The combined organic phase was dried over K_2CO_3 and evaporated to afford 389 mg (83%) of brilliant orange solid naphthacene. A portion was recrystallized from xylenes to give material with mp ca. 345 °C dec: ^1H NMR δ 7.39 (m, 4 H), 8.00 (m, 4 H), 8.67 (s, 4 H); MS, m/z (relative intensity) 229 (19.7), 228 (parent, 100), 227 (4.6), 226 (16.5), 114 (20.4), 113 (10.0).

Pentacene. A mixture of isomers of **20** (200 mg, 0.33 mmol) in 20 mL of benzene (heterogeneous) was treated with TFA (0.26 mL, 3.3 mmol), resulting in the development of a deep red color and after 3 h the formation of a pink precipitate. The volatiles were vacuum evaporated to afford 115 mg of pink solid, presumably diketone(s), virtually insoluble in common solvents: mp ca. 300 °C dec; MS, m/z (relative intensity) 311 (24.4), 310 (parent, 100), 309 (15.3), 281 (11.6), 278 (23.8), 252 (29.5); IR (KBr) 3060, 2880, 1660, 1601, 1286, 950, 718 cm^{-1}.

A slurry of this material (250 mg) in 40 mL of THF was treated with 400 mg of LAH; the initially pink suspension developed a green color which darkened with continued stirring for 2 h at ambient temperature. The excess hydride was quenched with moist ethyl acetate; rotary evaporation at this stage gave a black solid mass. This was washed extensively with 5% HCl, with warming on a steam bath, and suction filtered to give 256 mg (119% of theory) of crude blue-black solid. Recrystallization of a portion from benzene gave pentacene as a dark purple-blue powder. The UV spectrum (*o*-dichlorobenzene solvent) was in accord with that shown by Clar:[25] MS, m/z (relative intensity) 280 (5.2), 279 (25.8), 278 (parent, 100), 276 (14.1) 139 (20.2).

Acknowledgment. Financial support of this work by the University of California Cancer Research Coordinating Committee is gratefully acknowledged. We also thank Becca Hunt for carrying out preliminary work on the bromoanthracene derivatives, Russell White for preparing 2,3-dibromonaphthalene, Drs. Hugh Webb and Ata Shirazi for their expert assistance in obtaining MS and NMR spectra, and Professor Derek Boyd (Queen's University Belfast) for his helpful correspondence.

Registry No. **1**, 75802-19-6; **2**, 96913-93-8; **3**, 100790-65-6; **4**, 100790-66-7; **5a**, 100790-67-8; **5b**, 100790-68-9; **6**, 100790-69-0; **7**, 100790-70-3; **8a**, 100790-71-4; **8b**, 100790-72-5; **9**, 100790-73-6; **10**, 100790-75-8; **11**, 100790-77-0; **12**, 100790-78-1; **13**, 100790-79-2; **14**, 100790-80-5; **15**, 100790-82-7; **16**, 100790-82-7; **17**, 100790-86-1; **18**, 100790-87-2; **19**, 100790-89-4; **20** (isomer 1), 100790-90-7; **20** (isomer 2), 100895-73-6; **23**, 80716-38-7; **24**, 1523-24-6; **25**, 50259-89-7; **26**, 69653-12-9; **29**, 7470-93-1; **30**, 62170-37-0; **31**, 100790-92-9; **33**, 96913-95-0; **34**, 54687-41-1; **35**, 64615-22-1; **36**, 100790-93-0; **37**, 100790-94-1; **38**, 100790-95-2; **39**, 100790-96-3; **40**, 35187-43-0; **41**, 3073-99-2; **42**, 92-24-0; **43**, 135-48-8; 7,12-dihydro-7,12-epoxy-5-methylbenz[*a*]anthracene, 100790-74-7; 9,14-dihydro-9,14-epoxydibenz[*ac*]antrhacene, 100790-76-9; 9,10-dihydro-2,3-dimethylanthracene, 100790-81-6; 5,12-dihydro-5,12-epoxynaphthacene, 100790-83-8; 1-breomo-9,10-dihydro-9,10-epoxyanthracene, 100790-85-0; 6-bromo-7,12-dihydro-7,12-epoxybenz[*a*]anthracene, 100790-88-3; 5,14:7,12-diepoxy-5,7,12,14-tetrahydrpentacene, 100790-91-8; 1-bromoanthracene, 7397-92-4; dibenz[*a*,*c*]anthracene, 215-58-7; 9-(10*H*)-anthracene, 90-44-8; 2-bromoanthracene, 7321-27-9; naphthacene, 92-24-0; pentacene, 135-48-8; *o*-chlorotolune, 95-49-8; *p*-bromotoluene, 106-38-7; 1-bromo-4-methylnaphthalene, 6627-78-7; 9-bromophenanthrene, 573-17-1; *o*-bromoanisole, 578-57-4; 1-bromopyrene, 1714-29-0; 4-chloro-1,2-dimethylbenzene, 615-60-1; 2,3-dibromonaphthalene, 13214-70-5; *o*-dibromobenzene, 583-53-9; *p*-dibromobenzene, 106-37-6.

α,β-Unsaturated Acyl Cyanides. 6.[1] Self-Condensation and Conjugate Addition of Allyl-, Allenyl-, Propargyl-, and Alkynyltrimethylsilanes

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The base-induced reaction of α,β-unsaturated acyl cyanides leads to lactones resulting from a self-condensation reaction. Neutral nucleophiles such as trimethylsilyl derivatives react with α,β-unsaturated acyl cyanides in the presence of titanium tetrachloride. δ-Ethylenic acyl cyanides, δ-acetylenic acyl cyanides, γ-allenic acyl cyanides, and γ-acetylenic acyl cyanides (or the corresponding acids or methyl esters) are obtained from α,β-unsaturated acyl cyanides by condensation respectively with allyl-, allenyl-, propargyl- and alkynyltrimethylsilanes.

Although the chemistry of aromatic and saturated aliphatic acyl cyanides has been developed in some detail,[2] relatively few studies on the reactivity of α,β-unsaturated acyl cyanides have appeared.[2c,3] These latter conjugated systems are expected to be good acceptors for 1,2 and/or 1,4-nucleophilic additions, since the cyano group is inductively a strong electron-withdrawing substituent which does not show a compensating electron-donating resonance effect.[4] From a synthetic point of view, acyl cyanides are the equivalent of the corresponding acids and esters into which they can be readily converted. We described here a part of our program concerned with developing applications of α,β-unsaturated acyl cyanides in organic synthesis.

Results and Discussion

Reaction of the corresponding α,β-unsaturated acid chlorides with CuCN in acetonitrile leads to the desired

(1) For part 5, see: El-Abed, D.; Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1984**, *25*, 4503.

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(3) (a) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1980**, *21*, 731. (b) Bal, B. S.; Childers, W. E., Jr.; Pinnick, H. W. *Tetrahedron* **1981**, *37*, 2091. (c) Yanovskaya, L. A.; Shakhidayatov, Kh.; Kucherov, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2553; *Chem. Abstr.* **1968**, *69*, 67061p. (d) Normant, J. F.; Piechucki, C. *Bull. Soc. Chim. Fr.* **1972**, 2402. (e) Hoffmann, H. M. R.; Haase, K.; Ismail, Z.; Preftitsi, S.; Weber, A. *Chem. Ber.* **1982**, *115*, 3880. (f) Ismail, Z.; Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 859. (g) Pfaltz, A.; Anwar, S. *Tetrahedron Lett.* **1984**, *25*, 2977. (h) Murahashi, S. I.; Naota, T.; Nakajima, N. *Ibid.*, *26*, 925.

(4) (a) Schaefer, F. C. In "The Chemistry of the Cyano Group"; Rappoport, Z., Ed.; Wiley: London–New York, **1970**, p 239. (b) Anet, F. A. L.; Chiaci, M. *J. Chem. Soc., Chem. Commun.* **1979**, 588. (c) For a discussion on the balance between inductive destabilization and conjugative stabilization for the cyano group in the generation of a carbocation, see: Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279.

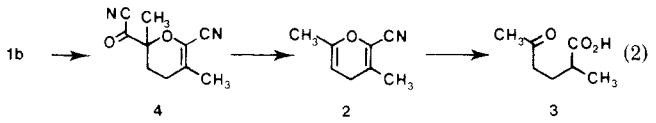
0022-3263/86/1951-1199$01.50/0

acyl cyanides **1c–1f** in good yields (equation 1). The use

(1)

a, $R^1 = R^2 = R^3 = H$
b, $R^1 = R^2 = H$; $R^3 = CH_3$
c, $R^1 = CH_3$; $R^2 = R^3 = H$
d, $R^1 = R^2 = CH_3$; $R^3 = H$
e, $R^1 = C_6H_5$; $R^2 = R^3 = H$
f, $R^1 = CH_3CH{=}CH$; $R^2 = R^3 = H$

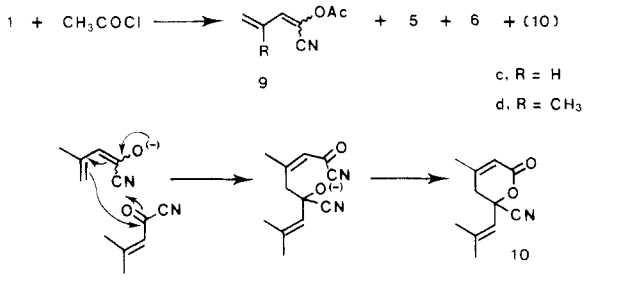
of benzonitrile as solvent is required for the preparation of **1a** and **1b** in moderate yields. Attempts to use acetonitrile resulted in the polymerization of **1a** and the further transformation of **1b** to pyran **2**. The structure of **2** was demonstrated by its quantitative hydrolysis of **3** upon treatment with aqueous hydrochloric acid. The formation of the interesting pyran **2** is attributed to Diels–Alder dimerization of **1b** followed by the spontaneous loss of CO and HCN from adduct **4** (eq 2).



