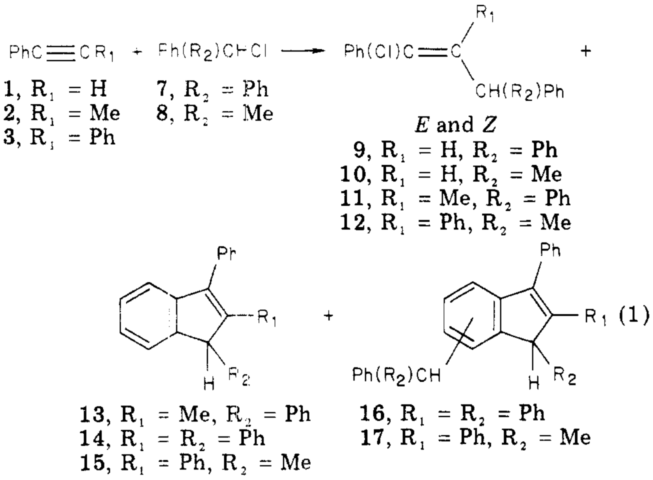
[a] Reagent ratio 1:1. [b] Reagent ratio 5:1 (alkyne/phenylalkyl chloride).

Table III. Addition of Phenylalkyl Chlorides 7 and 8 to Alkenes 5 and 6 (Eq 2)

alkene (R_1)	phenylalkyl chloride (R_2)	time, h	products (yield, %)
5a (Me)	7 (Ph)	25^a	18 (70)
5b (Me)	7 (Ph)	30^a	18 (73)
6a (Ph)	7 (Ph)	10^b	19 (84)
6a (Ph)	8 (Me)	18^a	20 (75)
6b (Ph)	7 (Ph)	96^a	19 (75)
6b (Ph)	8 (Me)	41^a	20 (81)

[a] Reagent ratio 1:1. [b] Reagent ratio 0.8:1 (6a:7).

The results of the addition of 7 and 8 to alkynes 1–3 following the general eq 1 are reported in Table II.



1, R_1 = H
2, R_1 = Me
3, R_1 = Ph

7, R_2 = Ph
8, R_2 = Me

E and *Z*
9, R_1 = H, R_2 = Ph
10, R_1 = H, R_2 = Me
11, R_1 = Me, R_2 = Ph
12, R_1 = Ph, R_2 = Me

(1)

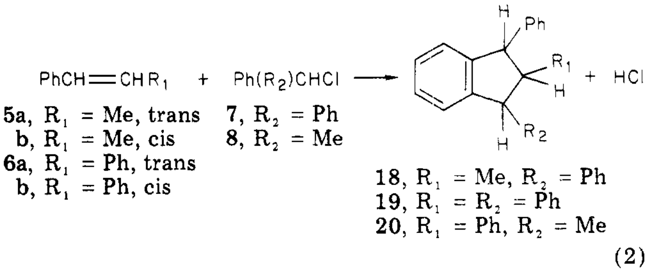
13, R_1 = Me, R_2 = Ph
14, R_1 = R_2 = Ph
15, R_1 = Ph, R_2 = Me

16, R_1 = R_2 = Ph
17, R_1 = Ph, R_2 = Me

Compounds 9, 14, and 16 were known from previous work.[2,3] 1,3-Diphenyl-2-methylindene (13) and 2,3-diphenyl-1-methylindene (15) were identified by comparison with authentic products prepared as reported in the literature.[20,21] The structure of the 1:1 addition products 10 and 11 was established on the basis of the ^{1}H NMR spectrum, from which the *E*:*Z* ratios were also evaluated. Full characterization of 12 was not possible owing to the small amount formed and to the difficulty of separation from 15. Indenes 16 and 17 were shown to be formed by a subsequent reaction of 7 and 8 with 14 and 15, respectively, as previously observed.[3] The position of the phenylalkyl residues in 16 and 17 was not established. No reaction of this kind was observed in the addition of 7 to 1-phenylpropyne (2), in which indene 13 was formed. The latter proved to be unreactive toward 7 even under conditions more forcing than those of the addition reaction.

All the above reaction products were stable to the reaction conditions. In the addition reactions in which cyclization to indene derivatives occurred some hydrogen chloride was formed, as required by the stoichiometry of the reaction. Products of addition of this to alkynes 2 and 3 were detected but were not taken into account owing to their small amount.

The results of the addition of 7 and 8 to alkenes **5a,b** and **6a,b** following the general eq 2 are reported in Table III.



