Anal. Calcd m/e for $C_{12}H_{10}F_6O_3S$: 348.0254. Found: 348.0221.[73]

(*E*)-2-(4-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-yl Trifluoromethanesulfonate (37d). Compound **37d** was obtained in 49% yield from **38d** by using method B: IR (neat) 1680, 1494, 1420, 1281, 1248, 1220, 1141, 1051, 960, 940, 835 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.09 (2 H, m), 6.11 (1 H, q of t, J = 7.5 Hz, J' = 2 Hz), 7.20 (2 H, d, J = 8.7 Hz), 7.36 (2 H, d, J = 8.7 Hz).

Anal. Calcd m/e for $C_{11}H_7ClF_6O_3S$: 367.9709. Found: 367.9698.[73]

Determination of the Reaction Kinetics. Anhydrous trifluoroethanol purchased from Matheson Coleman and Bell was used directly without further purification. Solutions of the appropriate triflates or the tosylates were prepared at 0.003–0.005 M. The solutions were buffered with 2,6-lutidine at 0.0045–0.0075 M, respectively. The kinetics were determined conductimetrically in a 10-mL conductance cell, which was sealed for each run. The mathematical treatment of the rate data was that described by Bamford and Tippen where a weighted least-squares treatment was used to determine the first-order rate constants.[74]

Determination of Yields. The yields for the trifluoroethanolysis of triflates **30a–d** and tosylates **31a–d** were determined by VPC, using the method of internal standards. Two sealed tubes with a known amount of triflate or tosylate in trifluoroethanol, buffered with 2,6-lutidine, were solvolyzed for 8–10 half-lives. An exact amount of internal standard was added to each tube, and the product peak areas as compared to the area of the standard were determined with the aid of a Hewlett-Packard Model 3370A electronic integrator. Prior standardization of the solvolysis products vs. the internal standards allowed precise determination of the yields.

Determination of the Stability of 36 to the Reaction Conditions. A solution was prepared by dissolving 30 mg (0.1 mmol) of 3-(4-methylphenyl)-1,1,1-trifluorobut-3-en-2-yl 2,2,2-trifluoroethyl ether (**36**) in 10 mL of anhydrous trifluoroethanol (0.01 M), previously buffered to 0.005 M with 2,6-lutidine. To the solution was added 26 mg of 2,6-lutidinium trifluoromethanesulfonate (0.1 mmol) (prepared by adding trifluoromethanesulfonic acid to a solution of 2,6-lutidine in ether). The resulting solution was refluxed for a time equal to 10 half-lives. Monitoring the reaction by analytical VPC on a 10 ft × $^1/_8$ in. 5% XF-1150 on 45/60 Chrom W column and also a 10 ft × $^1/_8$ in. 15% DEGS on 60/80 Chrom P column showed no change in **36**.

Determination of the Stereochemical Stability of (*E*)- and (*Z*)-35b–d to the Reaction Conditions. The (*E*)-2-aryl-4,4,4-trifluorobut-2-en-1-yl 2,2,2-trifluoroethyl ethers **35b–d** were obtained pure by preparative VPC as described above. Trifluoroethanol solutions were prepared that were 0.01 M in each ether, 0.005 M in 2,6-lutidine, and 0.01 M in 2,6-lutidinium trifluoromethanesulfonate. The individual solutions were refluxed for a time equal to 10 half-lives, and no detectable isomerization was found.

In a related experiment, a solution of the triflate **30b** in trifluoroethanol, buffered with a 50% excess of 2,6-lutidine, was examined for product formation at 10%, 25%, 50% 75%, and 100% reaction. The ratio of (*E*)- and (*Z*)-**35b** was found qualitatively to be quite constant throughout the reaction.

Acknowledgment. We are indebted to the National Science Foundation for a grant that supported this investigation.

