of triethylamine in 100 mL of dry THF was cooled with an ice-water bath, whereupon 1.354 g (6 mmol) of *N*-[(chlorocarbonyl)oxy]phthalimide was added. Stirring was continued at 5 °C for 15 min and further at room temperature for 3 h. Triethylamine hydrochloride precipitated and was removed by filtration and washed thoroughly with THF. The combined filtrates were evaporated under reduced pressure to give 2.01 g (95%) of DPC as a slightly yellow solid. On recrystallization from dry ethyl acetate, it gave 1.78 g (84%) of colorless granular crystals, which showed no clear melting point. It began to lose weight at 153 °C in thermogravimetry in air (5 °C/min): ^{1}H NMR ($CDCl_3$) δ 7.70–8.00 (m, Ar H); IR (KBr) 1740, 1790, 1850 (C=O) cm^{-1}.

Anal. Calcd for $C_{17}H_8N_2O_7$: C, 57.96; H, 2.30; N, 7.95. Found: C, 57.41; H, 2.20; N, 7.93.

Reaction of DPC with *N*-Carbobenzoxy Amino Acids. A typical example is as follows. *N*-(Carbobenzoxy)-L-proline (1.247 g, 5 mmol) was dissolved in 20 mL of dry THF, and 1.762 g (5 mmol) of DPC and a drop of triethylamine were added to the solution. The reaction mixture became a clear solution after about 4 h of stirring. The reaction was discontinued after 20 h. The solvent was evaporated under reduced pressure to give a pale-yellow oil. It was dissolved in chloroform, washed consecutively with an aqueous sodium bicarbonate solution and water, and then dried over sodium sulfate. After removal of chloroform, 1.94 g (98%) of the product was obtained as a colorless oil, which, on standing at room temperature, crystallized. It was recrystallized from ethyl acetate/petroleum ether to give 1.75 g (89%) of white granular crystals: mp 104–106 °C (lit.[7] mp 109 °C); $[\alpha]^{22}_D$ −82.1° (*c* 1.0, acetic acid) (lit.[7] $[\alpha]^{22}_D$ −81.9°); IR (KBr) 1690, 1740, 1790, 1810 (C=O) cm^{-1}.

Registry No. 1, 524-38-9; 2, 15263-19-1; DPC, 78816-91-8; *N*-hydroxyphthalimide benzoate, 58585-84-5; *N*-hydroxyphthalimide acetate, 17720-64-8; *N*-(carbobenzyloxy)-L-proline, 1148-11-4; *N*-(carbobenzoyloxy)-L-phenylalanine, 1161-13-3; *N*-(carbobenzoyloxy)-L-leucine, 2018-66-8; hydroxyphthalimide *N*-(carbobenzyloxy)prolinate, 83025-91-6; hydroxyphthalimide *N*-(carbobenzyloxy)phenylalanate, 83025-92-7; hydroxyphthalimide *N*-(carbobenzyloxy)leucinate, 83025-93-8.

Addition of Electrogenerated Cyanomethyl Anions to Fluorenone and Its Schiff Bases. Indirect Evidence of the Formation of an Unstable Cyclopropyl Cyanide Derivative as a Key Intermediate

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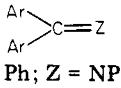
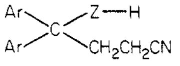
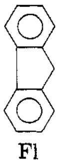
In a previous publication on the electroreductive cyclopropylcarbonylation in acetonitrile (MeCN) of fluorenone and of the Schiff bases 1 and 2, we have reported the unexpected formation of the nitrile derivatives 4–6 as minor compounds.[1]