5a, R_1 = Me, trans
b, R_1 = Me, cis
6a, R_1 = Ph, trans
b, R_1 = Ph, cis

7, R_2 = Ph
8, R_2 = Me

18, R_1 = Me, R_2 = Ph
19, R_1 = R_2 = Ph
20, R_1 = Ph, R_2 = Me

(2)

No linear 1:1 addition product of the two reagents was formed. The amount of products of addition of hydrogen chloride to 5 and 6 was negligible. Indans 18–20 were identified by comparison with authentic samples prepared by reduction with hydriodic acid and red phosphorus of the corresponding indenes 13–15, respectively. As reported in Table III, in all three cases only one geometrical isomer was formed from both cis and trans alkenes 5 and 6 with both chlorides 7 and 8. On the basis of their ^{1}H NMR spectra and by comparison with all the possible geometrical isomers synthesized independently[22] the *E,E* configuration was assigned to 1,3-diphenyl-2-methylindan 18 and to 1,2,3-triphenylindan 19. By analogy, the same configuration was tentatively assigned also to 2,3-diphenyl-1-methylindan 20. Indans 18–20 were stable to the reaction conditions.

The addition of diphenylmethyl chloride (7) to styrene (4) afforded 1-chloro-1,3,3-triphenylpropane (21) as the 1:1 addition product of the two reagents, together with some 1,3,3-triphenylprop-1-ene (22), of unknown configuration (eq 3).

$$\underset{4}{\mathrm{PhCH{=}CH_2}} + 7 \rightarrow \underset{21}{\mathrm{Ph(Cl)CHCH_2CHPh_2}} + \underset{22}{\mathrm{PhCH{=}CHCHPh_2}} \quad (3)$$

Compounds 21 and 22 were identified on the basis of their ^{1}H NMR spectrum and also by comparison with authentic samples prepared from 1,3,3-triphenylpropan-2-ol.[23] The alkene 22 was shown by independent experiments to be not a primary product of the addition reaction but a product of protiodechlorination of 21 both under the reaction conditions and, mostly, during the workup. Both products 21 and 22, and also styrene (4), were somewhat unstable to the reaction conditions. In fact, under the conditions described above only a 25% yield of

---

(20) C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 1493 (1933).

(21) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943); K. R. Huffman and E. F. Ullman, *ibid.*, **89**, 5629 (1967).

(22) A full account of the synthesis and of the determination of configuration of all the isomeric indans corresponding to structures **18** and **19** will be given in a forthcoming publication.

(23) B. J. Burckhalter and S. H. Johnson, *J. Am. Chem. Soc.*, **73**, 4830 (1951).

Table IV. Relative Reactivities of Alkynes and Alkenes in Electrophilic Additions[a]

	hydration or acid addn		bromination[b]		addn of RSCl
substrates	k_{alkyne}/k_{alkene}	conditions	k_{alkyne}/k_{alkene}	solvent	k_{alkyne}/k_{alkene}
PhC≡CH/PhCH=CH$_2$	1.6–2.2[c]	38–56% aq H_2SO_4	3.85×10^{-4} [e]	CH_3CO_2H	5.4×10^{-3} [e,k]
	1.54[d]	48.7% aq H_2SO_4	7.7×10^{-4} [g,h]	MeOH	
	1.54[e]	47% aq H_2SO_4 [f]	6.7×10^{-4} [g,h]	50% MeOH	
	1.25[c]	0.8 M CF_3CO_2H/CCl_4	2.8×10^{-3} [g,h]	H_2O	
p-MeC$_6$H$_4$C≡CH/p-MeC$_6$H$_4$CH=CH$_2$	2.5–3.2[c]	23–38% aq H_2SO_4	3.1×10^{-4} [g,h]	MeOH	
PhC≡CMe/*trans*-PhCH=CHMe	6.7×10^{-1} [e]	48.7% aq H_2SO_4	2.0×10^{-4} [e]	CH_3CO_2H	7.1×10^{-2} [e,k]
PhC≡CMe/*cis*-PhCH=CHMe			2.76×10^{-4} [e]	CH_3CO_2H	1.9×10^{-1} [e,k]
n-BuC≡CH/*n*-BuCH=CH$_2$	2.8×10^{-1} [e]	48.7% aq H_2SO_4	5.49×10^{-6} [e]	CH_3CO_2H	1.2×10^{-2} [e,k]
	1.9×10^{-1} [i,j]	CF_3CO_2H at 60 °C	2.44×10^{-4} [g,h,j]	MeOH	
			5.9×10^{-7} [g,h,j]	H_2O	
EtC≡CEt/*trans*-EtCH=CHEt	6.0×10^{-2} [e]	48.7% aq H_2SO_4	2.98×10^{-6} [e]	CH_3CO_2H	6.7×10^{-1} [e,k]
	3.8×10^{-1} [i]	CF_3CO_2H at 60 °C			
EtC≡CEt/*cis*-EtCH=CHEt	7.2×10^{-2} [e]	48.7% aq H_2SO_4	2.69×10^{-6} [e]	CH_3CO_2H	7.1×10^{-2} [e,k]
			1.28×10^{-5} [g,h]	MeOH	

[a] At 25 °C unless otherwise indicated. [b] Most widely investigated halogenation reaction. [c] From ref 8. [d] From ref 18. [e] From ref 9; see also ref 14 for bromination. [f] 3% MeOH added. [g] From ref 15-17. [h] From ref 13. [i] From ref 39. [j] 1-Pentene was used as a reference compound instead of 1-hexene. [k] p-Chlorobenzenesulfenyl chloride in tetrachloroethane.

