Anal. Calcd for $C_{12}H_{14}N_2O_5$: C, 54.13; H, 5.30; N, 10.52. Found: C, 53.69; H, 5.19; N, 10.54.

Dimethyl 3-(*p*-Methoxyphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) in 2 mL of acetonitrile and 0.12 mL (1 mmol) of *p*-methoxystyrene were stirred overnight at 25 °C. The solvent was removed under vacuum and subsequent recrystallization from diethyl ether/pentane produced 0.12 g (39%) of cyclobutane: mp 56–58 °C; NMR ($CDCl_3$) 7.4–6.8 (dd, 4 H), 4.7–4.3 (dd, J = 8, 11 Hz, 1 H), 3.9, 3.85, 3.80 (3 s, 9 H), 3.4–2.5 (m, AB, 2 H); mass spectrum, m/e 328, 208, 184, 134 (BP), 119, 113. Anal. Calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.91; N, 8.53. Found: C, 62.06; H, 4.86; N, 8.53.

Dimethyl 3-(*p*-Methylphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) and 0.13 mL (1 mmol) of *p*-methylstyrene were stirred in 2 mL of acetonitrile overnight at 25 °C. Removal of the solvent left an orange oil, to which a vacuum was applied to remove excess styrene. The oil was dissolved in diethyl ether and placed at −60 °C, whereupon the solution separated into two layers. The ether was decanted off and the oil again placed under vacuum: yield 0.17 g (54%); NMR δ 7.2–6.9 (m, 4 H), 4.8–4.4 (m, 1 H), 3.9 (2 s, 6 H), 3.6–3.0 (m, 2 H), 2.4 (s, 3 H). Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 66.17; H, 5.14; N, 9.02.

Dimethyl 3-Phenyl-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) and 0.12 mL (1 mmol) of styrene were allowed to react in 2 mL of acetonitrile at 25 °C for 18 h. After removal of solvent and excess styrene under vacuum, recrystallization from ether/pentane gave 0.10 g (33%) of cyclobutane: mp 41–43 °C; NMR ($CDCl_3$) δ 7.2 (Ar, 5 H), 4.7 (m, 1 H), 3.8 (2 s, 6 H), 3.5–3.2 (m, 2 H); Mass spectrum, m/e 298 (molecular ion), calcd m/e 298, 178, 154, 72. Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.77; H, 4.71; N, 9.30.

Note Added in Proof: After this manuscript had been accepted, it came to our attention that the analogous compound diethyl 1,1-dicyanoethene-2,2-dicarboxylate had been synthesized on two occasions (Regan, T. H. *J. Org. Chem.* **1962**, *27*, 2236; Kociolek, K.; Lephawy, M. T. *Synthesis* **1977**, 778). The former utilized the same synthesis as ours, namely, the condensation of an oxomalonic ester with malononitrile.

Also, ethyl 1,1-dicyanoethene-2-carboxylate has been described (Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 295; Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 301.

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Registry No. 1, 82849-49-8; 1-styrene copolymer, 82849-60-3; 1-ethyl vinyl ether copolymer, 82849-61-4; 1-*p*-methylstyrene copolymer, 82849-62-5; MDA, 82849-50-1; dimethyl oxomalonate, 3298-40-6; dimethyl 3-ethoxy-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-51-2; dimethyl 3-(*p*-methoxyphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-52-3; dimethyl 3-(*p*-methylphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-53-4; dimethyl 3-phenyl-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-54-5; malononitrile, 109-77-3; styrene, 100-42-5; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4; ethyl vinyl ether, 109-92-2; isobutyl vinyl ether, 109-53-5; methyl glyoxylate, 922-68-9; dimethyl 3-isobutoxy-2,2-dicyano-1,1-dicarboxylate, 82849-59-0.

Notes

Vinyl Cations in Organic Synthesis. A New Route to Disubstituted Alkynes

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Disubstituted alkynes are usually prepared by elimination or substitution reactions.[1] However, these methods suffer structural and/or regiochemical limitations, which makes alternative procedures desirable. New interesting synthetic routes have been proposed, through vinyl selenoxides,[2] nitrimines,[3] β-oxo sulfones,[4] [(methylthio)-methyl]lithium derivatives of carboxylic acids,[5] β-keto sulfones,[6] and diketones.[7] Starting materials and experimental procedures, however, are not always simple and involve, in any case, more than one step.