1, Ar = Ph; Z = NPh
2, Ar_2 = Fl; Z = NPh
3, Ar_2 = Fl; Z = NPh-*p*-Cl

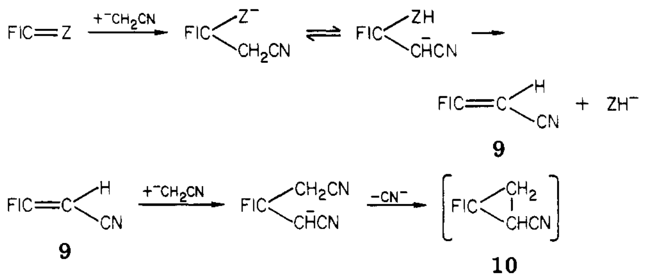


4, Ar_2 = Fl; Z = O
5, Ar = Ph; Z = NPh
6, Ar_2 = Fl; Z = NPh



Fl

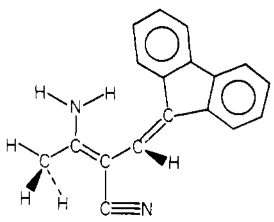
Scheme I[a]



[a] Z = O, NPh, NPh-*p*-Cl; for Fl, see structure 1–6.

To explain these results, we have suggested a mechanism in which a reductive cleavage of an intermediate acrylonitrile occurs (Scheme VI of ref 1).

We now report new results that have been obtained by adding electrogenerated $^-CH_2CN$ anions to fluorenone and its Schiff bases 2 and 3. The conjugated 3-aminoacrylonitrile (*E*)-7 is the major compound isolated from all experiments.



(*E*)-7

It is suggested that nucleophilic additions of CH_2CN to fluorenone and its Schiff bases 2 and 3 lead to an unstable key intermediate, 10, which is further transformed to (*E*)-7. Taking into account the results and their interpretation, we reconsider the origin of the nitrile derivatives 4–6 isolated by the experimental conditions of ref 1.

Results and Discussion

Cyanomethyl anions have been electrogenerated by two ways:[2–7] (1) A strong base, such as an aromatic ketone radical anion or the azobenzene dianion, is electrogenerated in MeCN, from which it abstracts a proton;[2–6] (2) a reductive cleavage of cyanomethyl derivatives is performed in DMF.[4–7] Prior to this work, the addition of electrogenerated CH_2CN^- to aromatic carbonyl groups has been reported for a series of aromatic aldehydes and ketones, including benzophenone,[2–5] the formation of 3-substituted glutaronitriles has been observed in several cases.

Under our experimental conditions, azobenzene (2×10^{-3} M) is reduced to its dianion in MeCN. After consumption of 2 F, one of the substrates (10^{-3} M) is added to the catholyte. The mixture is allowed to stand for 3 h. The compounds contained in the catholyte are then isolated.

Besides traces of unidentified nitrile derivatives and a mixture of azo- and hydrazobenzene, a major cyano com-

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(1) G. Belot, C. Degrand, and P. L. Compagnon, *J. Org. Chem.*, **47**, 325 (1982).

(2) E. M. Abbot, A. J. Bellamy, and J. Kerr, *J. Chem. Ind.*, 828 (1974).

(3) A. J. Bellamy, *J. Chem. Soc., Chem. Commun.*, 944 (1975).

(4) A. J. Bellamy, G. Howat, and I. S. Mackirdy, *J. Chem. Soc., Perkin Trans. 2*, 786 (1978).

(5) W. J. M. Van tilborg, C. J. Smit, and J. J. Scheele, *Tetrahedron Lett.*, 2113 (1977).

(6) K. G. Boto and F. G. Thomas, *Aust. J. Chem.*, **26**, 1251 (1973).

(7) A. J. Bellamy and I. S. Mackirdy, *J. Chem. Soc., Perkin Trans. 2*, 1093 (1981).