21 and 22 could be obtained. Correspondingly, a quite large amount of polymerization products was formed. In order to reduce the polymerization to a minimum we carried out the addition reaction in the presence of tetra-*n*-butylammonium chloride. This did not completely prevent polymerization of styrene but permitted a 62% yield of 21 and 22 to be obtained, with only a small amount of the latter. These conditions were therefore used also in the competition reactions in which styrene was involved. The addition of 8 to styrene was also attempted; the extensive polymerization observed prevented the use of this reaction in the competition experiments.

Discussion

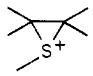
The results reported in Table I show that the reactivities of alkynes 1–3 and alkenes 4–6 toward phenylalkylcarbenium ions are, in general, of the same order of magnitude. The reactivity ratios between pairs of similarly substituted substrates range, in fact, between 0.2 and 3.5, with the exception of the reactions involving *cis*-stilbene, which will be discussed later. These small values compare very well with those reported in Table IV for the relative reactivities of alkynes and alkenes toward the proton but differ significantly from those of the same substrates toward halogens. The relative reactivities toward sulfenyl halides are similar to, though somewhat greater than, those of halogen addition.

The most important aspect of the results of this work is that the behavior of the proton in these addition reactions is no longer a special one, for which a rationale might be found in its unique properties. As a matter of fact, any rationale must explain why both proton and carbenium ions behave in one way and the halogens in a different one. It is our opinion, already advanced in previous papers,[7,13] that an answer to this problem can be found only if due account is given to the fact that the cationic intermediates may have either open or bridged structures and that the relative energies of the two valence tautomers depend on the electrophile (bridging atom or group) and on the structure of the substrates, either acetylenic or ethylenic.

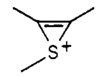
First, it must be recalled that bridged saturated chloronium and bromonium ions (A) have been observed, though under special conditions,[24,25] whereas the unsaturated analogues B have resisted any attempt of detection. On the other hand thiiranium (C) and thiirenium (D) ions have both been characterized, even though the former are definitively more stable than the latter.

A

B

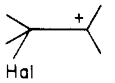


C

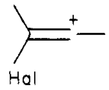


D

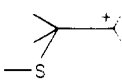
Second, extended theoretical calculations with ab initio methods indicate that A,[28] C,[29] and D[30] lie in energy minima while B[31] does not and that they may be either less or more stable than their valence tautomers, the open cations E–H, which represent other minima in the potential energy surfaces.[32] Calculations also show that the relative energies of bridged and open pairs are such that the bridging is more stabilizing (or less destabilizing) in the saturated than in the unsaturated series.



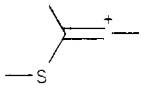
E



F

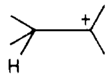


G

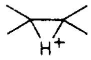


H

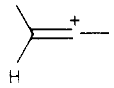
The outcome of theoretical studies on open and bridged ions I–L with hydrogen as a bridging atom is rather different.[33,34] In both saturated and unsaturated series either



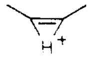
I



J



K



L

---

(24) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Org. Chem.*, **37**, 1169 (1972); G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 3387 (1973); G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *ibid.*, **96**, 3565 (1974), and references cited therein.

(25) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Am. Chem. Soc.*, **90**, 2587 (1968); R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *ibid.*, **99**, 5964 (1977), and references cited therein.

(26) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964); P. Raynolds, S. Zonnebelt, S. Bakker, and R. M. Kellogg, *J. Am. Chem. Soc.*, **96**, 3146 (1974); G. Capozzi, O. De Lucchi, V. Lucchini, and G. Modena, *Tetrahedron Lett.*, 2603 (1975).

(27) G. Capozzi, O. De Lucchi, V. Lucchini, and G. Modena, *J. Chem. Soc., Chem. Commun.*, 248 (1975); G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin, *Tetrahedron Lett.*, 911 (1977).

(28) A. Dargelos, D. Liotard, and M. Chaillet, *Tetrahedron*, **28**, 5595 (1972); A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **38**, 21 (1975), and references cited therein; *ibid.*, **44**, 385 (1977).

(29) Y. Kikuzono, T. Yamabe, S. Nagata, H. Kato, and K. Fukui, *Tetrahedron*, **30**, 2197 (1974); J. W. Gordon, G. H. Schmid, and I. G. Csizmadia, *J. Chem. Soc., Perkin Trans. 2*, 1722 (1975), and references cited therein.

(30) I. G. Csizmadia, F. Bernardi, V. Lucchini, and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, 542 (1977), and references cited therein.

(31) V. Lucchini, G. Modena, and I. G. Csizmadia, *Gazz. Chim. Ital.*, **105**, 675 (1975).