Registry No. **15**, 89619-07-8; **16**, 89619-09-0; **17**, 372-49-6; **18**, 89619-04-5; **19**, 89619-05-6; **20**, 89619-06-7; **22**, 89619-08-9; **23a**, 89618-98-4; **23b**, 89618-99-5; **23c**, 89619-00-1; **23d**, 89619-01-2; **23e**, 89619-02-3; **24a**, 29338-71-4; **24b**, 42107-37-9; **24c**, 98-81-7; **24d**, 89619-10-3; **24e**, 89619-13-6; **25a**, 89619-03-4; **25b**, 66520-90-9; **25c**, 6006-81-1; **25d**, 45941-96-6; **26**, 89619-11-4; **27**, 37614-59-8; **28**, 89619-15-8; **29**, 89619-16-9; **30a**, 89618-87-1; **30b**, 89618-88-2; **30c**, 89618-89-3; **30d**, 89618-90-6; **30e**, 89618-91-7; **31a**, 89618-92-8; **31b**, 89618-93-9; **31c**, 66303-64-8; **31d**, 89618-94-0; **32**, 2927-15-3; **33**, 89619-14-7; **34**, 6226-25-1; (*Z*)-**35a**, 89619-27-2; (*E*)-**35a**, 89619-28-3; (*Z*)-**35b**, 89619-23-8; (*E*)-**35b**, 89619-24-9; (*Z*)-**35c**, 89619-21-6; (*E*)-**35c**, 89619-22-7; (*Z*)-**35d**, 89619-25-0; (*E*)-**35d**, 89619-26-1; **36**, 89619-29-4; **37b**, 89618-95-1; **37c**, 89618-96-2; **37d**, 89618-97-3; **38b**, 89619-31-8; **38c**, 89619-30-7; **38d**, 89619-32-9; **42a**, 89619-20-5; **42b**, 89619-18-1; **42c**, 89619-17-0; **42d**, 89619-19-2; $H_2C{=}CHCH_2OTs$, 4873-09-0; p-$H_3COC_6H_4(CH{=}CH_2)$, 637-69-4; p-$H_3CC_6H_4(CH{=}CH_2)$, 622-97-9; $C_6H_5(CH{=}CH_2)$, 100-42-5; p-$ClC_6H_4(CH{=}CH_2)$, 1073-67-2; p-$F_3CC_6H_4(CH{=}CH_2)$, 402-50-6; 1-bromo-3,3,3-trifluoropropane, 460-32-2; ethyl trifluoroacetate, 383-63-1; ethyl bromide, 74-96-4; trifluoropropyne, 661-54-1; trifluoroacetaldehyde, 75-90-1; phenylacetylene, 536-74-3; formaldehyde, 50-00-0; (p-methoxyphenyl)acetylene, 768-60-5; 4-(trifluoromethyl)styrene, 402-50-6; 1-[4-(trifluoromethyl)phenyl]ethanol, 1737-26-4; 4-(1,2-dibromoethyl)benzotrifluoride, 89619-12-5.

(74) (a) "The Practice of Kinetics"; Bamford, C. H., Tippen, C. F. H., Eds.; Elsevier: New York, 1969; pp 364–377. (b) Weighting factor was $(C_\infty - C_t)^2$.

Vinylene 1,2-Bis(trifluoromethanesulfonates) from Azibenzils and Triflic Anhydride

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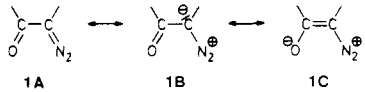
Received November 3, 1983

Trifluoromethanesulfonic anhydride reacts with azibenzil and its 4-Cl and 4-OMe derivatives (**2a–c**) to give predominantly 1,2-diarylvinylene 1,2-bis(trifluoromethanesulfonates) (*Z,E*)-**4a–c** besides small amounts of the corresponding benzils **5a–c**. The *Z* olefins are favored over their *E* isomers in all cases. The reaction begins with electrophilic attack on the oxygen of the diazo ketone by the anhydride; it represents a novel method of generating vinyl cations via vinyldiazonium ions.

According to their dominant resonance structures (**1A** ⇄ **1B** ⇄ **1C**), it is expected that α-diazo ketones exhibit ambident behavior toward electrophiles. C-Attack by the electrophile is the most frequently encountered reaction, with protons, acyl or silyl groups, metal ions, or halogen cations acting as electrophilic moieties.[1] Examples of O-attack include the kinetically controlled O-protonation,[2]



1A **1B** **1C**

(1) Regitz, M.; Maas, G. "Aliphatic Diazo Compounds"; Academic Press, in press.

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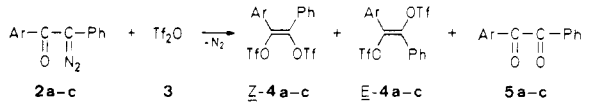
alkylation by Meerwein salts or carbenium ions,[3] and complexation by Lewis acids.[4]

In view of the well-established ability of trifluoromethanesulfonic anhydride (**3**) to transfer a trifluoromethanesulfonyl group to more or less polarized carbonyl groups[5-7] as well as to enolate systems,[8,9] we have investigated its reaction with azibenzils (1-diazo-1,2-diaryl-2-ethanones) **2a–c**. In case of electrophilic O-attack by the anhydride, this reaction would offer a novel entry into the chemistry of alkenediazonium and vinyl cations.