(2)

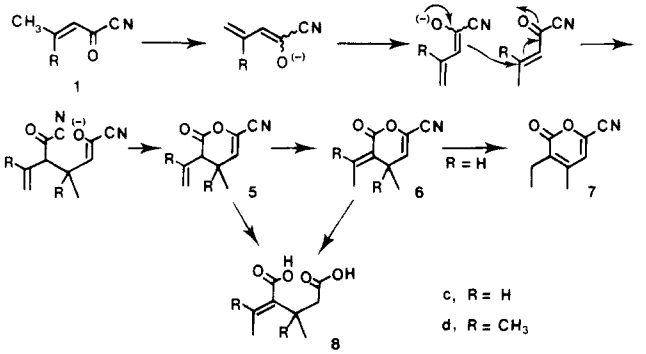
Treatment of **1c** and **1d** with weak bases results in formation of self-condensation products,[5] which are derived from the corresponding enolate anions as indicated in Scheme I. The best yields were observed under exceptionally mild conditions (pyridine or triethylamine in THF or KF in Me_2SO[6]). A reasonable mechanistic scheme involves addition of C-2 of an enolate anion to a second molecule of the acyl cyanide in a 1,4-manner followed by cyclization to **5**. Base-promoted bond migration converts **5** to **6**. In the case of **5d** further isomerization of **6c** to pyrone **7** takes place. These structures were confirmed by saponification of a mixture of lactones **5c** and **6c** to diacid **8c**; a mixture of **5d** and **6d** gives diacid **8d** in a similar manner.

When the above reaction of **1c** was performed in the presence of 10 equiv of methyl vinyl ketone, the major products were still lactones **5c** and **6c**, with only small amounts of other, as yet unidentified, condensation products. The enolates of **1c** and **1d** can be trapped by acetyl chloride, but again the enol acetates **9** are accompanied by major amounts of lactones **5** and **6**. In the case of **1d** a new condensation product **10** was obtained which becomes the major product when triethylamine is used as the base. The formation of **10** can be rationalized by



1,2-addition of C-4 of the enolate of **1d** to a second molecule of **1d** followed by ring formation (the addition of a d^5-reagent to an a^2-reagent[7]).[8,9]

Scheme I

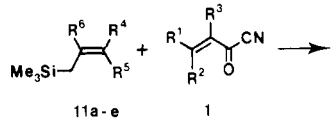


These base-induced reactions demonstrate that, on one hand, α,β-unsaturated acyl cyanides are very easily enolized and, on the other hand, they are extremely good acceptors for nucleophilic additions. In keeping with these observations, an attempt to add enamines such as 1-pyrrolidinocyclohexene to **1c** resulted once again in the formation of lactones **5c** and **6c** as major products. Thus, it appears that neutral nucleophilic reagents need to be used if self-condensation of these α,β-unsaturated acyl cyanides is to be avoided. These considerations have led us to examine the reactions of compounds of type **1** with various unsaturated trimethylsilane derivatives.[10]

Allyl transfer reactions are known to take place smoothly from allylsilanes to α,β-enones to give δ,ϵ-enones,[11] but attempts to alkylate α,β-unsaturated esters have been unsuccessful.[12] The reaction of allylsilanes **11** with acyl cyanides **1** in the presence of 1 equiv of $TiCl_4$ gives almost quantitative yields of the allylated product **12** in most cases. As usual, the new C–C bond is formed regioselectivity to the γ-carbon of the starting allylsilanes. The acyl cyanides **12** (X = CN) can be isolated intact from the reaction by hydrolysis of the reaction mixture and rapid extraction into pentane.[13,14] On the other hand, the corresponding acids **12** (X = OH) can be obtained directly after more prolonged hydrolysis and methanolysis gives the corresponding methyl esters **12** ($X = OCH_3$). In two cases, a dihydropyran of structure **13** was observed as a side product. This probably results from intramolecular O-alkylation of the titanium enolate by the β-silyl carbenium ion and further protolysis of the silicon–carbon bond.[15]

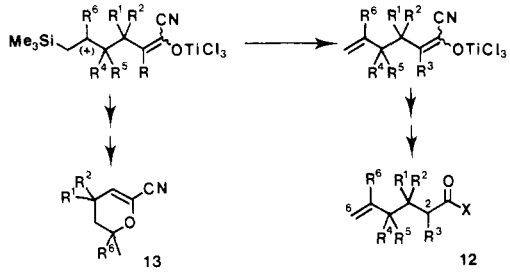
(5) Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1983**, *24*, 2847.
(6) Yakobson, G. G.; Akhmetova N. E. *Synthesis* **1983**, 169.
(7) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

(8) Slight differences in the solvent used can lead to a variation of 1,2 vs. 1,4 addition, for example, see: Corey, E. J.; Rucker C. *Tetrahedron Lett.* **1982**, *23*, 719.
(9) The lithium dienolates of α,β-unsaturated carbonyl compounds react with most electrophiles selectively at the α-position (d^3-reagent[7]); see: Fleming I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, *20*, 3205. For an example of γ-alkylation, see: Oppolzer W.; Strauss H. F.; Simmons D. P. *Ibid.*, **1982**, *23*, 4673.
(10) (a) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. (b) Chan T. H.; Fleming, I. *Synthesis* **1979**, 761. (c) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (d) Fleming, I.,; Terrett, N. K. *Ibid.* **1983**, *55*, 1707. (e) Weber W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, **1983**.
(11) (a) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673. See also: (b) Deleris, G.; Dunogues, J.; Calas, R. *J. Organomet. Chem.* **1975**, *93*, 43.
(12) (a) We do not observe any reaction between allyltrimethylsilane and methyl crotonate in the presence of 1 equiv of $TiCl_4$ (see also ref 11a). (b) This is presumably a reflection of the more negative reduction potential of esters vs. ketones, see: House, H. O.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 5495.
(13) (a) Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1980**, *21*, 4487. The stereochemistry of this conjugate addition has been discussed in our preliminary communication, see: (b) El-Abed, D.; Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1984**, *25*, 1463. **12h**: threo 77%, erythro 23%; **12i**: threo 42%, erythro 58%; **12k**: threo 48%, erythro 52%.
(14) By heating acyl cyanides **12f**, **12g**, **12i–12l** can be cyclized to cyclohexenones, see: 13b.



11a-e 1

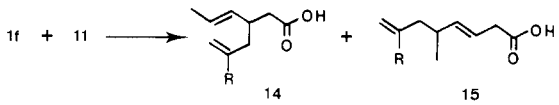
a, $R^4 = R^5 = R^6 = H$
b, $R^4 = R^5 = H$; $R^6 = CH_3$
c, $R^4 = CH_2SiMe_3$; $R^5 = R^6 = H$
d, $R^4 = CH_2SiMe_3$; $R^5 = H$; $R^6 = CH_3$
e, $R^4 = CH_2SiMe_3$; $R^5 = R^6 = CH_3$



13 12 (3)

a, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$
b, $R^1 = R^2 = H$; $R^3 = CH_3$; $R^4 = R^5 = R^6 = H$
c, $R^1 = CH_3$; $R^2 = R^3 = R^4 = R^5 = R^6 = H$
d, $R^1 = R^2 = CH_3$; $R^3 = R^4 = R^5 = R^6 = H$
e, $R^1 = C_6H_5$; $R^2 = R^3 = R^4 = R^5 = R^6 = H$
f, $R^1 = CH_3$; $R^2 = R^3 = R^4 = R^5 = H$; $R^6 = CH_3$
g, $R^1 = R^2 = CH_3$; $R^3 = R^4 = R^5 = H$; $R^6 = CH_3$
h, $R^1 = CH_3$; $R^2 = R^3 = H$; $R^4 = CH_2SiMe_3$; $R^5 = R^6 = H$
i, $R^1 = CH_3$; $R^2 = R^3 = H$; $R^4 = CH_2SiMe_3$; $R^5 = H$; $R^6 = CH_3$
j, $R^1 = R^2 = CH_3$; $R^3 = H$; $R^4 = CH_2SiMe_3$; $R^5 = H$; $R^6 = CH_3$
k, $R^1 = CH_3$; $R^2 = R^3 = H$; $R^4 = CH_2SiMe_3$; $R^5 = R^6 = CH_3$
l, $R^1 = R^2 = CH_3$; $R^3 = H$; $R^4 = CH_2SiMe_3$; $R^5 = R^6 = CH_3$

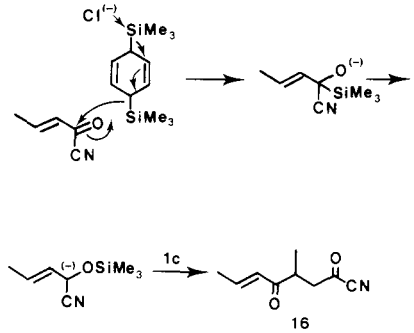
The dienyl acyl cyanide **1f** reacted with **11a** and **11b** to give both 1,4 and 1,6 addition. Comparable amounts of **14** and **15** were obtained from either starting material after hydrolytic work-up.