(32) Calculations have been carried out only with F and Cl. Although no data are available for Br, the similarity in the chemical behavior of Cl and Br suggests that dramatic changes should not be expected.

valence tautomer was found to be the more stable depending on the basis sets and, more generally, on the calculation method; the energy difference was, however, relatively small, particularly when more sophisticated calculations were made. For carbon as a bridging atom similar results have been reported, though less extensive computational work has been carried out.[34,35]

In conclusion, theoretical and experimental evidence suggests that the relative stability of cyclic and open ions is not much affected by the unsaturation in the case of either hydrogen or carbon as a bridging atom, whereas the unsaturation destabilizes significantly the bridged structure in the case of chlorine or bromine. The case of sulfur lies in between, with the saturated pair favored by the bridging but not as much as for halogens.

On these bases, the relative reactivities of alkynes and alkenes toward electrophiles may be rationalized as follows:

(i) Whenever the transition states for both reactions resemble the open ion or, alternatively, the bridging does not affect significantly the energies of the process, i.e., when open and bridged ions are of similar energy, the two systems show a similar reactivity. This may well be due to a compensation of the intrinsically lower stability of a vinyl cation with respect to a carbenium ion by the higher ground-state energy of the alkyne with respect to the alkene. Of course, the actual reactivity ratios depend on the very structure of the substrate; fluctuations may therefore be expected as it is a "casual" compensation. Larger differences may also be expected if the electrophile is a particle having an intrinsically strong electronic effect,[12,13] which may unbalance the system.

(ii) When the electrophile is a good bridging group, bridged character of the transition states may be expected. This should render the reactivity of the double bond greater than that of the triple bond. From the above discussion the maximum effect by the bridging has to be expected in halogenation reactions, as indeed found.

(iii) The intermediate position of the reactivity ratios for sulfenyl halide additions is likely due to the fact that in both series the bridged ions are relatively stable species, yet in this case alkenes are more favored than alkynes by the bridging.

The above arguments do not take into account differential solvent effects in the two systems. In fact, such an argument has been recently used[9,36] to offer a rationale for the different reactivity ratios of halogenation in nonpolar solvents and hydration in the very polar solvent water. In our opinion such differential effects are not significant; they may just give a minor contribution. First, the solvation energies of carbenium ions are generally small;[37] hence, it does not seem likely to obtain large differences with small numbers. Second, results from these laboratories[8] have shown that the solvation parameters for the acid-catalyzed hydration of pairs of similarly substituted alkynes and alkenes are very similar. Third, and not a negligible argument, is that the competition data reported here for carbenium ion addition refer to a medium of relatively low polarity, yet the reactivity ratios are, as already stated, very similar to those found in hydration reactions.

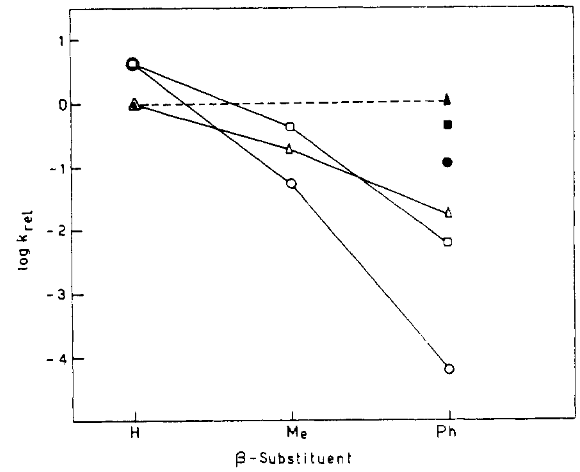


Figure 1. Effect of β-substituents on the rates of addition of Ph_2CHCl (**7**) (open signs, full lines) and PhCH(Me)Cl (**8**) (closed signs, broken line) to alkynes **2** and **3** and alkenes **4–6** relative to phenylacetylene (**1**): triangles, alkynes; squares, *trans*-alkenes; circles, *cis*-alkenes; square in a circle, styrene.

Let us now consider in more detail the effect of the structure on the reactivity of the set of compounds studied. To this purpose the rates relative to that of phenylacetylene with both electrophiles have been calculated from the experimental reactivity ratios and are graphically displayed in Figure 1.

The dominant effect within each series appears to be steric in origin. This can easily be seen in the reactions with diphenylmethyl chloride, where the rates are decreased in both alkyne and alkene series by β substitution, either with a methyl or a phenyl group. The effect is relatively small for alkynes but quite large for alkenes, particularly for the cis isomers. In the last series the retarding factor is quite high and reaches five powers of ten in the case of *cis*-stilbene (**6b**). The remarkably low reactivity of **6b**, even with respect to **6a**, has analogy in the literature in a study on the cationic oligomerization of stilbenes, where it was mainly imputed to steric factors.[38] The reactions with 1-phenylethyl chloride, instead, are much less affected by the crowding at the reaction center, as expected from the smaller size of the electrophile.