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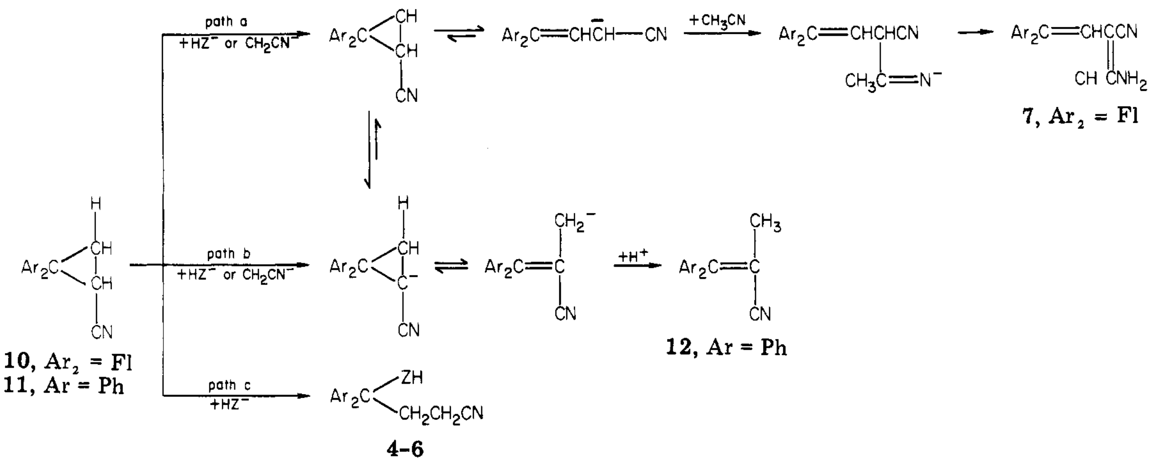
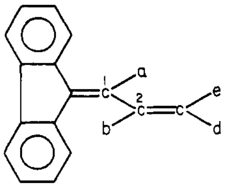
Scheme II^a



^{a} Z = O, NPh, NPh-*p*-Cl; for Fl, see structures **1-6**.

pound corresponding to (*E*)-**7** is obtained. In the case of the anil **3** *p*-chloroaniline is also isolated.

The stereochemistry of (*E*)-**7** has been assigned from spectroscopic data, which lead to a compound of type **8**. The IR spectrum shows the typical pattern of 3-aminoacrylonitrile derivatives:[8] a NH_2 stretching (3450, 3341 cm^{-1}) and a NH band (3240 cm^{-1}); a specially low frequency of a C≡N band at 2185 cm^{-1}; two very strong bands (1626, 1611 cm^{-1}) due to a NH_2 deformation; and a disymmetrical conjugated C=N or C=C stretching. The UV data present similitudes with those of 1-(9-fluorenylidene)-3-phenyl-2-propene;[9] however, a lower hyperchromic effect likely reflects a poor conjugation due to a steric strain and to a twisting of the C(1)–C(2) bond of **8**. The NMR spectrum presents a massif of aromatic protons whose aspect does not present the characteristic deshielding of the substituted fluorene **8** (a = CN). It shows also an amino group and a deshielded methyl group coupled with a vinylic H (J = 1 Hz). A priori, this low coupling constant can suggest a cis ^4J for b and d in **8**; however, it is inconsistent with the IR spectrum, particularly the C≡N stretching. This coupling is better explained through a ^5J between a (a = H) and d (d = CH_3) in **8**. It is shown in structure (*E*)-**7**.



8, a, b, d, e = H, CH_4, CN, NH_2

The origin of (*E*)-**7** may be explained if the intermediate formation of an unstable cyclopropyl derivative, **10**, is considered, according to Scheme I. The nitrile **10** would result from a substituted glutaronitrile anion via a cyclizing elimination. In Scheme I, all the anions ZH^- and CN^- are poor leaving groups; their ability decreases in the order $CN^- > HO^- > ArNH^-$. However, *p*-chloroaniline has been isolated in the case of the anil **3**. Moreover, acrylonitrile analogues of **9** have been also considered as intermediates by Bellamy and his co-workers[2-4] in reactions that implicate HO^- as the leaving group.