14 15

a, R = H
b, R = CH_3

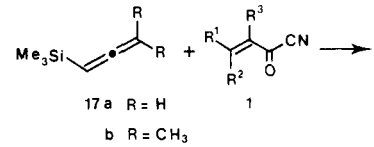
An interesting result is observed with 1,4-bis(trimethylsilyl)-3,5-cyclohexadiene[16] which leads to the condensation product **16** in 60% yield from acyl cyanide **1c**.



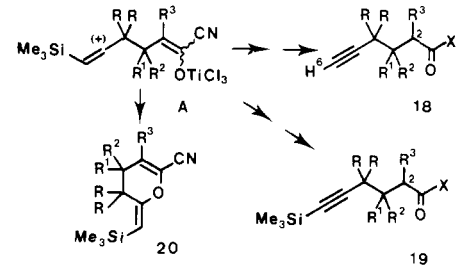
16

A possible mechanism for this conversion involves transfer of a trimethylsilyl group to **1c**, Brook rearrangement[17] and subsequent conjugate addition[18] to a second molecule of **1c** as illustrated below.[19]

A similar set of conversions of **1** with allenyltrimethylsilanes **17** gives the corresponding δ,ε-acetylenic acyl cyanides. In this case, mixtures of these compounds both with and without retention of the trimethylsilyl group (**18** and **19**, respectively) were observed. In a couple of instances the pyran derivatives **20** were also observed as minor products, that might result from intramolecular O-alkylation of the titanium enolate by the vinyl cation A. The reaction of **17b** with **1d** leads to **18g** and **19g** in which a new bond between two quaternary carbon atoms is generated. This is rarely encountered because of F-strain[20] and underlines the efficiency of α,β-unsaturated acyl cyanides as electrophilic acceptors.



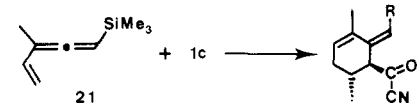
17a R = H
b R = CH_3 1



A 18 20 19 (4)

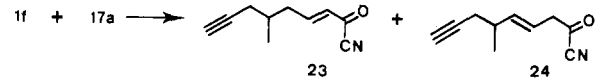
a, $R = R^1 = R^2 = R^3 = H$
b, $R = R^1 = R^2 = H$; $R^3 = CH_3$
c, $R = H$; $R^1 = CH_3$; $R^2 = R^3 = H$
d, $R = CH_3$; $R^1 = R^2 = R^3 = H$
e, $R = CH_3$; $R^1 = R^2 = H$; $R^3 = CH_3$
f, $R = R^1 = CH_3$; $R^2 = R^3 = H$
g, $R = R^1 = R^2 = CH_3$; $R^3 = H$

The condensation of **1c** with 3-methyl-1-trimethylsilylpentane-1,2,4-triene[21] **21** generates a mixture of **22a** and **22b** resulting from a Diels–Alder addition.[22]



21 22a, R = H
b, R = $SiMe_3$

The dienyl acyl cyanide **1f** reacts with **17a** to give only **23** and **24** by reaction at C-6.



23 24

(15) During the addition of allylsilane to enones, a trimethylsilylmethyl cyclobutyl derivative is obtained from C-alkylation of the titanium enolate: (a) Pardo, R.; Zahra J. P.; Santelli, M. *Tetrahedron Lett.* **1979**, *20*, 4557. (b) Hosomi, A.; Kobayashi, H.; Sakurai, H. *Ibid.* **1980**, *21*, 955. (c) Danishefsky, S.; Kahn, M. *Ibid.* **1981**, *22*, 485. (d) House, H. O.; Gaa, P. C.; Van Derveer, D. *J. Org. Chem.* **1983**, *48*, 1661.

(16) Laguerre, M.; Dunogues, J.; Calas, R.; Duffaut, N. *J. Organometal. Chem.* **1976**, *112*, 49.

(17) Brook A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(18) Conjugate addition of a masked acyl anion is seldom observed, see: Hertenstein, U., Hünig, S.; Oller, M. *Synthesis*, **1976**, 416.

(19) One referee suggests that **16** might arise from an acid catalyzed self-condensation of 2 mol of **1c**. A solution of **1c** and $TiCl_4$ in ahydrous methylene chloride is stable during 1 week at room temperature.

(20) (a) Gold, V. *Prog. Stereochem.* **1962**, *3*, 169. (b) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Organic Reactions* **1959**, *10*, 179.

(21) Dulcere, J. P.; Grimaldi, J.; Santelli, M. *Tetrahedron Lett.* **1981**, *22*, 3179.

(22) The regioselectivity of this cycloaddition is the reverse from the one observed with 3-methyl-penta-1,2,4-triene and α,β-enones, see: Bertrand, M.; Grimaldi, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1971**, 962; and consequently, may be a stepwise, ionic reaction, see: Fleming, I. "Frontier Orbitals Organic Chemical Reactions"; Wiley: London, **1976**, p 132.

Table I. ^{1}H NMR Spectral Data for Unsaturated Acyl Cyanides[a,b]

no.	R^3	R^1	R^2
1a		6.83–6.17 (3 H, m)	
1b	2.03 (3 H) (d, J = 1.6)	6.56 (1 H) (q, J = 1.6)	6.68 (1 H) (br s)
1c	6.33 (1 H) (d, q, J = 15.6, J = 1.6)	2.19 (3 H) (d, d, J = 7.0, J = 1.6)	7.52 (1 H) (d, q, J = 15.6, J = 7.0)
1d	6.24 (1 H) (sept., J = 1.2)	2.12 (3 H) (d, J = 1.2)	2.32 (3 H) (d, J = 1.2)
1e	6.95 (1 H) (d, J = 16.8)	7.72 (5 H) (m)	8.17 (1 H) (d, J = 16.8)
1f	6.22 (1 H) (d, J = 15.4)	6.40 (1 H) (d, d, J = 14.6, J = 9.5) 6.72 (1 H) (dq, J = 14.6, J = 5.3) 2.04 (3 H) (d, J = 5.3)	7.65 (1 H) (d, d, J = 15.4, J = 9.5)

[a] J values are in hertz; CCl_4 was used in all cases. [b] For numbering, see eq 1.

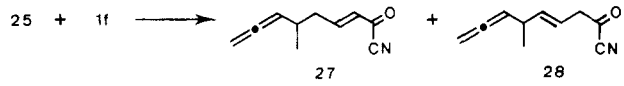
Table II. Self-Condensation of α,β-Unsaturated Acyl Cyanides 1c and 1d

	isomer distribution, % and yield, %						
	5c	**6c**	**7**	overall yield	**5d**	**6d**	overall yield
pyridine or triethylamine	15	85	0	87	40	60	80
KF/Me_2SO	0	0	100	90	65	35	80

The condensation of propargyltrimethylsilane **25** with acyl cyanides **1** gives good yields of γ-allenic acyl cyanides **26**. The addition of propargylsilane **25** to **1f** also occurs uniquely at C-6 to give **27** and **28**.

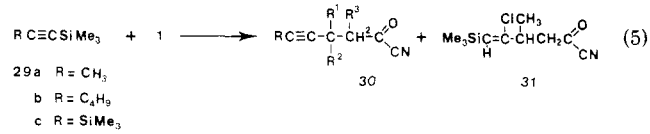
25 **26**

b, $R^1 = R^2 = H$; $R^3 = CH_3$
c, $R^1 = CH_3$; $R^2 = R^3 = H$
d, $R^1 = R^2 = CH_3$; $R^3 = H$



27 **28**

Finally, the $TiCl_4$ catalyzed conjugate addition of alkynylsilanes **29** to acyl cyanides **1** to give the γ-alkynyl derivatives **30** has been achieved in moderate yields.[23] This constitutes a very interesting synthetic conversion which requires only 1 equiv of **29**. Facile conversion of the



(5)

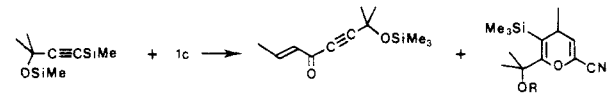
29a R = CH_3
b R = C_4H_9
c R = $SiMe_3$

30 **31**

a, R = CH_3; $R^1 = R^2 = R^3 = H$
b, R = CH_3; $R^1 = R^2 = H$; $R^3 = CH_3$
c, R = $R^1 = CH_3$; $R^2 = R^3 = H$
d, R = $R^1 = R^2 = CH_3$; $R^3 = H$
e, R = CH_3; $R^1 = C_6H_5$; $R^2 = R^3 = H$
f, R = C_4H_9; $R^1 = CH_3$; $R^2 = R^3 = H$
g, R = $SiMe_3$; $R^1 = CH_3$; $R^2 = R^3 = H$

corresponding acids and esters gives an overall 1,4 formal addition of an alkynyl group to a conjugated acid derivative.[24] Condensation of **1c** with bis(trimethylsilyl)-acetylene leads to minor product **31** resulting from hydrochloric acid addition on acetylenic bond.