The prevalence of steric effects makes difficult the assessment of the role eventually played by polar effects of the β substituents. These should be small, however, as indicated by the reactivity ratio close to unity of alkynes 1 and 3 in the reaction with 1-phenylethyl chloride, where, as discussed above, steric effects are less important. This observation is indeed consistent with the hypothesis, previously advanced, that the transition state for these reactions has an open-ion character.

The intrinsically rather low accuracy of the competition method and the further complications which may arise from the heterogeneous nature of our reactions prevent us from analyzing in more detail the results obtained. Nevertheless, the main features of the relative reactivity of double and triple bonds toward carbenium ions unveiled by this study should be regarded with confidence. As a matter of fact in several instances nearly identical relative rates were obtained with different sets of reagent ratios.

As a conclusion we emphasize once again that the intrinsic reactivity of alkynes toward electrophilic reagents

---

(33) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971); P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972); B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *ibid.*, **21**, 309 (1973); J. Weber, M. Yoshimine, and A. D. McLean, *J. Chem. Phys.*, **64**, 4159 (1976), and references cited therein.

(34) H. Lischka and H.-J. Köhler, *J. Am. Chem. Soc.*, **100**, 5297 (1978), and references cited therein.

(35) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973), and references cited therein.

(36) K. Yates and T. A. Modro, *Acc. Chem. Res.*, **11**, 190 (1978).

(37) V. Lucchini, G. Modena, G. Scorrano, and U. Tonellato, *J. Am. Chem. Soc.*, **99**, 3387 (1977); see also ref 39.

(38) D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, 3563 (1958).

(39) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966), and references cited therein.

Table V. ^{1}H NMR Data for Compounds 9-11 and 13-22 (Eq 1-3)

compd	δ (multiplicity,[a] intensity, J (Hz))
(*E*)-9	4.74 (d, 1 H, J = 11, C=CH), 6.39 (d, 1 H, J = 11, Ph_2CH), 6.95-7.35 (m, 15 H, aromatic)
(*Z*)-9	5.39 (d, 1 H, J = 9.5, C=CH), 6.51 (d, 1 H, J = 9.5, Ph_2CH), 6.90-7.45 (m, 15 H, aromatic)
(*E*)-10	1.21 (d, 3 H, J = 7.3, CH_3), 3.25-3.70 (m, 1 H, PhCH), 6.07 (d, 1 H, J = 10.5, C=CH), 6.50-7.40 (m, 10 H, aromatic)[b]
(*Z*)-10	1.36 (d, 3 H, J = 7, CH_3), 3.40-4.30 (m, 1 H, PhCH) 6.14 (d, 1 H, J = 9.5, C=CH), 6.50-7.40 (m, 10 H, aromatic)[b]
(*E*)-11	1.90 (s, 3 H, CH_3), 5.14 (s, 1 H, Ph_2CH), 7.00-7.40 (m, 15 H, aromatic)[b]
(*Z*)-11	1.57 (s, 3 H, CH_3), 5.93 (s, 1 H, Ph_2CH), 7.00-7.40 (m, 15 H, aromatic)[b]
13	1.87 (s, 3 H, CH_3), 4.32 (s, 1 H, PhCH), 7.00-7.50 (m, 14 H, aromatic)
14	4.95 (s, 1 H, PhCH), 6.90-7.45 (m, 19 H, aromatic)
15	1.26 (d, 3 H, J = 7.3, $CHCH_3$), 3.90 (q, 1 H, J = 7.3, $CHCH_3$), 7.20-7.30 (m, 14 H, aromatic)
16	4.95 (s, 1 H, PhCH), 5.45 (s, 1 H, Ph_2CH), 6.90-7.45 (m, 28 H, aromatic)
17	1.25 (d, 3 H, J = 7.3, $CHCH_3$), 1.65 (d, 3 H, J = 7.0, $PhCHCH_3$), 3.88 (q, 1 H, J = 7.3, $CHCH_3$), 4.16 (q, 1 H, J = 7.0, $PhCHCH_3$), 6.80-7.30 (m, 18 H, aromatic)
(*E*,*E*)-18	1.07 (d, 3 H, J = 7.0, $CHCH_3$), 1.90-2.40 (m, 1 H, $CHCH_3$), 3.76 [d, 2 H, J = 12, PhC(1,3)H], 6.70-7.50 (m, 14 H, aromatic)
(*E*,*E*)-19	3.44 [br t, 1 H, J = ca. 10, PhC(2)H], 4.51 [br d, 2 H, J = ca. 10, PhC(1,3)H], 6.80-7.30 (m, 19 H, aromatic)
(*E*,*E*)-20	1.30 (d, 3 H, J = 7.2, $CHCH_3$), 2.90 [t, 1 H, J = 11.5, PhC(2)H], 3.15-3.60 (m, 1 H, $CHCH_3$), 4.29 [d, 1 H, J = 11.5, PhC(3)H], 6.85-7.30 (m, 14 H, aromatic)
21	2.70 (br t, 2 H, J = ca. 7, $CHCH_2CH$), 4.12 (br t, 1 H, J = ca. 7, Ph_2CHCH_2), 4.55 (br t, 1 H, J = ca. 7, $PhCHCH_2$), 7.00-7.40 (m, 15 H, aromatic)
22	4.81 (br d, 1 H, J = ca. 7, Ph_2CH), 6.10-6.70 (m, 2 H, CH=CH), 7.00-7.40 (m, 15 H, aromatic)

[a] Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. [b] Mixture of the two isomers.

is not much lower than that of similarly substituted alkenes; rather it is quite similar.