As shown in Scheme II, the unstable key intermediate **10**, or its analogue **11** in the case of benzophenone, may undergo different attacks, followed by molecular rearrangements. An attack by a base, such as ZH^- or CH_2CN on H at C-3 (path a), gives an anion that, through a nucleophilic addition on a solvent molecule, leads to (*E*)-**7** in the case of **10**.

A similar attack of **10** or **11** on H at C-1 (path b) should yield acrylonitrile derivatives. From this point of view, a thorough reinvestigation of the byproducts obtained in ref 1 has been performed. In the case of experiment 5 (electroreduction of benzophenone anil in MeCN), we have isolated traces (≤2%) of the acrylonitrile **12**.[10]

Path c of Scheme II corresponds to a nucleophilic attack by ZH^- on C-2 of the key intermediate. It leads to the butyronitriles **4–6** described in ref 1.

Experimental Section

Anils **2** and **3** are prepared according to ref 11. MeCN of analytical grade is carefully dried on neutral alumina. An Amel-552 potentiostat and a Tacussel-IG5-N integrator are used. Solutions of 0.36 g of azobenzene (2 mmol) were electrolyzed under argon atmosphere at −2.0 V vs. SCE (mercury pool cathode; Bu_4NPF_6 0.1 M as supporting electrolyte). After consumption of 2 F, the substrate (1 mmol) is added to the catholyte. The mixture is allowed to stand under argon atmosphere for 3 h. The compounds contained in the catholyte are then isolated according to the procedure described in ref 12 and purified by column chromatography with acetone–hexane (30:70) as eluant.

(*E*)-1-(9′-Fluorenylidene)-2-cyano-3-amino-2-butene (7): Greenish yellow crystals; mp 189 °C (chloroform–hexane); IR (KBr) 3450, 3341, 3240 (primary amino and imino groups), 2185 ($NC{=}CC{\equiv}N^-$), 1626 and 1611 (NH_2 deformation and disymmetric conjugated C=C or C=N stretching), 1544, 1426, 774, 730 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (d, J = 1 Hz, 3 H, CH_3), 4.80 (br s, 2 H, exchangeable by D_2O, NH_2), 6.88 (broad signal, 1 H, vinylic H; at 100 MHz, with scale extension: quadruplet, which becomes a fine singlet by irradiation of the Me group), 7.2–7.5 (massif, 4 H, fluorenyl H); mass spectrum, *m/e* (relative intensity) 258 (100, $M^{+}\cdot$), 243 (48, M − CH_3), 241 (72, M − 2 − CH_3), 216 (32, 243 − HCN), 214 (29, 241 − HCN), 189 (63, 216 − HCN), 187 (21, 214

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[8] S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961).

[9] UV λ_{max} 242 nm (log ϵ 4.66), 262 (4.47), 272 (4.35), 376 (4.66). "UV Atlas of Inorganic Compounds", Vol. II, Butterworth, London, 1966–1971; p E 7/4.

[10] **2-Methyl-3,3-diphenylacrylonitrile** [lit.: W. Chodkiewicz, P. Cadiot, and A. Willemart, *Bull. Soc. Chim. Fr.*, 1586 (1958)], which we have determined the spectral properties: IR (KBr) 2217 (conjugated CN), 1600 cm^{-1}; NMR ($CDCl_3$) δ 2.10 (s, 3 H), 7.0–7.5 (m, 10 H, aromatic H); mass spectrum, *m/e* (relative intensity) 219 (100, $M^{+}\cdot$), 218 (47), 204 (40, M − CH_3), 192 (25, M − HCN), 191 (36, M − 1 − HCN), 167 (58), 166 (30), 165 (86, fluorenyl cation), 164 (30), 152 (30, biphenylene cation), 140 (27), 115 (40), 77 (53).

[11] G. Reddelien, *Ber. Dtsch. Chem. Ges.*, **43**, 2479 (1910).