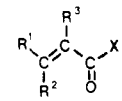
The condensation of propargyl alcohol derivatives **32** with **1c** leads to the 1,2-addition product **33** and pyran derivative **34** (**33**/**34** = 7/3).[25] To increase the yield, it is necessary to use a large excess of alkynylsilane **32** (60% yield with 5 mol equiv of **32** and 2 mol equiv of $TiCl_4$).



32 **33** **34a**, R = H
b, R = $SiMe_3$

Conclusion

In conclusion, if we compare the behaviour of α,β-enones,[10,11] α,β-unsaturated acyl cyanides, α,β-unsaturated acyl chlorides,[26] and α,β-unsaturated esters[12] toward unsaturated trimethylsilane derivatives in the presence of Lewis acids, we find that the reactivity of α,β-unsaturated acyl cyanides is close to that of α,β-enones and even better:



X = alkyl: conjugate addition
X = CN: easier conjugate addition
X = Cl: chlorine substitution
X = OCH_3: no reaction

Alkynylsilanes react only with α,β-unsaturated acyl chlorides (chlorine substitution) and α,β-unsaturated acyl cyanides (conjugate addition).

This remarkable activation of the γ-carbon atom of α,β-unsaturated acyl cyanides might be the result of the electronic properties of cyano group (e.g., σ_p of X, OCH_3, −0.28; CH_3, −0.14; Cl, 0.24; CN, 0.70)[27] and from its poor ability as a leaving group.

Experimental Section

General Methods. ^{1}H NMR spectra were determined on a Varian EM 360 (60 MHz) or Varian XL 200 (200 MHz) spectrometers. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL 200 (50.309 MHz) with Me_4Si as the internal standard. Mass spectra were obtained on a Varian MAT 311 mass spectrometer. IR spectra were obtained on a Perkin-Elmer 298 spectrometer. Melting points are uncorrected. New compounds gave satisfactory C, H, N, Si analyses, which were submitted per review. All reactions were done under a nitrogen atmosphere.

Synthesis of α,β-Unsaturated Acyl Cyanides 1a–1f. The acyl cyanides were prepared according to the procedure reported previously:[3d] To a 250-mL flask containing cuprous cyanide (18 g, 0.2 mol) in 80 mL of acetonitrile (or benzonitrile) the corresponding acyl chloride (0.2 mol) was added at room temperature. This mixture was stirred under reflux during 20 min and the resulting solution was rapidly removed by distillation under vacuum. The crude distillate was carefully fractionated to obtain

(23) Conjugate addition of an alkynyl unit to α,β-enones is achieved with alkynylalanes: (a) Hooz, J.; Layton, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 7320. (b) Bhanu, S.; Scheinmann, F. *J. Chem. Soc., Chem. Commun.* **1975**, 817. (c) Pappo R.; Collins, P. W. *Tetrahedron Lett.* **1972**, 2627. (d) Collins, P. W.; Dajani E. Z.; Bruhn, M. S.; Brown, C. H.; Palmer, J. R.; Pappo, R. *Ibid.* **1975**, 4217. (e) Hansen, R. T.; Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2244. Or alkynylboranes: (f) Bruhn, M. S.; Brown, C. H.; Collins, P. W.; Palmer, J. R.; Dajani, E. Z.; Pappo, R.; *Tetrahedron Lett.* **1976**, 235. (g) Sinclair, J. A.; Molander, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1977**, *99*, 954.

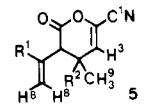
(24) Jellal, A.; Zahra, J. P.; Santelli, M. *Tetrahedron Lett.* **1983**, *24*, 1395.

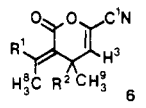
(25) The 1,2 addition of alkynylsilane **32** is apparently ascribable to steric hindrance of its γ-carbon atom.

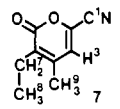
(26) Pillot, J. P.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1976**, 1871.

(27) March, J. "Advanced Organic Chemistry", 3rd ed.; Wiley: New York, 1985; p 244.

Table III. ^{1}H NMR Spectral Data for Lactones 5c, 6c, 7, 5d, and 6d[a]


5


6


7

no.	H^3	H^8	R^1	R^2	H^9	others
5c[b]	5.54 (d, J = 3.7)	6.87–5.50 (3 H) (m)		1.24 and 1.19 (3 H) (d, J = 7.0) (d, J = 7.0)		
6c	6.18 (d, J = 5.8)	1.95 (d, J = 7.0)	7.13 (1 H) (q, J = 7.0)	3.53 (1 H) (m)	1.25 (d, J = 7.2)	
7	6.63 (br s)	1.12 (t, J = 7.3)			2.22 (br s)	H^7: 2.57 (q, J = 7.3)
5d	5.65 (s)	6.08 (br s)	1.83 (3 H) (br s)	1.07 (3 H) (s)	1.07 (s)	H^5: 2.01 (s)
6d	5.83 (br s)	1.98 (s)	2.17 (3 H) (s)	1.12 (3 H) (s)	1.12 (s)	

[a] J values are in hertz; CCl_4 was used in all cases. [b] Mixture of cis-trans isomers.

the desired product. The following were obtained in this manner: acryloyl cyanide (**1a**) (50% yield, benzonitrile): bp 46–48 °C (180 torr); ^{13}C NMR δ 172.4 (s), 133.8 (t), 128.5 (d), 118.3 (s); IR (neat) 2225, 1680 cm^{-1}; mass spectrum, m/e 81 (M^+, 62) 55 (100), 54 (14), 53 (14), 49 (19). Methacryloyl cyanide (**1b**) (50% yield, benzonitrile):[3e] bp 48–50 °C (50 torr); IR (neat) 2225, 1680 cm^{-1}; mass spectrum, m/e 95 (M^+, 6), 69 (92), 41 (100), 40 (12), 39 (77). Crotonoyl cyanide (**1c**) (85–90% yield, acetonitrile):[3d,e] bp 68–70 °C (48 torr); ^{13}C NMR δ 168.0 (s), 159.2 (d), 131.8 (d), 117.3 (s), 19.3 (q); IR (neat) 2225, 1665 cm^{-1}; mass spectrum, m/e 95 (M^+, 18), 69 (19), 41 (100), 40 (44), 39 (37). Senecioyl cyanide (**1d**) (85% yield, acetonitrile):[3d,e] bp 70 °C (20 torr); ^{13}C NMR δ 169.9 (s), 165.1 (s), 123.4 (d), 115.5 (s), 28.5 (q), 22.5 (q); mass spectrum, m/e 109 (M^+, 4), 83 (30), 82 (40), 55 (17), 54 (18), 53 (11), 41 (100), 40 (55) 39 (50); IR (neat) 2225, 1655, 1610 cm^{-1}. Cinnamoyl cyanide (**1e**) (80% yield, acetonitrile):[3c,e] bp 140 °C (0.4 torr): mp 111 °C (vacuum sublimation); ^{13}C NMR δ 168.0 (s), 155.5 (d), 133.5 (d), 133.2 (s), 130.0 (d), 129.9 (d), 125.6 (d), 112.9 (s); mass spectrum, m/e 157 (M^+, 57) (HRMS calcd for $C_{10}H_7NO$ 157.0527, found 157.051), 156 (100), 131 (14), 129 (12), 128 (12), 103 (27), 102 (23), 77 (29), 51 (23); IR ($CDCl_3$) 2225, 1660, 1620 cm^{-1}. Sorboyl cyanide (**1f**) (75% yield, acetonitrile): bp 60 °C (15 torr); ^{13}C NMR δ 168.1 (s), 155.8 (d), 148.9 (d), 130.4 (d), 127.1 (d), 113.1 (s), 19.4 (q); mass spectrum, m/e 121 (M^+, 27) (HRMS calcd for C_7H_7NO 121.0527, found 121.053), 106 (100), 95 (13), 78 (15), 67 (15), 66 (19), 65 (18), 51 (10), 41 (22); IR (neat) 2225, 1665, 1625, 1595 cm^{-1}. (See Table I for ^{1}H NMR data.)

Preparation of 2. During the attempted preparation of **1b** using the above procedure with acetonitrile as solvent, pyran **2** is formed: (60% yield); bp 60 °C (3 torr); ^{1}H NMR ($CDCl_3$) δ 4.53 (1 H, t of q J = 3.18 Hz, J = 1.45 Hz), 2.73 (2, m), 1.85 (3, t J = 1.13 Hz), 1.76 (3, m); ^{13}C NMR δ 147.6 (s), 125.9 (s), 122.8 (s), 113.4 (s.), 94.7 (d), 27.2 (t), 18.7 (2C) (q); mass spectrum, m/e 135 (M^+, 38) (HRMS calcd for C_8H_9NO 135.0684, found 135.068), 134 (47), 120 (100), 92 (13), 79 (19), 77 (10), 65 (16), 43 (16), 39 (11); IR (CCl_4) 2220, 1770, 1665 cm^{-1}.

Preparation of 3. Refluxing 1 g of **2** with 25 mL of hydrochloric acid (30%) for 4 h gave crude keto acid. After diethyl ether extraction, **3** was isolated by distillation: bp 90 °C (2 torr) (90% yield); ^{1}H NMR ($CDCl_3$) δ 2.58 (1 H, sext J = 7.0 Hz), 2.27 (3, s), 1.28 (3, d J = 7.0 Hz); IR ($CDCl_3$) 3600–2860, 1770–1660 cm^{-1}.