Experimental Section

General Procedures. Melting and boiling points are uncorrected. Solvents and starting materials were purified following standard procedures. Phenylacetylene, 1-phenylpropyne, *trans*-1-phenylpropene, *cis*- and *trans*-stilbene, styrene, and diphenylmethyl chloride were commercially available products. Diphenylacetylene,[40] *cis*-1-phenylpropene,[41] and 1-phenylethyl chloride[42] were prepared by literature methods. 1,3,3-Triphenylpropan-1-ol[23] was prepared by reduction of 3,3-diphenylpropiophenone[43] with $LiAlH_4$ in ether. In the column chromatographies (silica gel slurries, 70–230 mesh, Merck) petroleum ether, bp 40–70 °C, was used. Proton magnetic resonance (^{1}H NMR) spectra were recorded in CCl_4 solution with Me_4Si as an internal standard on a Perkin-Elmer Model R 12 60-MHz spectrometer and in some cases on a Bruker Model HFX 90-MHz high-resolution spectrometer. The NMR data for all the reaction products are collected in Table V.

Competition Reactions. A typical run was as follows. To a suspension of powdered anhydrous zinc chloride (0.5 mmol) in a solution of the chosen pair of unsaturated substrates (25 mmol of each) in anhydrous dichloromethane (60 mL) a solution of the appropriate phenylalkyl chloride (5 mmol) in the same solvent (20 mL) was added dropwise, with stirring, at room temperature. After a few minutes the mixture was refluxed until no phenylalkyl chloride could be detected by TLC (1–10 h). After cooling, the mixture was filtered through a 20 mm thick layer of dry silica gel, and the solvent was evaporated to give a dark residue, which was column chromatographed. Elution with petroleum ether gave the mixture of unreacted unsaturated substrates. Further elution with appropriate mixtures of petroleum ether and benzene afforded the mixture of addition products, which was then analyzed by ^{1}H NMR.

The competition reactions of phenylacetylene (**1**) and styrene (**4**) toward diphenylmethyl chloride (**7**) were carried out in the presence of tetra-*n*-butylammonium chloride (see Results). The reaction conditions were identical with those described above, except for the reagent ratio, which was as follows: **1**, 24.5 mmol; **4**, 24.5 mmol; **7**, 5.0 mmol; zinc chloride, 2.9 mmol; $n\text{-}Bu_4N^+Cl^-$, 2.1 mmol.

The results of the competition reactions are reported in Table I.

Addition of Diphenylmethyl Chloride (7) to Phenylacetylene (1), 1-Phenylpropyne (2), and Diphenylacetylene (3). A typical run was as follows. To a suspension of anhydrous zinc chloride (0.14 g, 1 mmol) in a solution of the appropriate alkyne (10 mmol) in dichloromethane (30 mL) at room temperature was added a solution of **7** (2.03 g, 10 mmol) in the same solvent (10 mL). After a few minutes of stirring at room temperature the mixture was refluxed for ca. 3 h. After cooling, the mixture was filtered and the solvent was evaporated to give a brownish residue, which was chromatographed. Elution with petroleum ether gave first some unreacted alkyne.

In the addition to phenylacetylene (**1**) further elution with petroleum ether–benzene (9:1) afforded a mixture of (*E*)- and (*Z*)-1-chloro-1,3,3-triphenylprop-1-ene (**9**) in the ratio of 9:1 (*E*:*Z*), which were recognized as previously reported.[2]

In the addition to 1-phenylpropyne (**2**) further elution with petroleum ether–benzene (9:1) afforded a mixture of (*E*)- and (*Z*)-1-chloro-2-methyl-1,3,3-triphenylprop-1-ene (**11**) in the ratio of ca. 19:1 (*E*:*Z*) and of 1,3-diphenyl-2-methylindene (**13**), which were partially separated by fractional recrystallization from ethanol. The mixture of the isomeric **11**, mp 128–133 °C (from ethanol), was identified on the basis of its analytical and NMR data.

Anal. Calcd for $C_{22}H_{19}Cl$: C, 82.87; H, 6.01; Cl, 11.12. Found: C, 82.89; H, 6.03; Cl, 11.00.

1,3-Diphenyl-2-methylindene (**13**), mp 111 °C (from ethanol) (lit.[20] mp 108 °C), was identified by comparison with an authentic sample prepared by the literature method.