[12] C. Degrand, P. L. Compagnon, G. Belot, and D. Jacquin, *J. Org. Chem.*, **45**, 1189 (1980).

– HCN), 165 (33, fluorenyl cation), 163 (21), 149 (18); UV (95% EtOH) λ_{max} 207 nm (log ϵ 4.45), 239 (4.58), 255 (4.40), 376 (4.36). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.84; H, 5.43; N, 10.73.

Registry No. 2, 10183-82-1; **3**, 5455-00-5; (*E*)-**7**, 83026-87-3; MeCN, 75-05-8; fluorenone, 486-25-9.

Silicon-Substituted Cyclopropylcarbinyl Cations

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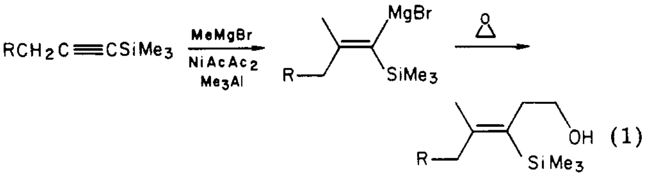
The electrophilic substitution of allyl- and vinylsilanes has proven to be a useful synthetic method.[2] We set out to explore the use of vinylsilanes as terminating groups for cation–olefin cyclizations.[3] The nickel-catalyzed addition of MeMgBr to alkynylsilanes which we have recently reported[4] leads directly to the fully substituted vinylsilane **1** (eq 1) with control of double bond stereochemistry.



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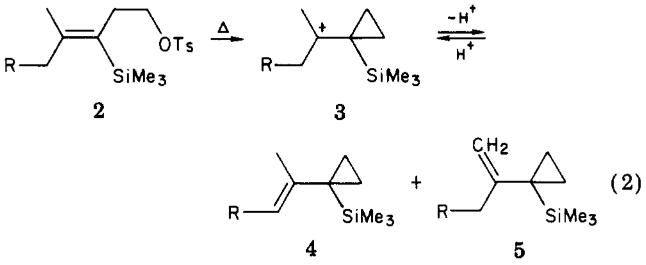
Unfortunately, treatment of the sodium salt of Hagemann's ester with the tosylate **2a** gave none of the desired alkylation product, even though the procedure used[5] led to a high yield of product when similar homoallylic bromides, which lacked the trimethylsilyl group, were used as alkylating agents.[6,7] Analysis of the reaction mixture indicated that **2a** had reacted to give a mixture of **4a** and **5a** (eq 2).



a, R = C_5H_{11}; b, R = H

Solvolysis of the tosylate **2a** in refluxing *tert*-butyl alcohol for 12 h gives the cyclopropylsilane **4a** in ca. 70% yield.[8] If this solvolysis is carried out in the presence of an excess of sodium *tert*-butoxide, a 1.6:1 mixture of **4a** and **5a** is obtained in 57% yield.[8] Solvolysis of **2a** gives the cyclopropylcarbinyl cation[9] **3a** which loses a proton to give allylsilanes **4a** and **5a**. In the absence of a proton scavenger, equilibration of **4a** and **5a**, via **3a**, occurs to give a ca. 16:1 mixture of **4a** and **5a**. As expected, isomerization of a 1.6:1 mixture of **4a** and **5a** in refluxing benzene containing a trace of *p*-toluenesulfonic acid gives the same 16:1 mixture.[8]

The tosylate **2b** behaves similarly, giving the cyclopropylsilane **4b** on solvolysis in refluxing *tert*-butyl alcohol containing potassium carbonate as a proton scavenger.[8]

Two points of general interest emerge from these reactions. The allylic silanes **4** and **5**, unlike other allylic silanes,[2] do not undergo desilylation with double bond migration on treatment with acid. Although the double bond is readily protonated to give the cyclopropyl cation **3a**, as evinced by the conversion of **5a** to **4** in acid, desilylation would require rehydribidization of the cyclopropyl carbon with introduction of additional strain into the molecule. Cation **3** can react with nucleophiles to give homoallylic species analogous to **2** in which the vinylsilane can readily desilylate. Analogous results have been obtained by Paquette, Horn, and Wells.[10]

The presence of silicon on the double bond appears to accelerate the solvolysis of the tosylate **2a**, since the analogous compound 1-bromo-4-methyl-3-pentene alkylates Hagemann's ester under conditions which lead only to solvolysis of **2a**. More detailed studies will be required to establish this since these differences could also result from steric interactions.