Self-Condensation of 1c and 1d. First procedure: a magnetically stirred solution of anhydrous pyridine (25 mL) and anhydrous THF (10 mL) was cooled (0 °C) and acyl cyanide **1c** or **1d** (10 mmol) was slowly added. The solution was allowed to stir at room temperature for 3 days. Hydrolysis and extractive workup (acidic) with diethyl ether gave lactones (total yield 90%). **Second procedure**: a magnetically stirred solution of potassium fluoride (60 mg) in Me_2SO (25 mL) and THF (5 mL) was cooled (0 °C) and acyl cyanide (10 mmol) in ahydrous THF (10 ml) was slowly added. The solution was allowed to stir at room temperature for 3 h. Hydrolysis and extractive workup (acidic) with diethyl ether gave lactones: mixture of **5c** **6c**, and **7**, bp 95 °C (0.3 torr). Pure lactones were isolated by preparative GLC (Carbowax 20 M) (during storage, the lactones **5c** and **6c** are isomerized to very large white cristals of the pyrone **7**). (See Table II for self-condensation products of **1e** and **1d**.)

5c: mass spectrum, m/e 163 (M^+, 75), 135 (25), 120 (54), 106 (33), 95 (38), 92 (63), 67 (67), 66 (100), 53 (38), 42 (46), 41 (67), 39 (71); IR (CCl_4) 2240, 1800, 1740, 1645 cm^{-1}. **6c**: ^{13}C NMR δ 160.4 (s), 145.5 (d), 126.9 (s), 125.5 (s), 123.8 (d), 112.4 (s), 29.7 (d), 20.5 (q), 14.5 (q); mass spectrum, m/e 163 (M^+, 50) (HRMS calcd for $C_9H_9NO_2$ 163.0633, found 163.063), 148 (44), 135 (18), 120 (100), 92 (22), 81 (44), 68 (90), 53 (20); IR (CCl_4) 2240, 1800, 1770–1755, 1670 cm^{-1}. **7**: ^{13}C NMR δ 160.2 (s), 147.6 (s), 134.7 (s), 130.5 (s), 120.2 (d), 112.3 (s), 21.0 (t), 18.7 (q), 12.0 (q); mass spectrum, m/e 163 (M^+, 42) (HRMS calcd for $C_9H_9NO_2$ 163.0633, found 163.063), 148 (7), 135 (18), 134 (11), 120 (100), 92 (14), 78 (12), 65 (27), 53 (8), 41 (8), 39 (15); IR (CCl_4) 2220, 1785, 1725, 1635 cm^{-1}. **5d**: IR (CCl_4) 2225, 1790, 1725, 1645 cm^{-1}. **6d**: mass spectrum, m/e 164 (M^+ – HCN, 4) (HRMS calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.084), 139 (10), 138 (100), 136 (6), 133 (5), 123 (12), 121 (5), 110 (8), 95 (28), 83 (35), 82 (26), 79 (12), 77 (13), 67 (18), 55 (28), 54 (70), 41 (29), 39 (51); IR (CCl_4) 2225, 1790, 1770, 1660 cm^{-1}. (See Table III for spectral data **5c**, **6c**, **7**, **5d**, and **6d**.)

Table IV. Enolization of 1c and 1d in the Presence of Acetyl Chloride (2 mol equiv)

	product distribution, %						
	5c	**6c**	**9c**	**5d**	**6d**	**9d**	**10**
pyridine	10	50	35				
				25	35	25	10
triethylamine				4	6	10	65

Preparation of 8c and 8d. To a solution of sodium hydroxide (2.5 N, 20 mL) and dioxane (15 mL) was added lactones **5c** and **6c** (for **8c**) (10 mmol, 1.63 g) or **5d** and **6d** (for **8d**) (10 mmol, 1.91 g). The reaction mixture was stirred at reflux for 4 h. After hydrolysis, the solution was acidified to pH 1 and extracted with diethyl ether. **8c**: mp 118 °C (CCl_4–light petroleum); ^{1}H NMR (CCl_4) δ 7.07 (1 H, q, J = 7.2 Hz), 3.73–3.0 (1, m), 2.8 (2, m), 1.92 (3, d, J = 7.2 Hz), 1.25 (3, d, J = 7.0 Hz); ^{13}C NMR δ 179.7 (s), 172.7 (s), 141.7 (d), 134.6 (s), 39.2 (t), 28.5 (d), 18.9 (q), 14.3 (q); IR ($CDCl_3$) 3460–2740, 1730–1660, 1635 cm^{-1}. **8d**: mp 128 °C (CCl_4–light petroleum); ^{1}H NMR (CCl_4) δ 2.17 (2 H, s), 1.98 (3, s), 1.93 (3, s), 1.06 (6, s); IR (CCl_4) 3460–2740, 1730–1630, 1615 cm^{-1}.

Preparation of 9 and 10. A solution of acyl cyanide (25 mmol) in THF (15 mL) was added dropwise to a mixture of acetyl chloride (4g, 50 mmol) in dry pyridine or triethylamine (10 mL) at 0 °C with stirring. The reaction was allowed to proceed at 25 °C with stirring for 24 h. The reaction mixture was poured onto ice and extracted with pentane (6 × 30 mL). The combined extracts were washed with aqueous solution of ammonium chloride and brine, dried on $MgSO_4$, filtered, evaporated in vacuo, and distilled. **9c** (Z and E, 1/1): bp 55 °C (1.5 torr); ^{1}H NMR (CCl_4) δ 7.00–6.23 (2 H, m.), 5.90–5.35 (2, m), 2.26 (1.5, s), 2.22 (1.5, s); IR (CCl_4) 2235, 1790, 1680, 1640 cm^{-1}. **9d** (one isomer): bp 70 °C (1.5 torr); ^{1}H NMR (CCl_4) δ 6.17 (1 H, s), 5.19 (2, s(br)), 2.17 (3, s), 1.93 (3, s); IR (neat) (2220, 1775, 1745, 1635, 1190 cm^{-1}. **10**: bp 120 °C (0.3 torr); mp 78 °C (vacuum sublimation); ^{1}H NMR (CCl_4) δ 5.90 (1 H, q, J = 2.0 Hz), 5.32 (1, sept J = 2.0 Hz), 2.74 (2, s), 2.08 (3, d, J = 2.0 Hz), 2.05 (3, d J = 2.0 Hz), 1.89 (3, d, J = 2.0 Hz); ^{13}C NMR δ 161.4 (s), 155.1 (s), 146.3 (s), 119.7 (d), 117.9 (s), 116.6 (d), 72.4 (s), 39.6 (t), 26.5 (q), 23.0 (q), 19.7 (q); mass spectrum, m/e 191 (M^+, 2.5), 190 (M^+ – H, 8), (HRMS calcd for $C_{11}H_{12}NO_2$ 190.0868, found 190.087), 146 (28), 107 (8), 83 (13), 82 (100), 79 (5), 54 (18), 53 (10), 39 (16); IR (CCl_4) 2225, 1735, 1660, 1645, 1260, 1240 cm^{-1}. (See Table IV for products distribution.)

Preparation of allyltrimethylsilanes: 11b,[28] 11c–11e.[29]