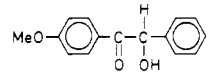
Results and Discussion

When azibenzils **2a–c** are allowed to react with trifluoromethanesulfonic anhydride (**3**, triflic anhydride, Tf_2O) in dichloromethane, nitrogen evolution takes place even well below room temperature. After column chromatography, 1,2-diarylvinylene 1,2-bis(triflates) (*Z*)-**4a–c** were obtained as major products, accompanied by small amounts of their isomers (*E*)-**4a–c** and benzils **5a–c**. The *E,Z* yields of **4a,b** given below are isolated yields, but the *Z*/*E* ratio of **4c** is likely to be higher than indicated by the isolated yields. Control experiments with each of the two diastereomers showed that (*Z*)-**4c** was partly hydrolyzed to the benzoin **6** when subjected to flash column chromatography over silica gel, whereas (*E*)-**4c** was recovered quantitatively. Also, the fact that **6** is detected (by TLC) directly after (*Z,E*)-**4c**, i.e., before other products with higher R_f values, in the original chromatographic separation of the reaction mixture, points to its formation by vinylene bis(triflate) hydrolysis on the silica gel column. This different solvolytic stability of (*Z*)- and (*E*)-**4c** is also confirmed, when methanol is the solvent (see below). The

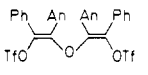


2a–c **3** Z-**4a–c** E-**4a–c** **5a–c**

Ar	Yield [%]		
a: Ph	83	3	3
b: 4-Cl-C_6H_4	55.5	9.5	6
c: 4-OMe-C_6H_4	~33	~4	12



6



7

An = MeO-

mechanism of benzil formation is not yet clear at present.

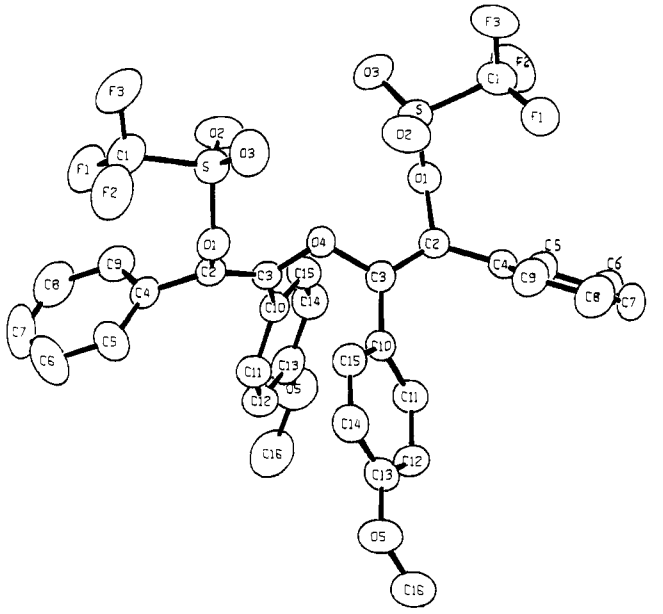


Figure 1. ORTEP drawing of **7**. The molecule has crystallographic C_2 symmetry, with O4 lying on the symmetry axis.

According to TLC control, the benzils **5a–c** are already present in the crude reaction mixtures rather than being formed during workup.

An additional product was isolated from the reaction mixture of **2c** with Tf_2O to which structure **7** was assigned by an X-ray analysis (Figure 1). A symmetrical structure was already indicated by the ^1H NMR spectrum (only one OMe signal and one AA'BB' system for the 4-methoxyphenyl group), and the *Z,Z* configuration was in accord with UV data (see below for the configurational assignment of the parent vinylene bis(triflates) (*Z,E*)-**4** by UV spectroscopy), but the positional interchange of the phenyl and anisyl groups was also considered possible a priori.

The configurational assignment of the vinylene bis(trifluoromethanesulfonates) could be established by comparison of the UV spectra with those of *cis*- and *trans*-stilbene[10] (see Table I). In the *Z* series, two UV maxima are present, of which the one at shorter wavelength has the more intense absorption. For the *E* olefins, only the long-wave absorption is observed, its intensity being higher than that of the corresponding absorption in the *Z* olefins but lower than in *trans*-stilbene. Similar features have been found in α,α'-dialkyl derivatives of *cis*- and *trans*-stilbene.[10] Also, α,α'-dialkoxy-substituted stilbenes exhibit the same intensity characteristics as our compounds, even though two absorptions were observed for both *Z* and *E* isomers.[11] Another noteworthy difference betwen the two stereoisomers is apparent in the ^1H NMR spectra. It has been found earlier, that (*Z*)-α,α'-dimethoxystilbene shows a "singlet" for the aromatic protons, whereas for the *E* isomer, a broad multiplet is observed.[12] The same distinction is valid for the *E* and *Z* isomers of **4a–c**.

E and *Z* olefins can often be interconverted photochemically in the presence of a sensitizer. Indeed, benzophenone-sensitized irradiation of (*Z*)-**4a** or (*Z*)-**4b** leads to a mixture of (*Z,E*)-**4a** or (*Z,E*)-**4b** besides small amounts of the corresponding diaryl acetylene; the reaction is, however, accompanied by extensive decomposition.[13]

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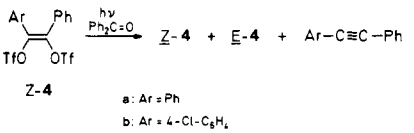
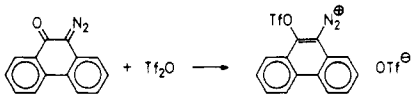