Our interest in the chemistry of vinyl cations[8] prompted us to investigate the feasibility of a new synthetic approach to disubstituted alkynes through such intermediates. Electrophilic additions of carbenium ions to triple bonds are well-known reactions: depending on the characteristics of the system and on the experimental conditions, different products can be obtained, deriving from addition and/or addition–elimination routes.[9] In particular, the latter can provide a simple way to transform 1-alkynes into disubstituted alkynes.

We report here the preliminary results of our study.

Results and Discussion

Phenylacetylene (1) was allowed to react in boiling dichloromethane with a series of diphenylmethyl sulfonic esters **2a–c**, prepared in situ by the reaction of di-

(1) (a) Kobrich, G.; Buck, P.; Ziegenbein, W. "Chemistry of Acetylenes"; Viehe, H. G., Ed., Marcel Dekker: New York, 1969; Part II, p 99. (b) Jäger, V.; Viehe, H. G. "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1977; Band V/2a, p 1.
(2) Reich, H. J.; William, W. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5967.
(3) Büchi, G.; Wüest, H. *J. Org. Chem.* **1979**, *44*, 4116.
(4) Lythgoe, B.; Waterhouse, J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2429.
(5) Kano, S.; Yokomatsu, T.; Shibuya, S. *J. Org. Chem.* **1978**, *43*, 4366.
(6) Bartlett, P. A.; Green, F. R., III; Rose, E. H. *J. Am. Chem. Soc.* **1978**, *100*, 4852.
(7) Bauer, D. P.; Macomber, R. S. *J. Org. Chem.* **1976**, *41*, 2640.
(8) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979, and references therein.
(9) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 249.

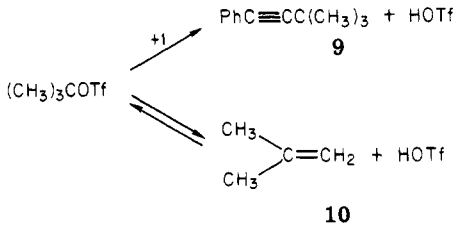
0022-3263/82/1947-4577$01.25/0

Table I. Reactions of Alkynes 1 and 11 with Sulfonic Esters 2a-c and 8

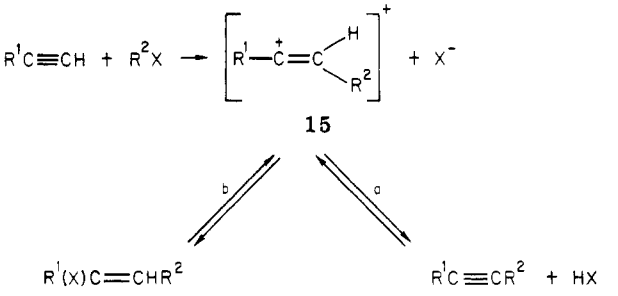
reactants, mmol		rctn time, h	products (isolated yield, %)		
$R^1C{\equiv}CH$	R^2X		$R^1C{\equiv}CR^2$	$R^1(X)C{=}CHR^2$	$R^1COCH_2R^2$
1 (5.0)	2a (5.0)	15	3 (10.8)	4a (28.5)	5 (22.3)
1 (5.0)	2a (5.0)	15[a]	3 (36.8)	4a (trace)	5 (8.9)
1 (25.0)	2a (5.0)	15	3 (67.8)	4a (trace)	5 (17.6)[b]
1 (5.0)	2a (5.0)	15[c]	3 (25.0)	4a (21.5)	5 (20.1)
1 (5.0)	2a (5.0)	15[d]	3 (42.5)	4a (4.6)	5 (9.1)
1 (15.0)	2b (15.0)	10[e]	3 (9.0)	4b (46.0)	5 (4.0)
1 (12.5)	2c (5.0)	7	3 (73.0)		5 (17.0)[f]
1 (25.0)	2c (5.0)	15	3 (72.3)		5 (9.0)[f]
1 (25.0)	8 (5.0)	15	9 (6.7)		
11 (10.0)	2a (5.0)	4	12 (14.5)		13 (4.5)[g]