Preparation of 12 and 13: Titanium chloride (1.9 g, 10 mmol) and anhydrous methylene chloride were cooled (−20 °C), and acyl cyanide (10 mmol) in anhydrous methylene chloride was added. The reaction mixture was cooled to −78 °C and the silane derivative (15 mmol) was added. The solution was allowed to stir at −78 °C for 3 h and at −30 °C during 4 h. The reaction mixture was poured into ice water, followed by rapidly extractive workup with pentane. The reaction mixture was stirred with water during 1 h followed by extractive workup with diethyl ether to isolate the acids. The reaction mixture was diluted with 30 mL of anhydrous methanol, after which it was allowed to stand at room temperature for about 24 h to isolate the methyl esters. Hydrolysis and extractive workup gave methyl ester. Products were isolated by distillation and purified by preparative GLC (Carbowax 20 M). **12a** (X = CN) (30 %) and **13a** (35 %): bp 30 °C (0.7 torr). **12a** (X = CN): IR (neat) 2225, 1720, 1645 cm^{-1}. **13a**: ^1H NMR (CCl_4) δ 5.48 (1 H, t, J = 4.0 Hz), 3.93 (1, m), 1.33 (3, d, J = 7.0 Hz); mass spectrum, m/e 123 (M^+, 65) (HRMS calcd for C_7H_9NO 123.0684, found 123.067), 108 (14), 94 (21), 82 (31), 80 (23), 69 (21), 67 (13), 55 (40), 54 (17), 42 (100), 41 (50), 39 (21); IR (neat) 2225, 1735, 1645 cm^{-1}. **12b** (X = CN) (30 %): bp 70 °C (2.2 torr); IR (neat) 2220, 1715, 1645 cm^{-1}. **12c** (X = CN) (95 %): bp 60 °C (0.7 torr); mass spectrum, m/e 137 (M^+, 2), 122 ($M^+ - CH_3$, 2) (HRMS calcd for C_7H_8NO 122.06505, found 122.060), 111 (5), 69 (37), 68 (99), 67 (62), 55 (31), 53 (16), 42 (45), 41 (100), 39 (49); IR (CCl_4) 2225, 1725, 1645 cm^{-1}. **12d** (X = CN) (95 %): bp 45 °C (0.4 torr); IR (CCl_4) 2225, 1730, 1715, 1645 cm^{-1}. **12e** (X = CN) (80 %): bp 110 °C (0.1 torr); IR (neat) 2230, 1725, 1645, 1610 cm^{-1}. **12f** (X = CN) (95 %): bp 50 °C (0.3 torr); IR (CCl_4) 2225, 1725, 1650 cm^{-1}. **12g** (X = CN (60 %) and **13g** (35 %): bp 70 °C (0.3 torr). **12g** (X = CN): ^{13}C NMR δ 176.6 (s), 142.0 (t), 116.0 (s), 115.1 (s), 55.7 (t), 49.7 (t), 35.8 (s), 27.8 (q), 25.2 (q); mass spectrum m/e 165 (M^+, 25) (HRMS calcd for $C_{10}H_{15}NO$ 165.1153, found 165.115), 150 (17), 110 (14), 108 (20), 95 (10), 83 (33), 69 (17), 59 (10), 56 (100), 55 (23), 43 (14), 41 (28); IR (neat) 2220, 1715, 1645 cm^{-1}. **13g**: ^1H NMR (CCl_4) δ 5.32 (1 H, s), 1.68 (2, s), 135 (6, s), 1.15 (6, s); ^{13}C NMR δ 125.9 (s), 125.7 (d), 115.4 (s), 47.1 (t), 30.1 (s), 30.3 (q), 27.5 (q), 27.4 (s); mass spectrum, m/e 165 (M^+, 22) (HRMS calcd for $C_{10}H_{15}NO$ 165.1153, found 165.115), 150 (17), 110 (14), 108 (17), 83 (31), 69 (14), 56 (100), 55 (14), 43 (9), 41 (24); IR (neat) 2235, 1690, 1640 cm^{-1}. **12h** (X = CN) (80 %): bp 100–110 °C (1.5 torr). **12h** (X = CN) erythro (62 %): ^{13}C NMR δ 177.5 (s), 140.6 (d), 116.9 (t), 114.0 (s), 50.8 (t), 44.8 (d), 35.8 (d), 20.4 (t), 15.2 (q), −0.3 (q); mass spectrum, m/e 208 ($M^+ - CH_3$, 0.5) (HRMS calcd for $C_{11}H_{18}NOSi$ 208.1157, found 208.116), 181 (5) (HRMS calcd for $C_{10}H_{17}OSi$ 181.1048, found 181.105), 141 (5), 127 (17), 84 (7), 75 (12), 73 (100), 55 (5), 45 (7); IR (neat) 2220, 1725, 1645 cm^{-1}. **12h** (X = CN) threo (18 %): ^{13}C NMR δ 177.7 (s), 141.9 (d), 116.9 (t), 114.0 (s), 49.8 (t), 46.1 (d), 36.2 (d), 19.8 (t), 17.9 (q), −0.3 (q); **12i** (X = CN) (85 %) (threo 42%; erythro 58%): bp 75 °C (1 torr); mass spectrum, m/e 210 (M^+ − HCN, 3) (HRMS calcd for $C_{12}H_{22}OSi$ 210.1439, found 210.143), 195 (8), 141 (23), 75 (13), 73 (100), 59 (6), 45 (6), 41 (5); IR (neat) 2220, 1720, 1665, 1250 cm^{-1}. **12j** (X = CN) (80 %): bp 90 °C (1.5 torr); IR (neat) 2220, 1715, 1640, 1250 cm^{-1}. **12k** (X = CN) (80 %)(threo 48 %; erythro 52%): 90 °C (0.2 torr; IR 2220, 1715, 1645, 1250 cm^{-1}. **12l** (X = CN) (85 %): bp 90 °C (0.2 torr); IR (CCl_4) 2220, 1715, 1645, 1250 cm^{-1}. (For ^1H NMR spectral data for **12a–l**, see Table V.) **14a + 15a**: bp 70–80 °C (0.15 torr). **14a** (30 %): ^1H NMR (CCl_4) δ 6.0 (1, m), 5.47 (2, m), 5.07 (1, m), 5.02 (1, m), 2.73–1.83 (5, m), 1.67 (3, d, J = 5.0 Hz); IR (neat) 3300–2500, 1790, 1725, 1710, 1645 cm^{-1}. **15a** (45 %): ^1H NMR (CCl_4)) δ 5.77 (1 H, m.), 5.55 (2, m), 5.02 (1, d, J = 11 Hz), 5.00 (1, d, J = 15.0 Hz), 3.05 (1, m), 2.12 (2, m), 1.03 (3, d, J = 6.4 Hz); IR (neat) 3400–2400, 1715, 1645 cm^{-1}. **14b + 15b**: 110 °C (0.5 torr). **14b** (45 %): ^1H NMR (CCl_4) δ 5.42 (2 H, m), 4.76 (2, s (br)), 2.33 (2, m), 2.10 (2, d, J = 7.0 Hz), 1.75 (3, s(br)), 1.70 (3, d, J = 5.0 Hz); IR (CCl_4) 3400–2400, 1710, 1645 cm^{-1}. **15b** (30 %): ^1H NMR (CCl_4) δ 5.52 (2H, m), 4.70 (2, s(br)), 3.03 (2, m), 1.71 (3, s (br)), 0.99 (3, d, J = 6.8 Hz); IR (CCl_4) 3400–2400, 1710, 1650 cm^{-1}. **16** (70%): bp 100 °C (0.5 torr); ^1H NMR (CCl_4) δ 6.36 (1 H, d, J = 15.5 Hz, q, J = 6.5 Hz), 5.57 (1, d, J = 15.5 Hz, q, J

Table V. ^1H NMR Spectral Data for Unsaturated Acyl Cyanides[a,b]

no.	H^2	R^3	R^1	R^2	R^4	R^5	R^6	H^6	R^4–Si(CH_3)$_3$
12a	2.66 (2 H) (t, J = 7.0)						6.70–4.70 (3 H) (m)		
12b		1.30 (3 H) (d, J = 7.0)					6.10–4.65 (3 H) (m)		
12c	2.82 (d, J = 10.0)	2.60 (1 H) (d, J = 4.8)	1.05 (3 H) (d, J = 5.0)		2.17 (2 H) (m)		6.13–4.83 (3 H) (m)		
12d	2.65 (2 H) (s)		1.13 (6 H) (s)		2.13 (2 H) (d, J = 7.0)		6.10–4.85 (3 H) (m)		
12e	2.73 (d, J = 6.1)	2.70 (1 H) (d, J = 8.0)	7.03 (5 H) (s)	3.13 (1 H) (m)	2.13 (2 H) (t, J = 7.0)		6.10–4.80 (3 H) (m)		
12f	2.60 (2 H) (m)		0.97 (3 H) (d, J = 6.0)				1.70 (3 H) (br s)	4.80 (2 H) (m)	
12g	2.63 (2 H) (s)		1.12 (6 H) (s)		2.07 (2 H) (s)		1.78 (3 H) (br s), 4.83 (1 H) (br s), and 4.60 (1 H) (br s)		
12h[c]	2.67 (2 H) (m)		1.06 (3 H) (d, J = 7.0)		0.73 (2 H) (d, J = 7.0)		6.43–4.86 (3 H) (m)		0.13 (9 H) (s)
12i[c]	2.60 (2 H) (m)		1.03 (3 H) (d, J = 6.0)		0.68 (2 H) (m)		1.80 (3 H) (br s), 4.97 (1 H) (br s), and 4.81 (1 H) (br s)		0.13 (9 H) (s)
12j	2.73 (2 H) (s)		1.27 (6 H) (s)		0.53 (2 H) (m)		1.87 (3 H) (br s)	4.87 (2 H) (m)	0.11 (9 H) (s)
12k[c]	2.70 (2 H) (m)		1.03 (3 H) (d, J = 6.0)		0.40 (2 H) (m)	1.23 (3 H) (s)	1.90 (3 H) (br s)	4.93 (2 H) (m)	0.11 (9 H) (s)
12l	2.10 (2 H) (s)		1.20 (3 H) (s)	1.12 (3 H) (s)	0.50 (2 H) (m)	1.30 (3 H) (s)	1.87 (3 H) (br s)	5.03 (2 H) (m)	0.11 (9 H) (s)

[a] J values are in hertz; CCl_4 was used in all cases. [b] For numbering, see eq 3. [c] Mixture of threo–erythro isomers. **12h**: threo, 77%; erythro, 23%. **12i**: threo, 42%; erythro, 58%. **12k**: threo, 48%; erythro, 52%.

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Table VI. ^{1}H NMR Spectral Data for Acetylenic Derivatives 18 and 19[a,b]

no.	H^2	R^3	R^1	R^2	R	H^6 or $(CH_3)_3Si$
18a	2.67 (2 H) (t, J = 7.0)					2.31 (1 H) (t, J = 2.0)
19a	2.77 (2 H) (t, J = 6.5)					0.17 (9 H) (s)
18b		1.43 (3 H) (d, J = 6.5)				2.27 (1 H) (t, J = 2.0)
18c	2.77 (2 H) (m)		1.13 (3 H) (d, J = 7.0)			2.30 (1 H) (t, J = 2.0)
19d	2.90 (2 H) (m)				1.37 (6 H) (s)	0.2 (9 H) (s)
19e		1.20 (3 H) (d, J = 4.0)	1.90 (2 H) (m)		1.27 (6 H) (s)	0.17 (9 H) (s)
18f	2.98 (2 H) (part AB of ABC patt)		2.30 (1 H) (m)	1.05 (3 H) (d, J = 6.6)	1.28 (3 H) (s) 1.22 (3 H) (s)	2.13 (1 H) (s)
18g	2.90 (2 H) (s)		1.23 (6 H) (s)		1.25 (6 H) (s)	2.18 (1 H) (s)
19g	2.82 (2 H) (s)		1.18 (6 H) (s)		1.21 (6 H) (s)	0.15 (9 H) (s)

[a] J values are in hertz; CCl_4 was used in all cases. [b] For numbering, see eq 4.