In the addition to diphenylacetylene (**3**) elution with petroleum ether–benzene (6:1) afforded 1,2,3-triphenylindene (**14**), mp 135–136 °C (from ethanol). Further elution with petroleum ether–benzene (3:1) gave diphenylmethyl-1,2,3-triphenylindene (**16**), mp 165–166 °C (from absolute ethanol). Indenes **14** and **16** were recognized as previously reported.[3]

The results of these addition reactions are reported in Table II.

Addition of 1-Phenylethyl Chloride (8) to Phenylacetylene (1) and Diphenylacetylene (3). These reactions were carried out as described for the corresponding addition of chloride **7**.

In the addition to phenylacetylene (**1**) the chromatography of the brown reaction residue, with petroleum ether as eluent, gave first some unreacted **1**. Further elution with petroleum ether–benzene (9:1) afforded a mixture of (*E*)- and (*Z*)-1-chloro-1,3-diphenylbut-1-ene (**10**) in the ratio of 4.8:1 (*E*:*Z*) (colorless oil), which was purified by distillation in vacuo, bp 230–237 °C (10^{-4} torr). The two isomeric compounds **10** could not be satisfactorily separated by adsorption chromatography and were therefore identified on the basis of the analytical and NMR data of their mixture.

Anal. Calcd for $C_{16}H_{15}Cl$: C, 79.16; H, 6.23; Cl, 14.61. Found: C, 79.12; H, 6.13; Cl, 14.62.

---

[40] L. F. Fieser, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 606.

[41] M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963).

[42] A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 694 (1911).

[43] P. R. Shildneck, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 236.

In the addition to diphenylacetylene (**3**) the chromatography of the residue, with petroleum ether–benzene (8:1) as eluent, afforded 2,3-diphenyl-1-methylindene (**15**), mp 106–107 °C (from ethanol) (lit.[21] mp 106.5 °C), which was identified by comparison with an authentic sample prepared by the literature method. Further elution with petroleum ether–benzene (6:1) afforded 2,3-diphenyl-1-methyl-(1-phenylethyl)indene (**17**), mp 112–113 °C (from ethanol).

Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.29; H, 6.78.

Indene **17** was identified by comparison with a sample prepared in 90% yield by reaction of chloride **8** (5 mmol) with indene **15** (5 mmol) in boiling dichloromethane (30 mL) in the presence of zinc chloride (0.5 mmol) for 1 h.

In the NMR spectrum of the mother liquor of recrystallization of indene **15** signals of very low intensity at δ 1.32 (d) and 4.98 (q) were detected, which did not belong to compounds **15** and **17** and could indicate the presence of a small amount of (*E*)- or (*Z*)-1-chloro-1,2,3-triphenylbut-1-ene (**12**), i.e., the product of 1:1 addition of **8** to **3**. This could not be obtained in pure form and was therefore not characterized.

The results of these addition reactions are reported in Table II.

Addition of Diphenylmethyl Chloride (7) to *cis*- and *trans*-1-Phenylpropene (5a,b) and *cis*- and *trans*-Stilbene (6a,b). The procedure described for the corresponding addition to alkynes was followed.

In the addition to the 1-phenylpropenes **5a,b** the chromatography of the reaction mixtures, with petroleum ether–benzene (9:1) as eluent, afforded in both cases (*E,E*)-1,3-diphenyl-2-methylindan (**18**), mp 91–92 °C, which was recrystallized from ethanol and identified by comparison with a sample synthesized independently (vide infra).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.77; H, 7.06.

In the addition to the stilbenes **6a,b** the chromatography of the reaction mixtures, with petroleum ether–benzene (3:1) as eluent, afforded in both cases (*E,E*)-1,2,3-triphenylindan (**19**), mp 125–126 °C, which was recrystallized from ethanol and identified by comparison with a sample synthesized independently.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.63; H, 6.35.

Synthesis of (*E,E*)-1,3-Diphenyl-2-methylindan (18). The procedure described by Kohler and Mydans[45] for the reduction of 1,2,3-triphenylindene was followed. A suspension of indene **13** (0.4 g, 1.4 mmol) and red phosphorus (0.44 g) in 57% hydriodic acid (5 mL) was refluxed for 46 h under nitrogen. After cooling, the mixture was diluted with water and extracted with ether. The ether solution was washed with aqueous sodium thiosulfate and dried ($CaCl_2$). Evaporation of the solvent gave a solid residue which was chromatographed. Elution with petroleum ether–benzene (9:1) gave **18** (0.28 g, 70%), which was recrystallized from ethanol; mp 91–92 °C.

Synthesis of (*E,E*)-1,2,3-Triphenylindan (19). The procedure described for indan **18** was followed, using 1.45 g (4.2 mmol) of indene **14** and 0.47 g of red phosphorus in 10 mL of 57% hydriodic acid. The chromatography of the reaction residue, with petroleum ether–benzene (3:1) as eluent, afforded **19** (1.08 g, 74%), which was recrystallized from ethanol; mp 125–126 °C.