Z-4

a: Ar = Ph
b: Ar = 4-Cl-C$_6$H$_4$

In a formal sense, 9,10-phenanthrenequinone-10-diazide (8) can be looked at as a bridged azibenzil; reaction with



8 9

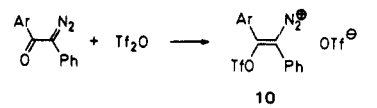
Tf_2O, however, does not produce a vinylene bis(triflate) but the diazonium salt **9** in high yield. **9** is clearly characterized as an arenediazonium salt by its IR band at 2283 cm^{-1} for the CN_2^+ stretching vibration, which is in the typical range for such compounds.[14]

It should be mentioned that this reaction represents a novel access to the synthetically important class of arenediazonium salts, with possible applications to other *o*- or *p*-benzoquinone diazides.[15]

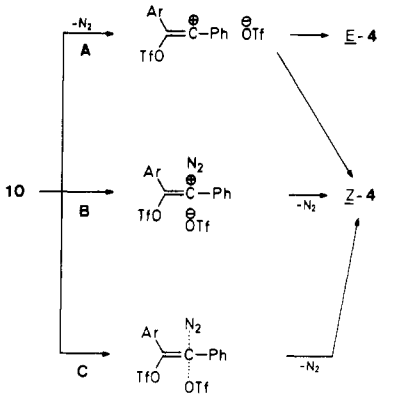
A mechanistic scheme (Scheme I) for the formation of vinylene 1,2-bis(triflates) **4** begins with an electrophilic attack of the trifluoromethanesulfonyl group on the oxygen atom of the α-diazo ketone. The concurrent sulfonylation at the nucleophilic diazo carbon is not observed. The alkenediazonium salts **10**, formed by O-sulfonylation, can then lose nitrogen with formation of a vinyl cation, which finally reacts with the triflate ion to yield **4**. Vinyl cation generation via a vinyldiazonium ion has been observed in a few other cases before.[16,17] The instability of **10** compared with **9** may be correlated with the anticipated energy level of the resulting vinyl cations; contrary to the vinyl cation derived from **10**, the positive charge in the vinyl cation resulting from **9** cannot be stabilized by delocalization into the orthogonally fixed π-system.

An explanation for the observed highly stereoselective formation of (*Z*)-**4a–c** must take into consideration the fact that azibenzil exists in only one conformation even at −90 °C according to its NMR spectrum.[18] LIS experiments showed this to be the *s*-trans conformation which was also found in the solid state by an X-ray analysis.[18] Therefore, the vinyldiazonium ion **10** formed by O-sulfonylation of **2** must exist in the *E* form (Scheme I). Several possibilities now exist for the transformation of **10** into the products. As much evidence has been assembled for a linear geometry of open-chain vinyl cations,[19] the intermediacy of a free vinyl cation (path A) should cause formation of both *E* and *Z* olefins. Preferential capture of a 1,2-diaryl-substituted vinyl cation from its least hindered side by an anion has been observed,[20] and the high preference for attack from the side of the trifloxy group (leading to *Z* olefins) may be the consequence of steric shielding of the

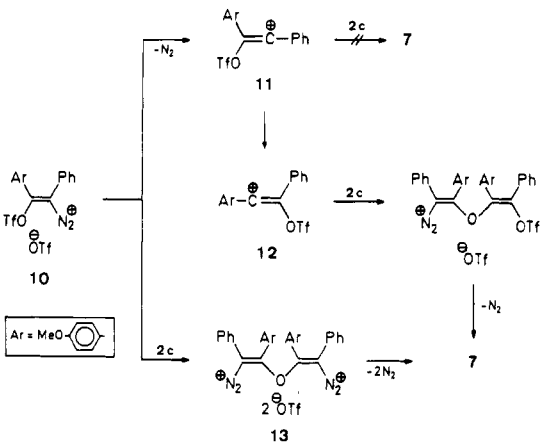
Scheme I



10



Scheme II



10 11 12 13

opposite side by the β-aryl ring lying in-plane with the vinylic system. This mechanistic pathway may be accompanied by the collapse of a vinyl cation/triflate ion pair, before the N_2 molecule liberated from **10** has completely left the coordination sphere of the vinyl cation (path B). The shielding of the β-aryl side in the vinyl cation by the leaving dinitrogen group would lead to exclusive formation of *Z* olefins along this pathway. An ion–molecule pair seems not very likely in view of the neutral leaving group N_2; on the other hand, its formation may be supported by the β-trifloxy group which destabilizes the vinyl cation and hence decreases its lifetime as a free ion.