Table VII. ^{1}H NMR Spectral Data for Acetylenic Acyl Cyanides 30[a,b]

no.	H^2	R^3	R^1	R^2	R
30a	2.87 (2 H) (t, J = 6.5)		2.42 (2 H) (m)		1.72 (3 H) (t, J = 2.5)
30b		1.46 (3 H) (d, J = 7.2)			1.87 (3 H) (br s)
30c	2.89 (2 H) (m)		1.27 (3 H) (d, J = 6.8)		1.80 (3 H) (d, J = 2.5)
30d	2.73 (2 H) (s)		1.33 (6 H) (s)		1.82 (3 H) (s)
30e	2.60 (2 H) (d, J = 7.5)		7.2 (5 H) (br s)	4.00 (1 H) (tq, J = 7.5, J = 2.0)	1.73 (3 H) (d, J = 2.0)
30f	2.77 (2 H) (d, J = 7.0)		1.27 (3 H) (d, J = 6.8)	3.23 (1 H) (m)	2.15 (2 H) (td, J = 6.2, J = 2.0) 0.92 (3 H) (t, J = 6.5)
30g	2.85 (2 H) (br s)		1.25 (3 H) (d, J = 6.5)		0.15 (9 H) (s)

[a] J values are in hertz; CCl_4 was used in all cases. [b] For numbering, see eq 5.

= 1.5 Hz), 3.10–2.17 (3, m), 1.92 (3, d, J = 6.5 Hz, d, J = 1.5 Hz), 1.12 (3, d, J = 7.0 Hz); ^{13}C NMR δ 173.1 (s), 172.9 (s), 134.4 (d), 124.5 (d), 115.0 (s), 41.1 (d), 35.2 (t), 17.6 (q), 14.5 (q); mass spectrum, m/e 165 (M^+, 10) (HRMS calcd for $C_9H_{11}NO_2$ 165.0789, found 165.078), 137 (7), 96 (43), 84 (22), 82 (31), 79 (14), 70 (14), 69 (95), 47 (28), 43 (24), 42 (100), 41 (33), 39 (25); IR (CCl_4) 2225, 1805, 1680, 1200 cm^{-1}.

Preparation of 17a and 17b.[28]

Preparation of 18, 19, and 20. The procedure for the obtention of these products was the same as that for allylsilane addition. **18a** (X = OH) (20 %): bp 70 °C (0.8 torr); IR (CCl_4) 3360–2800, 3320, 2125, 1710 cm^{-1}. **19a** (X = OH) (30 %): bp 100 °C (0.8 torr); mass spectrum, m/e 184 (M^+, 4), 169 ($M^+ - CH_3$, 18) (HRMS calcd for $C_8H_{13}O_2Si$ 169.0684, found 169.069), 151 (14), 142 (9), 116 (18), 113 (79), 89 (32), 77 (18), 75 (100), 73 (30), 71 (20), 67 (18), 60 (86), 55 (21), 53 (20), 40 (41), 39 (23); IR (CCl_4) 3300–2800, 2210, 1715, 1250 cm^{-1}. **18b** (X = CN) (65 %): bp 50 °C (0.6 torr); IR (CCl_4) 3300, 2220, 1720 cm^{-1}. **18c** (X = CN) (80 %): bp 70 °C (0.4 torr); IR (CCl_4) 3300, 2220, 2120, 1710 cm^{-1}. **20c** (5 %): bp 85 °C (0.4 torr); ^{1}H NMR (CCl_4) δ 5.76 (1 H, s), 5.16 (1, d, J = 5.0 Hz), 1.10 (3, d, J = 7.0 Hz), 0.10 (9 H, s); mass spectrum, m/e 207 (M^+, 4), 192 ($M^+ - CH_3$) (HRMS calcd for $C_{10}H_{14}ONSi$ 192.0844, found 192.085), 165 (74), 147 (10), 145 (19), 137 (20), 129 (11), 120 (28), 108 (19), 105 (29), 104 (38), 103 (75), 102 (100), 93 (29), 91 (23), 84 (15), 75 (65), 73 (46), 69 (60), 67 (50), 41 (62), 39 (40); IR (neat) 2220, 1715, 1605, 1250 cm^{-1}. **19d** (X = CN) (60 %): bp 90 °C (0.15 torr); IR (CCl_4) 2225, 2180, 1690, 1250 cm^{-1}. **18e** (X = CN)(30 %): bp 70–75 °C (0.5 torr); IR (CCl_4) 3310, 2230, 2120, 1720 cm^{-1}. **19e** (X = CN) (20 %): bp 100 °C (0.5 torr); IR (neat) 2220, 2185, 1710, 1250 cm^{-1}. **18f** (X = CN) (75 %): bp 55 °C (0.2 torr); IR (CCl_4) 3310, 2230, 2120, 1720 cm^{-1}. **20f** (10 %): bp 80 °C (0.2 torr); ^{1}H NMR (CCl_4) δ 5.72 (1 H, d, J = 4.8 Hz), 5.57 (1, s), 1.48 (6, s), 1.32 (3, d, J = 7.0 Hz); mass spectrum, m/e 235 (M^+, 1) (HRMS calcd for $C_{13}H_{21}NOSi$ 235.1392, found 235.139), 220 (7) (HRMS calcd for $C_{12}H_{18}NOSi$ 220.1157, found 220.113), 192 (21), 146 (17), 93 (21), 91 (16), 75 (26), 73 (100), 70 (15), 58 (16), 43 (36), 41 (16); IR (CCl_4) 2240, 2230, 1720, 1680, 1655 cm^{-1}. (For H^1 NMR spectral data for **18** and **19** see Table VI.)

18g (X = CN) (55 %): bp 75 °C (0.15 torr); IR (CCl_4) 3305, 2220, 2110, 1730, 1710 cm^{-1}. **19g** (X = CN) (25 %): bp 80 °C (0.15 torr); IR (CCl_4) 2220, 2170, 1720, 1250 cm^{-1}. **20g** (10 %): bp 80 °C (0.15 torr): ^{1}H NMR (CCl_4) δ 5.68 (1 H, s), 5.56 (1, s), 1.53 (6, s), 1.27 (6, s), 0.20 (9, s). Stereochemistry E of the exocyclic double bond of **20g** was established using shift reagent Eufod; mass spectrum, m/e 249 (M^+, 3) (HRMS calcd for $C_{14}H_{23}NOSi$ 249.1548, found 249.155), 234 (10), 140 (22), 125 (16), 107 (22), 97 (23), 83 (42), 75 (20), 73 (100), 68 (40), 67 (43), 59 (43), 55 (18), 43 (18), 41 (26); IR (CCl_4) 2235, 2220, 1660, 1250 cm^{-1}.

Preparation of 21.[21]

Preparation of 22. 22a (25 %) (preparative GLC): ^{1}H NMR (CCl_4) δ 5.67 (1 H, s (br)), 5.43 (1, s), 5.02 (1, s), 1.95 (3, s (br), 1.07 (3, d, J = 7.0 Hz); IR (CCl_4)) 2220, 1720, 1650, 905 cm^{-1}. **22b** (35 %) (preparative GLC): ^{1}H NMR (CCl_4) δ 6.00 (1 H, s.), 5.57 (1, s (br)), 1.95 (3, s (br)), 1.10 (3, d. J = 7.0 Hz), 0.20 (9, s); mass spectrum, m/e 247 (M^+, 16) (HRMS calcd for $C_{14}H_{21}NOSi$ 247.1392, found 247.138), 232 (34), 204 (24), 175 (14), 160 (21), 148 (28), 147 (22), 133 (41), 121 (26), 106 (22), 105 (59), 91 (22), 77 (21), 75 (31), 73 (100), 45 (19); IR (CCl_4) 2225, 1710, 1650, 1250 cm^{-1}.

Preparation of 23 and 24. 23 + 24: bp 70–80 °C (0.2 torr). **23** (42 %): ^{1}H NMR (CCl_4) δ 7.83–7.10 (1 H, m), 6.26 (1, d, J = 16.0 Hz, t, J = 1.8 Hz), 2.30 (1, t. J = 2.0 Hz), 1.13 (3, d. J = 6.0 Hz); IR (CCl_4) 3320, 2225, 1670, 1630 cm^{-1}. **24** (30 %): ^{1}H NMR (CCl_4) δ 5.40 (2 H, m), 2.97 (2, d, J = 5.0 Hz), 2.30 (1, t, J = 2.0 Hz), 1.23 (3, d, J = 6.0 Hz); IR (CCl_4) 3320, 2225, 1710 cm^{-1}.