Experimental Section

All GC analyses were performed on a 0.25 in. × 9 ft Carbowax 20M on Chromoasorb PNAW column. Benzene and THF were distilled from sodium/benzophenone ketyl. *tert*-Butyl alcohol was distilled from calcium hydride.

Preparation of 1a. Nickel acetylacetonate (128.5 mg, 0.5 mmol) was introduced into a flame-dried Schlenk flask. The flask was flame dried again and purged with nitrogen. THF (5 mL) was added, and the solution was stirred until all the solid had dissolved. Then, as rapidly as possible, the following were added: Me_3Al (0.91 M in hexane, 0.36 mL, 0.33 mmol; the solution turns brown in 15 s); 1-(trimethylsilyl)-1-octyne (0.91 g, 5.0 mmol); MeMgBr (2.03 M in THF/benzene, 9.85 mL, 20.0 mmol). The reaction mixture was stirred for 24 h at 25 °C, diluted with 15 mL of THF, and cooled to −78 °C. Ethylene oxide was bubbled through the solution for 5 min, and the mixture was allowed to warm to 25 °C. Quenching with water and sodium dihydrogen phosphate solution gave a thick precipitate. The entire mixture was filtered with suction. The residue was washed with 100 mL of pentane. The layers were separated, and the aqueous layer was washed with three portions of pentane. The combined organic layers were washed with water, dried (Na_2SO_4), and evaporated to give 1.16 g of crude product. Chromatography of 1.05 g of crude product on silica gel (3:1 pentane–ether) gave 0.58 g (53%) of **1a**

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(1) Address correspondence to this author at the Department of Chemistry, Brandeis University, Waltham, MA 02254.

(2) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(3) For the use of allyl-, propargyl- and alkynylsilanes as terminators see ref 2 and: Johnson, W. S.; Yarnell, T. M.; Myers, R. B.; Morton, D. R.; Boots, S. G. *J. Org. Chem.* **1980**, *45*, 1254. Schmid, R.; Huesmann, P. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 5122.

(4) Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624.

(5) Johnson, W. S.; Dawson, M. J.; Ratcliffe, B. E. *J. Org. Chem.* **1977**, *42*, 153.

(6) Snider, B. B.: Rodini, D. J.; Van Straten, J. W. *J. Am. Chem. Soc.* **1980**, *102*, 5872.

(7) Other procedures which effect the net alkylation of 3-methyl-2-cyclohexenone were also unsuccessful in this case. See: Tsukasa, H.; Saito, S. *Nippon Kagaku Kaishi* **1974**, 1555. Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337. See also: Amupitan, J.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 852.

(8) Several minor products, most of which no longer contained silicon, were present in these reactions. Reactions in acidic media gave a greater percentage of desilylated products, none of which, however, appears to arise from an alkylidenecyclopropane. Specifically, homoallylic tosylates resulting from disilylation of **2** were formed along with products derived from them such as the corresponding *tert*-butyl ether and cyclopropylcarbinyl *tert*-butyl ether.

(9) For a review see: Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, pp 1295–1345.

(10) Alkenyl(trimethylsilyl)cyclopropanes have been prepared by acid-catalyzed dehydration of (trimethylsilyl)cyclopropylcarbinols: Paquette, L. A.; Horn, K. A.; Wells, G. J. *Tetrahedron Lett.* **1982**, *23*, 259.

0022-3263/82/1947-4588$01.25/0