An alternative to the ion-pair mechanism (path B), namely, a nucleophilic displacement of N_2 in **10** by the triflate ion with inversion of configuration (vinyl equivalent of an S_N2 reaction), is highly unlikely in view of the low nucleophilicity of the anion; up to now, such an S_N2-type displacement has never been observed in neutral vinylic systems.[21]

Our experiments furnished *Z*/*E* ratios of ca. 28, 6, and 9 for the vinylene bis(triflates) **4a–c**. Significant differences have also been found when the corresponding vinylene bis(nonaflates) were prepared from azibenzils and nonafluorobutanesulfonic anhydride.[22] Taking into account that these ratios result from isolated yields of the isomers and perhaps do not represent the true isomer

(13) For this reason, isomerization of the *E* to the *Z* isomers was not tried with the small quantities of *E* isomers which were at hand.
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Table I. Spectral Data of Compounds 4

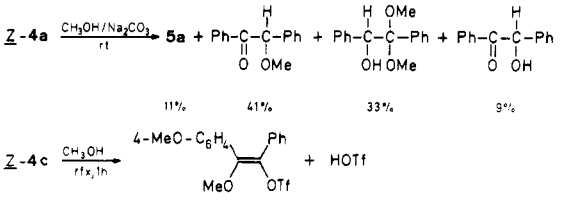
compd	UV[a] λ_{max}, nm (log ϵ)	^{1}H NMR,[b] ppm	^{13}C NMR,[b] ppm	^{19}F NMR,[c] ppm	IR,[d] cm^{-1} C-O-SO_2R	IR,[d] cm^{-1} others
(*Z*)-**4a**	220 (4.30), 267 (4.11)	7.36 (s)	118.5 (q, CF_3, $^1J_{CF}$ = 317.2 Hz), 129.2 and 129.9 (*o*-, *m*-C), 129.6 (ipso-C), 131.4 (*p*-C), 141.4 (C-olefin)	88.2	1440–1420 (br, s)	1605 (vw), 1585 (vw), 1240–1210 (br, s), 1135, 1048, 1002 (all s)
(*E*)-**4a**	259 (4.27)	7.40–7.86 (m)		87.8	1430, 1420 (s)	1628 (w), 1592 (w), 1270, 1245–1210 (br, vs), 1140, 1038, 1032 (all vs)
(*Z*)-**4b**	227.5 (4.32), 274 (4.12)	7.1–7.45 (m)	118.7 (q, CF_3, $^1J_{CF}$ = 320.3 Hz), 128.3, 129.4, 129.7, 130.0, 130.9, 131.2, 131.7, 137.9 (C-Cl), 140.4 and 141.8 (C-olefin)	88.12, 88.20	1439 (s)	1605 (w), 1230 (br, vs), 1145 (vs), 1105 (s), 1052 (s), 1003 (vs)
(*E*)-**4b**	266 (4.32)	7.43–7.80 (m)		87.72, 87.80	1445, 1431 (s)	1600 (m), 1245–1205 (br, vs), 1136 (vs, 1098, 1045, 1032 (all s), 992, 906 (vs)
(*Z*)-**4c**	232 (4.29), 289.5 (4.11)	3.77 (OMe), 6.81, 7.20 (AA'BB'), 7.30 (s, 5 H)	55.4 (OMe), 118.7 (q, CF_3, $^1J_{CF}$ = 320.3 Hz), 114.8, 121.6, 129.2, 130.0, 130.1, 131.2, 131.7, 140.1 and 141.6 (C-olefin), 162.2 (*p*-C-anisyl)	88.5	1445, 1435 (s)	1620 (s), 1525 (s), 1319 (s), 1270 (s), 1233 (br, vs), 1183, 1142, 1047, 1033, 1020, 994 (all s)
(*E*)-**4c**	280 (4.29)	3.90 (OMe), 7.03, 7.68 (AA'BB'), 7.43–7.70 (m, 5 H)		87.56, 87.64	1428 (s)	1620 (s), 1520 (m), 1315 (s), 1270 (s), 1250, 1232, 1218 (all s), 1183 (s), 1143, 1040 (vs)

[a] (*E*)-**4a** and (*E*)-**4c** in ethanol, all others in cyclohexane. [b] In $CDCl_3$, internal Me_4Si. [c] In $CDCl_3$, internal C_6F_6. [d] KBr pellets.

distribution in synthesis because of the lability of single isomers under workup conditions (as described above for (*Z*)- and (*E*)-**4c**), we cannot be sure at present about the influence of para substituents on the *Z*/*E* ratio of the vinylene bis(triflates). If such an influence really exists, it cannot affect the stereoselective approach of the triflate anion on a linear vinyl cation (path A). A rather weak electronic stabilization of a vinyl cation by β-aryl groups is, however, conceivable, which should increase in the order 4-ClC_6H_4 < 4-HC_6H_4 < 4-$OCH_3C_6H_4$ and could be operating in a mechanism according to path B. This ion–molecule pair mechanism will become the less important the more stabilized a vinyl cation is, thus giving place to the free vinyl cation route (path A). The amount of (*E*)-**4** should, therefore, increase in the given sequence. However, the isomer ratios of **4b** do not fit these expectations.