Contrary to the report of the authors cited,[45] no evidence for the formation of an isomer of 1,2,3-triphenylindan having mp 154 °C was obtained.

Addition of 1-Phenylethyl Chloride (8) to *cis*- and *trans*-Stilbenes 6a,b. The usual procedure was followed. The chromatography of the reaction mixtures, with petroleum ether–benzene (9:1) as eluent, gave in both cases 2,3-diphenyl-1-methylindan (**20**), which was recrystallized from ethanol; mp 81–82 °C.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.69; H, 7.06.

Indan **20** was recognized by comparison with a sample synthesized independently by the usual procedure, i.e., by reduction of indene **15** (1.0 g, 3.5 mmol) with red phosphorus (1.1 g) in 7 mL of hydriodic acid. There was obtained 0.66 g (66%) of **20**, to which the (*E,E*) configuration was tentatively assigned by analogy with indans **18** and **19**.

Addition of Diphenylmethyl Chloride (7) to Styrene (4). To a suspension of anhydrous zinc chloride (0.44 g, 3.2 mmol) in a solution of n-$Bu_4N^+Cl^-$ (0.64 g, 2.3 mmol) in dichloromethane (20 mL) at room temperature was added a solution of **7** (1.1 g, 5.4 mmol) and **4** (2.8 g, 27 mmol) in the same solvent (30 mL). The mixture was refluxed for 6 h, cooled, and filtered through a layer of dry silica gel. Evaporation of the solvent afforded a dark green residue, which was chromatographed. Elution with petroleum ether gave first the unreacted **4**. Further elution with petroleum ether–benzene (9:1) afforded a mixture of 1-chloro-1,3,3-triphenylpropane (**21**) (0.9 g, 54%) and 1,3,3-triphenylprop-1-ene (**22**) (0.12 g, 8%).

Separation of compounds **21** and **22** could not be satisfactorily achieved by fractional recrystallization owing to the instability of **21**. Attempts to obtain separation by column chromatography led to further transformation of **21** into **22**. They were therefore identified on the basis of the NMR spectrum of their mixture and by comparison with the spectrum of authentic samples synthesized independently.

The synthesis of **21** was performed by treatment of 1,3,3-triphenylpropan-1-ol with excess thionyl chloride in refluxing ether for 6 h. The crude product (56% yield) was purified by recrystallization from petroleum ether containing a few drops of benzene; mp 90–91 °C.

Anal. Calcd for $C_{21}H_{19}Cl$: C, 82.20; H, 6.24; Cl, 11.56. Found: C, 82.48; H, 6.44; Cl, 11.33.

The synthesis of **22** was performed following the procedure of the literature,[23] i.e., by dehydration of 1,3,3-triphenylpropan-1-ol with 20% aqueous sulfuric acid. The crude product (87% yield) was purified by recrystallization from ethanol; mp 97–98 °C (lit.[23] mp 98–99 °C). The configuration of **22** was not established.

Acknowledgments. The assistance of Mr. Roberto Salmaso in recording the high-resolution ^1H NMR spectra is gratefully acknowledged.

Registry No. **1**, 536-74-3; **2**, 673-32-5; **3**, 501-65-5; **4**, 100-42-5; **5a**, 873-66-5; **5b**, 766-90-5; **6a**, 103-30-0; **6b**, 645-49-8; **7**, 90-99-3; **8**, 672-65-1; (*E*)-**9**, 51117-48-7; (*Z*)-**9**, 51117-51-2; (*E*)-**10**, 70550-39-9; (*Z*)-**10**, 70550-40-2; (*E*)-**11**, 70550-41-3; (*Z*)-**11**, 70550-42-4; (*E*)-**12**, 70550-43-5; (*Z*)-**12**, 70550-44-6; **13**, 51310-26-0; **14**, 38274-35-0; **15**, 51310-25-9; **16**, 52589-09-0; **17**, 70550-62-8; (*E,E*)-**18**, 70550-45-7; (*E,E*)-**19**, 70550-46-8; (*E,E*)-**20**, 70550-47-9; **21**, 70550-48-0; **22**, 5424-75-9; p-$MeC_6H_4C{\equiv}CH$, 766-97-2; p-$MeC_6H_4CH{=}CH_2$, 622-97-9; n-$BuC{\equiv}CH$, 693-02-7; n-$BuCH{=}CH_2$, 592-41-6; $EtC{\equiv}CEt$, 928-49-4; *trans*-$EtCH{=}CHEt$, 13269-52-8; *cis*-$EtCH{=}CHEt$, 7642-09-3; 1,3,3-triphenylpropan-1-ol, 70550-49-1.

---

(44) M. Vaillant, *Ann. Chim.* (*Paris*), **9**, 5 (1954); J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, **27**, 4187 (1962); L. L. Miller and R. F. Boyer, *J. Am. Chem. Soc.*, **93**, 650 (1971), and references cited therein.

(45) E. P. Kohler and W. E. Mydans, *J. Am. Chem. Soc.*, **54**, 4667 (1932).