[a] Experiment carried out by adding *very slowly* diphenylmethyl chloride to the reaction mixture. Consistent amounts of 6a and 7 were also isolated among the reaction products. [b] Consistent amounts of 6a and 7 also isolated. [c] In the presence of 5.0 mmol of *cis*-stilbene, which was recovered almost completely isomerized to the trans form at the end of the reaction. [d] In the presence of 5.0 mmol of cyclohexene oxide. 1,2-Cyclohexanediol and picric acid were also identified among the reaction products. [e] From ref 9. [f] Consistent amount of 7 also isolated. [g] Small amount (ca. 7.6%) of 14 also isolated.

Scheme I



Scheme II



phenylmethyl chloride with the silver salts of the corresponding acids[10] (eq 1).

$$\underset{1}{PhC{\equiv}CH} + Ph_2CHX \xrightarrow{CH_2Cl_2} \underset{\substack{2a,\ X=OTNBS\\ b,\ X=OTs\\ c,\ X=OTf}}{} \underset{3}{PhC{\equiv}CCHPh_2} + \underset{\substack{4a,\ X=OTNBS\\ b,\ X=OTs}}{Ph(X)C{=}CHCHPh_2} + \underset{5}{PhCOCH_2CHPh_2} + \underset{\substack{6a,\ X=OTNBS\\ b,\ X=OTs}}{Ph(X)C{=}CH_2} + \underset{7}{PhCOCH_3} + HX \quad (1)$$

The reaction was tested under a variety of conditions (see Table I), obtaining in every case a mixture of products, whose composition depends on several factors; among them the nucleophilicity of the acid anion appears to play a major role: the highest yield of disubstituted alkyne 3 (73%) was obtained with the poorest nucleophile, the triflate anion.

The presence in the system of acid scavengers, such as cyclohexene oxide[11] or *cis*-stilbene, which shows a rather low reactivity toward carbenium ions,[12] increased somewhat the yield of 3, whereas more traditional bases (e.g., amines or sodium carbonate) as well as solvents of higher ionizing power (e.g., nitromethane) were not particularly useful. These reaction mixtures were rather complex and the yields of disubstituted alkyne poor. Therefore, such systems were not further investigated.

The ratio of the reagents is critical. In the case of trinitrobenzenesulfonate 2a, with a 5:1 molar excess of 1 over 2a, a significant increase of the yields of 3 and adduct 6a was obtained; meanwhile the yield of 4a sharply decreased.

Moreover, with the triflate 2c, smaller excess (2.5:1) of phenylacetylene and even shorter reaction times were required to obtain almost the same result.

As an extension of the above reactions, *tert*-butyl triflate (8) was allowed to react with 1. The reaction was slow, even in the presence of a large excess (5:1) of alkyne, and the desired product 9 was obtained in low yield. Probably, under these conditions, the competitive elimination reaction to isobutene (10) becomes predominant (Scheme I).

The reaction of 1-hexyne (11) with 2a (molar ratio 2:1) afforded a complex mixture of products; among them were identified disubstituted alkyne 12, ketone 13, and adduct 14 (eq 2).

$$\underset{11}{C_4H_9C{\equiv}CH} + 2a \longrightarrow \underset{12}{C_4H_9C{\equiv}CCHPh_2} + \underset{13}{C_4H_9COCH_2CHPh_2} + \underset{14}{C_4H_9(TNBSO)C{=}CH_2} \quad (2)$$