The formation of the divinyl ether **7** is remarkable, as it does not arise from reaction of excess diazo compound **2c** with the primarily formed vinyl cation **11**, which would lead to an unsymmetrical product (Scheme II). The vinyl cation route requires the presence of **12**, which could arise from the less stabilized **11** by trifloxy group migration. Another possibility is the attack of diazo compound **2c** on the vinyldiazonium ion **10** to give the bis(vinyldiazonium) ion **13**, from which **7** is available in a manner which is analogous to vinylene bis(triflate) formation. The latter mechanism is supported by the well-known β-attack of nucleophiles on alkenediazonium salts.[3]

The vinylene 1,2-bis(triflates) **4** are crystalline, stable compounds. When heated in refluxing mesitylene (164 °C), they decompose with evolution of SO_2 to yield quantitatively the corresponding benzils **5**. Preliminary solvolysis experiments display a different behavior of **4a** and **4c**. (*Z*)-**4a** was found not to be solvolyzed in boiling methanol; in Na_2CO_3-buffered methanol, however, it yields



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benzil, benzoin methyl ether, benzoin dimethyl ketal, and benzoin at room temperature. (*Z*)-**4c**, on the other hand, is converted to enol ether **14**, which has *Z* configuration according to its UV spectrum. This reaction is rather slow at room temperature but proceeds readily in boiling methanol. The replacement of only one triflate group in (*Z*)-**4c** by OMe, as well as the stability of (*Z*)-**4a** in neat methanol, reflect the higher stability of α-anisyl vs. β-anisyl and α-phenyl substituted vinyl cations which are intermediates in the solvolysis of vinyl triflates. (*E*)-**4c** reacts much slower in methanolysis than its *Z* isomer. Even after 10.5 h in boiling methanol, unsolvolyzed material was detected by TLC. This is in contrast to the acetolysis of structurally related α,β-dibromo-4,4'-dimethoxystilbenes, where $k_Z < k_E$.[20a]

Experimental Section

All melting points were determined in a heat block and are

uncorrected. The following instruments were used: ^1H NMR spectra, Varian EM 390; ^{19}F NMR spectra, Varian EM 390, chemical shifts relative to hexafluorobenzene; ^{13}C NMR spectra, Bruker WP 200, tetramethylsilane as internal standard; IR spectra, Beckman Acculab 3; UV spectra, GCA/McPherson instrument; mass spectrum, Varian MAT 311; elemental analyses, Perkin-Elmer Analyzer 240. All reactions were carried out in a nitrogen atmosphere in dry solvents. Triflic anhydride (**3**)[23] was redistilled from P_2O_5 if not used for several days. Separation of product mixtures was done by column chromatography on silica gel (0.063–0.2 mm), which had been heated to 175 °C/0.03 mmHg for 8 h. So-called flash chromatography[24] (nitrogen pressure, column size 3 × 100 cm, elution time ca. 15–30 min) was applied in some cases.

Reaction of 2a with Triflic Anhydride. To a solution of 2.00 g (9 mmol) of azibenzil[25] in 150 mL of dichloromethane, cooled to −65 °C, was added 2.54 g (9 mmol) of **3** in 10 mL of dichloromethane slowly. The reaction mixture was allowed to warm up to room temperature and kept there for 1.5 h. The solvent was removed at 14 mmHg, and the dark residue was separated by flash chromatography with 2400 mL of $CHCl_3$: (a) 3.68 g of a mixture of (*Z*)- and (*E*)-4a; (b) 0.06 g (3%) of benzil **5a**. The mixture of (*Z,E*)-**4a** was dissolved in 80 mL of refluxing pentane. From this solution, (*E*)-1,2-diphenylvinylene 1,2-bis(trifluoromethanesulfonate) (*E*-**4a**) crystallized after 1 day at room temperature (0.135 g = 3%): mp 169 °C (from ether). Anal. Calcd for $C_{16}H_{10}F_6O_6S_2$ (476.4): C, 40.34; H, 2.12. Found: C, 40.2; H, 2.25. From the mother liquor, 3.54 g (83%) of (*Z*)-**4a** were obtained: mp 67 °C (from pentane); mass spectrum (70 eV), *m/e* (relative intensity) 476 (1.5, M^+), 343 (12, $M^+ - CF_3SO_2$), 278 (2), 250 (9, $M^+ - CF_3SO_3$,Ph), 210 (4, $M^+ - 2CF_3SO_2$), 194 (5, $M^+ - CF_3SO_2$, CF_3SO_3), 178 (5, $M^+ - 2CF_3SO_3$), 165 (18), 105 (100, PhCO), 77 (55, Ph). Anal. Calcd for $C_{16}H_{10}F_6O_6S_2$ (476.4): C, 40.34; H, 2.12. Found: C, 40.70; H, 2.25.