Preparation of 26, 27, and 28. 26b (65 %): bp 50 °C (0.6 torr); ^{1}H NMR (CCl_4) δ 6.3–5.07 (3 H, m), 3.63 (1, sextuplet, J = 6.5 Hz), 1.36 (3, d, J = 6.5 Hz); IR (neat) 2220, 1960, 1700, 850 cm^{-1}. **26c** (80 %): bp 60 °C (0.4 torr); ^{1}H NMR (CCl_4) δ 5.40–4.73 (3, m), 2.80 (2, m), 1.17 (3, d, J = 7.0 Hz); IR (CCl_4) 2220, 1960, 1720, 850 cm^{-1}. **26d** (80 %): bp 70 °C (0.5 torr); ^{1}H NMR (CCl_4) δ 5.85–4.87 (3 H, m.), 2.80 (2, s), 1.20 (6, s); IR (neat) 2225, 1960, 1715 cm^{-1}, **27 + 28**: 70–80 °C (0.2 torr). **27** (45 %): ^{1}H NMR (CCl_4) δ 7.76–7.10 (1 H, m), 6.26 (1, d, J = 16.0 Hz, t, J = 1.8 Hz), 5.17 (1, m), 4.80 (2, m), 1.10 (3, d, J = 6.0 Hz); IR (CCl_4) 2225, 1960, 1670, 1630, 850 cm^{-1}. **28**: ^{1}H NMR (CCl_4) δ 5.57 (2 H, m), 5.17 (1, m), 4.80 (2, m), 2.97 (2, d, J = 5.0 Hz), 1.23 (3, d, J = 7.0 Hz); IR (CCl_4) 2225, 1960, 1730, 850 cm^{-1}.

Preparation of 30–33. Titanium tetrachloride (1.9 g, 10 mmol) and anhydrous methylene chloride (20 mL) were cooled (−20 °C) and acyl cyanide (10 mmol) in anhydrous methylene chloride (10 mL) was added. The reaction mixture was cooled to −78 °C and alkynylsilane derivative (12 mmol) was added. The solution was allowed to stir at −78 °C for 1 h and at −35 °C for 16 h (70 h for addition on **1d**). The reaction mixture was poured into ice water followed by rapidly extractive workup with pentane. **30a** (55 %): bp 70 °C (0.7 torr); IR (neat) 2220, 1720 cm^{-1}. **30b** (55 %): bp

90 °C (0.8 torr); IR (neat) 2220, 1725 cm^{-1}. **30c** (65 %): bp 70 °C (0.4 torr); IR (CCl_4) 2215, 1720 cm^{-1}. **30d** (70 %): bp 100 °C (2.5 torr); IR (CCl_4) 2220, 1715, 1220–1210 cm^{-1}. **30e** (80%): bp 140 °C (0.2 torr); IR (CCl_4) 2220, 1720 cm^{-1}. **30f** (65 %): bp 70 °C (0.2 torr); mass spectrum, m/e 177 (M^+, 2) (HRMS calcd for $C_{11}H_{15}NO$ 177.1153, found 177.114), 162 (7), 108 (5), 69 (100), 57 (23), 43 (21); IR (CCl_4) 2215, 1720 cm^{-1}. **30g + 31**: bp 75 °C (2 torr). **30g** (55 %): IR (CCl_4) 2220, 1720, 1250 cm^{-1}. **31** (*Z* isomer) (6 %): ^1H NMR (CCl_4) δ 5.60 (1 H, s (br)), 1.17 (3, d, J = 7.0 Hz), 0.18 (9, s). **31** (E isomer) (3 %): ^1H NMR (CCl_4) δ 5.75 (1 H, s), 1.10 (3, d, J = 7.0 Hz), 0.18 (9, s); IR (CCl_4) 2220, 1720, 1600, 1250 cm^{-1}. (See Table VII for ^1H NMR spectral data for **30a–g**.)

Preparation of 33 and 34. The procedure is repeated with 3.8 g (20 mmol) of titanium tetrachloride and 11.4 g (50 mmol) of **32**, **33** and **34**: bp 90 °C (0.8 torr). **33** (40%): ^1H NMR (CCl_4) δ 7.40–6.70 (2 H, part AB of ABX_3pattern), 1.95 (3, d, J = 6.0 Hz), 1.65 (6, s), 0.13 (9, s); IR (CCl_4) 2170, 1700, 1630, 1250 cm^{-1}. **34a** (10 %): ^1H NMR (CCl_4) δ 5.47 (1 H, d, J = 3.0 Hz), 1.57 (6, s), 1.14 (3, d, J = 7.0 Hz), 0.17 (9, s); mass spectrum, m/e 233 ($M^+ - H_2O$, 1) (HRMS calcd for $C_{13}H_{19}NOSi$ 233.1235, found 233.121), 218 (9), 205 (7), 190 (10), 138 (16), 124 (14), 123 (100), 106 (9), 97 (8), 73 (33), 69 (27), 43 (10), 41 (9); IR (CCl_4) 3620, 3560–3200, 2240, 1250 cm^{-1}. **34b** (10%): ^1H NMR (CCl_4) δ 5.64 (1 H, d, J = 3.0 Hz), 1.69 (6, s), 1.37 (3, d, J = 7.0 Hz), 0.37 (9, s), 0.17 (9, s); mass spectrum, m/e 233 ($M^+ - OSiMe_3$, 1), 218 ($M^+ - OSiMe_3 - CH_3$, 5) (HRMS calcd for $C_{12}H_{16}NOSi$ 21.1001, found 218.099), 205 (3), 190 (11), 163 (4), 138 (11), 136 (10), 124 (14), 123 (100), 106 (7), 97 (11), 73 (24), 69 (32), 43 (7), 41 (8); IR (CCl_4) 2240, 2185, 1680, 1250 cm^{-1}.

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Synthesis of Potential Phenolic Metabolites of Benzo[*b*]fluoranthene[1,2]

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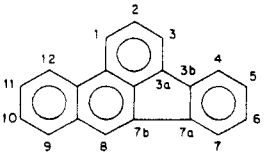
The syntheses of the 12 isomeric hydroxybenzo[*b*]fluoranthenes (hydroxy-BbF, 1–12) are described. 1-Hydroxy-BbF was prepared by treatment of 1-oxo-1,2,3,3a-tetrahydro-BbF (**13**) with Pd/C. 2-Hydroxy-BbF was synthesized by reduction of **13** with $NaBH_4$, followed by dehydration, epoxidation, and treatment with Pd/C. 3-Hydroxy-BbF was obtained by reduction of **13** with Zn(Hg) followed by oxidation with Triton-B, dehydration, epoxidation, and aromatization. 4-Hydroxy-BbF and 7-hydroxy-BbF were prepared by reaction of acephenanthrylene with 1-acetoxybutadiene, aromatization, hydrolysis, and separation by HPLC. 5-Hydroxy-BbF was synthesized by reaction of *o*-bromobenzaldehyde with 3-methoxyfluorene, followed by cyclization with KOH and quinoline, hydrolysis, and purification by HPLC. 6-Hydroxy-BbF was obtained by regiospecific cyclization of 3-methoxy-11*H*-benzo[*b*]fluorene-11-propionic acid (**33**), followed by reduction, dehydration, aromatization, and hydrolysis. 8-Hydroxy-BbF was synthesized by dehydration of 7b,8-dihydro-7b,8-dihydroxy-BbF (**39**). 9-Hydroxy-BbF and 12-hydroxy-BbF were prepared by treatment of the corresponding oxotetrahydro-BbFs with Pd/C. 10-Hydroxy-BbF and 11-hydroxy-BbF were synthesized by reaction of fluorene with the appropriate bromomethoxybenzaldehyde followed by cyclization with hydrolysis.

Polynuclear aromatic hydrocarbons (PAH) are metabolically converted to epoxides, dihydrodiols, phenols, tetrols, quinones, and a variety of related metabolites and conjugates. Some of these metabolites such as dihydrodiol epoxides and phenolic dihydrodiol epoxides are involved in the DNA binding properties and carcinogenic activities of PAH.[3] Thus, an understanding of PAH metabolism is important for determining the mechanisms by which they cause cancer. Benzo[*b*]fluoranthene (BbF) is a widely distributed environmental carcinogen.[4] It is metabolically converted in vitro and in vivo to dihydro diols, phenols, and other metabolites.[5,6] The dihydro diols have been identified by comparison to synthetic samples.[5,7] There are 12 possible phenols which can be formed from BbF. In this report, we describe the synthesis of these potential metabolites, **1–12**.



BbF

Results and Discussion

The starting material for the syntheses of 1-hydroxy-BbF (**1**), 2-hydroxy-BbF (**2**), and 3-hydroxy-BbF (**3**) was 1-oxo-1,2,3,3a-tetrahydro-BbF (**13**), which we had previously prepared by regiospecific cyclization of 11*H*-benzo[*b*]fluorene-11-propionic acid chloride.[7] Treatment of **13** with Pd/C yielded **1**. Reduction of **13** with $NaBH_4$ followed by dehydration and epoxidation with *m*-chloroperbenzoic acid gave **14**, which was treated with Pd/C to give **2**. 1-Hydroxy-BbF was not observed in this reaction. As an alternate approach to **2**, we investigated the reaction of 1,2-(dibenzoyloxy)-1,2,3,3a-tetrahydro-BbF with *p*-toluenesulfonic acid (PTSA), followed by hydrolysis and

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