The formation of the observed products can be rationalized in terms of a common vinyl cation intermediate 15 (Scheme II), which can either lose a proton (route a) or coordinate the nucleophile X^- (route b) to give the primary reaction products, namely, disubstituted alkynes 3, 9, and 12, and/or adducts 4a,b. Obviously, the properties of X^- and HX (e.g., the nucleophilicity of X^- and, perhaps, the solubility of the sulfonic acids HX in the reaction medium) play an important role in determining the product distribution. Scheme II can also explain the formation of the secondary products, namely, vinyl esters 6a,b and 14, which arise from the addition of the acids HX to the unreacted 1-alkynes. The other secondary products, e.g., ketones 5, 7, and 13, likely derive from hydrolysis or thermal decomposition of the rather unstable vinyl sulfonates during the workup or, to a small extent, even in the course of the reaction. The effect of bases other than X^- in the system, namely, cyclohexene oxide, *cis*-stilbene,

(10) Abbreviations used are as follows: OTNBS, trinitrobenzenesulfonate; OTs, *p*-toluenesulfonate; OTf, CF_3SO_3.
(11) Calò, V.; Lopez, L.; Valentino, D. S. *Synthesis* **1978**, 139.
(12) Marcuzzi, F.; Melloni, G.; Modena, G. *J. Org. Chem.* **1979**, *44*, 3022.

Table II. Physical and Spectral Data for Compounds 4a, 6a, 12, 13, and 14

compd	mp, °C	IR, cm^{-1}	^1H NMR, δ	elemental analysis found, %	elemental analysis calcd, %
4a[a]	124–126 dec (CH_2Cl_2/*n*-pentane)	1550, 1345 (vs, NO_2) 1400, 1200 (vs, OSO_2)	8.17 (s, 2 H, arom), 7.90–6.75 (m, 15 H, arom), 6.23 (d, 1 H, C=CH, J = 11 Hz), 5.39 (d, 1 H, Ph_2CH, J = 11 Hz)	C 57.86 H 3.22 N 7.35 S 5.71	C 57.75 N 3.38 N 7.48 S 5.70
6a	118–120 dec (CH_2Cl_2/*n*-pentane)	1560, 1360 (vs, NO_2) 1410, 1210 (vs, OSO_2)	8.63 (s, 2 H, aromatic), 7.83–6.66 (m, 5 H, aromatic), 5.62 and 5.37 (AB q, 2 H, $C=CH_2$, J_{AB} = 4 Hz)	C 42.27 H 2.26 N 10.55 S 8.38	C 42.53 H 2.28 N 10.63 S 8.10
12	high boiling, pale yellow liquid	2210 (vw, C≡C)	7.41–6.97 (m, 10 H, arom), 4.95 (t, 1 H, $C{\equiv}CCHPh_2$, J = 2.2 Hz), 2.26 (m, 2 H, $C{\equiv}CCH_2$), 1.42 (m, 4 H, $CH_2(CH_2)_2CH_3$), 0.91 (m, 3 H, CH_3)	C 91.4 H 8.1	C 91.8 H 8.1
13	high boiling, pale yellow liquid	1710 (vs, C=O)	7.90–6.74 (m, 10 H, arom), 4.60 (t, 1 H, Ph_2CH, J = 7.3 Hz), 3.14 (d, 2 H, $COCH_2$, J = 7.3 Hz), 2.31 (m, 2 H, RCH_2CO), 1.43 (m, 4 H, $CH_2(CH_2)_2CH_3$), 0.87 (m, 3 H, CH_3)	C 85.0 H 7.95	C 85.6 H 8.3
14	109–111 dec (CH_2Cl_2/*n*-pentane)	1550, 1345 (vs, NO_2) 1380, 1200 (vs, OSO_2)	8.66 (s, 2 H, arom), 5.04 and 4.93 (AB q, 2 H, $C=CH_2$, J_{AB} = 3.5, J_{BCH_2} = 1.1, $J_{ACH_2} \approx 0$ Hz), 2.48 (m, 2 H, $C=CCH_2$), 1.48 (m, 4 H, $CH_2(CH_2)_2CH_3$), 0.92 (m, 3 H, CH_3)	C 38.0 H 3.5 N 10.8 S 9.0	C 38.4 H 3.5 N 11.2 S 8.5

[a] The *E* configuration is suggested on the basis of the ^1H NMR data by comparison with compounds of similar structure.[9,15,16]

and the excess of the starting 1-alkyne itself, which are more or less able to act selectively as proton scavengers, is also consistent with the proposed reaction scheme.