Reaction of 2b with Triflic Anhydride. The solution of 2.20 g (7.8 mmol) of triflic anhydride in 10 mL of dichloromethane was added dropwise at −50 °C to 2.00 g (7.8 mmol) of **2b**[26] in 40 mL of dichloromethane. Stirring at −50 °C was continued for 1 h, before the solution was allowed to warm up to room temperature. The solvent was removed in vacuo, and the residue was subjected to flash column chromatography (250 g of silica gel, 1100 mL of pentane/ether, 10:1, v/v): (a) 2.59 g (65%) of partly separated (*E,Z*)-**4b**; (b) 0.12 g (6%) of *p*-chlorobenzil. Complete separation of the (*E,Z*)-mixture of **4b** was effected by MPLC (eluent: pentane/ether, 10:1, v/v), the *E* isomer being eluted first. (*E*)-1-(4-Chlorophenyl)-1-phenylvinylene 1,2-bis(trifluoromethanesulfonate) (*E*-**4b**); total yield 0.365 g (9.5%); mp 105 °C. Anal. Calcd for $C_{16}H_9ClF_6O_6S_2$ (510.8): C, 37.62; H, 1.78. Found: C, 37.5; H, 1.88. *Z*-**4b**: total yield 2.225 g (55.5%); mp 40 °C. Anal. Calcd for $C_{16}H_9ClF_6O_6S_2$ (510.8): C, 37.62; H, 1.78. Found: C, 37.8; H, 1.86.

Reaction of 2c with Triflic Anhydride. The solution of 3.00 g (12.1 mmol) of **2c**[27] in 30 mL of dichloromethane was added dropwise to 3.40 g (12.1 mmol) of triflic anhydride in 40 mL of dichloromethane, kept at −40 °C. After being stirred for 2.5 h, the reaction mixture was allowed to warm up to room temperature, stirred with 5 g of Na_2CO_3, and filtered. The solvent was removed in vacuo, and the residue was separated by flash column chromatography (250 g of silica gel, 6000 mL of $CHCl_3$): (a) 2.26 g (37%) of a mixture of (*E,Z*)-**4c**, isomer ratio 9:1 (by NMR); (b) 0.20 g of an unidentified compound which could not be purified because of decomposition; (c) 0.084 g (9%) of bis[1-(4-methoxyphenyl)-2-phenyl-2-[[(trifluoromethyl)sulfonyl]oxy]vinyl] ether (**7**) [mp 137 °C (from pentane/ether); IR (KBr) 1663 (w), 1615, 1520, 1430, 1309 (all s), 1260 (vs), 1222 (vs, br), 1182 (s), 1144 (vs), 1092, 1079, 1038 (all s), 985 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.75 (s, OMe), 6.64 and 6.83 (AA′BB′), 7.17 (H-phenyl); UV (cyclohexane) λ_{max} 232 nm (log ϵ 4.48), 294 (4.33). Anal. Calcd for $C_{32}H_{24}F_6O_9S_2$ (730.7): C, 52.6; H, 3.31. Found: C, 52.7; H, 3.45]; (d) 0.36 g (12%) of 4-methoxybenzil (**5c**).

When the reaction between **2c** and triflic anhydride was carried out with inverse addition of the components, the following results were obtained: (*E,Z*)-**4c** (14%); 4-methoxybenzoin (**6**) (6%), mp 105–106 °C (lit.[28] 105.5–106.5 °C); **7** (6%); and **5c** (8.4%).

Separation of the *E,Z* mixture of **4c** was done by flash column chromatography with pentane/ether (4:1, v/v). From 2.26 g of this mixture, we obtained (a) (*E*)-1-(4-methoxyphenyl)-2-phenylvinylene 1,2-bis(trifluoromethanesulfonate) (*E*-**4c**) [0.25 g, mp 118 °C. Anal. Calcd for $C_{17}H_{12}F_6O_7S_2$ (506.4): C, 40.32; H, 2.39. Found: C, 40.3; H, 2.46] and (b) (*Z*)-**4c** [1.67 g, mp 88 °C. Anal. Calcd C, 40.32; H, 2.39. Found: C, 40.5; H, 2.48].

In two separate control experiments, 72 mg of either (*E*)-**4c** or (*Z*)-**4c** were subjected to flash column chromatography (40 g of silica gel, 200 mL of pentane/ether, 4:1, v/v). For (*E*)-**4c**, 71 mg of unchanged material were recovered; (*Z*)-**4c** gave only 59 mg back; and 4-methoxybenzoin (**6**) was detected by TLC.

Photosensitized Isomerization of (*Z*)-4a. The solution of 1.00 g of (*Z*)-**4a** and 2.3 g of benzophenone in 50 mL of anhydrous benzene was irradiated (Philips HPK 125 W) for 3 h in a nitrogen atmosphere. Separation of the mixture by column chromatography with pentane/dichloromethane (4:1, v/v) gave (a) 20 mg (5%) of diphenylacetylene, (b) 266 mg (27%) of (*E*)-**4b**, and (c) 336 mg (34%) of (*Z*)-**4b**.