The above results suggest that direct alkylation of terminal alkynes, in particular arylacetylenes, under electrophilic conditions is a viable path, even though further experiments are needed in order to define scope and limitations of the reaction and its merits in comparison with alternative routes.

Experimental Section

Phenylacetylene, 1-hexyne, *cis*-stilbene, diphenylmethyl chloride and silver triflate were commercial products. Cyclohexene oxide and silver 2,4,6-trinitrobenzenesulfonate were prepared according to liaterature methods.[13,14] Melting points are uncorrected. ^1H NMR spectra were taken at 60 MHz on Varian EM 360 A or Brucker-Spectrospin WP 60 spectrometers, using $CDCl_3$ as a solvent; chemical shifts are given in δ relative to Me_4Si as internal standard. IR spectra were recorded (KBr pellets or liquid films) on a Perkin-Elmer 457 spectrometer.

General Procedure. A solution of the alkyl or phenylalkyl chloride (R^2Cl) in anhydrous dichloromethane (30 mL) was added dropwise to a stirred suspension of the appropriate silve salt (AgX, equimolar amounts with respect to R^2 Cl) in a solution of the 1-alkyne ($R^1C{\equiv}CH$) in the same solvent (35 mL), at room temperature.

The reaction mixture was refluxed for the time indicated in Table I, and the products that were insoluble in CH_2Cl_2 (AgCl and the sulfonic acid HX) were filtered off.

The dichloromethane solution was concentrated under reduced pressure, and sulfonates **4a,b**, **6a,b**, and **14** were fractionally preciptated by slow addition of anhydrous *n*-pentane at 0 °C.

After filtration of the sulfonates, the solution was evaporated and the residue was chromatographed on silica gel. Elution with light petroleum yielded alkynes **3**, **9**, and **12**; further elution with light petroleum containing 3–5% diethyl ether afforded the ketones **5**, **7**, and **13**.

In this procedure, stirring and rate of addition of the chloride R^2Cl are critical. In one experiment, performed with a very low rate of addition of diphenylmethyl chloride to equimolar amounts of silver 2,4,6-trinitrobenzenesulfonate and phenylacetylene in dichloromethane, the product distribution changed significantly (see Table I).

The reaction products **3**, **4b**, **5**, **6b**, **9**, and **7** were identified by comparison with authentic samples prepared by literature methods.[9] Physical and spectral data for the new compounds isolated are reported in Table II.

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Registry No. **1**, 536-74-3; **2a**, 51117-47-6; **2b**, 5435-24-5; **2c**, 82951-42-6; **3**, 5467-43-6; **4a**, 82963-10-8; **4b**, 51117-52-3; **5**, 606-86-0; **6a**, 82951-43-7; **8**, 82951-44-8; **11**, 693-02-7; **12**, 82951-47-1; **13**, 82951-45-9; **14**, 82951-46-0; silver 2,4,6-trinitrobenzenesulfonate, 18681-53-3; silver tosylate, 16836-95-6; silver triflate, 2923-28-6; *tert*-butyl chloride, 507-20-0; diphenylmethyl chloride, 90-99-3.

(13) Swern, D. "Organic Peroxides"; Wiley: New York, 1971; Vol. 2, p 355.
(14) Pettitt, D. J.; Helmkamp, G. K. *J. Org. Chem.* **1964**, *29*, 2702.
(15) Capozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc. C* **1970**, 2617.
(16) Eckes, L.; Hanack, M. *Chem. Ber.* **1978**, *111*, 1253.

Conformational Studies by Dynamic Nuclear Magnetic Resonance. 23.[1] Stereodynamics of Cyclic Sulfinylhydrazines

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Restricted rotation about the NN bond can be detected by NMR in molecules where conjugative effects produce partial double bond character. Compounds of the general formula $R_2NN{=}X$ frequently display slow NN rotation, owing to the contribution of structures of the type $R_2N^+{=}N{-}X^-$.

(1) Part 22: Lunazzi, L.; Macciantelli, D.; Spinelli, D.; Consiglio, G., *J. Org. Chem.* **1982**, *47*, 3759.

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