Photosensitized Isomerization of (*Z*)-4b. A similar treatment as described above for (*Z*)-**4a** yields (0.40 g of (*Z*)-**4b**, irradiation time 1.5 h): (a) 13 mg (8%) of (4-chlorophenyl)-phenylacetylene, (b) 44 mg (11%) of (*E*)-**4b**, and (c) 47 mg (12%) of (*Z*)-**4b**.

10-[[(Trifluoromethyl)sulfonyl]oxy]phenanthrene-9-diazonium Trifluoromethanesulfonate (9). Triflic anhydride (2.00 g, 7.1 mmol) was added dropwise to a solution of 1.50 g (7.1 mmol) of **8**[29] in 100 mL of dichloromethane chilled to 0 °C. After addition was completed, the mixture was stirred for another 30 min. Precipitation of the diazonium salt was completed by cooling to −50 °C and addition of 100 mL of ether. The mixture was then filtered with suction and the solid washed with cold ether to yield 2.75 g of yellow **9**: mp 86 °C dec. From the mother liquor, which was concentrated to a volume of 30 mL and allowed to stand at −70 °C, another 0.36 g of **9** was obtained: total yield 3.11 g (87%); IR (KBr) 2283 (s, CN_2), 1620 (m), 1453, 1391 (both s), 1265 (br, vs), 1185 (sh), 1170 (vs), 1137, 1085, 1056 (all s), 1041 (vs) cm^{-1}; ^1H NMR (CD_3CN) δ 7.95–8.47 (m, 6 H), 8.86–9.08 (m, 2 H); ^{19}F NMR (CD_3CN) δ 84.3 (anionic CF_3SO_3), 92.1 (covalent CF_3SO_3). Anal. Calcd for $C_{16}H_8N_2F_6O_6S_2$ (502.4): C, 38.25; H, 1.61; N, 5.58. Found: C, 37.4; H, 1.68; N, 5.5.

Thermal Decomposition of 4a–c. A solution of 1 mmol of **4** in 15 mL of xylene was heated to reflux for 3.5 h during which time SO_2 evolution was observed (detection by passing the gas through an aqueous solution of $BaCl_2$, redissolving the precipitate ($BaSO_3$) by concentrated HCl, and precipitation of $BaSO_4$ after oxidation with hydrogen peroxide). After evaporation of the solvent, the corresponding benzil **5** was obtained in quantitative yield.

Solvolysis of (*Z*)-4a in Methanol. A solution of 1.00 g of (*Z*)-**4a** in 25 mL of methanol was stirred for 13 h at room temperature in the presence of Na_2CO_3 (2.00 g). The residue, which remained after filtering and removal of the solvent, was separated by flash column chromatography on 85 g silica gel. Elution with 2800 mL of pentane/ether (4:1, v/v) gave (a) 47 mg (11%) of benzil; (b) 193 mg (41%) of benzoin methyl ether, mp 47 °C (lit.[30] mp 48–49 °C); (c) 181 mg (33%) of benzoin dimethyl ketal, purified by Kugelrohr distillation at 135 °C (0.03 mmHg) [IR (KBr) 3610–3460 (OH, s, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.77 (d, ^3J = 2.5 Hz, OH), 3.26 and 3.50 (both s, diastereotopic OMe groups), 5.09 (d, ^3J = 2.5 Hz), 6.79–7.42 (m, 10 H). The compound was identified by comparison with an independently prepared sample.[30] Subsequent elution of the column with 300 mL of ether/methanol (4:1, v/v) gave 41 mg (9%) of benzoin.

Solvolysis of (*Z*)-4c in Methanol. The solution of (*Z*)-**4c** (389 mg) in 30 mL of methanol was refluxed for 1 h. Back at room

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temperature, the solution was neutralized with solid Na_2CO_3 (0.5 g). After filtering and removal of the solvent, pentane was added to the residue. Upon cooling, 258 mg (86%) of (*Z*)-2-(4-methoxyphenyl)-2-methoxy-1-phenylvinyl trifluoromethanesulfonate (**14**) were obtained; mp 52–53 °C; IR (KBr) 1666 (m), 1617 (m), 1522 (s), 1422 (s), 1315/1306 (m), 1267, 1248, 1228, 1211 (all vs), 1182, 1144, 1103, 1013, 967 (all s) cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 234 nm (4.21), 289 nm (4.07); ^1H NMR ($CDCl_3$) δ 3.52 (s, 3 H), 3.79 (s, 3 H), 6.83 and 7.18 (AA'BB'), 7.20 (s, 5 H); ^{19}F NMR ($CDCl_3$) δ 87.7. Anal. Calcd for $C_{17}H_{15}F_3O_5S$ (388.4): C, 52.58; H, 3.89. Found: C, 52.6; H, 3.95.

X-ray Analysis of 7. Crystal data: monoclinic space group $C2/c$; a = 20.175 (5) Å, b = 9.475 (7) Å, c = 18.279 (4) Å, β = 101.78 (2)°; 4 molecules per unit cell, calculated density D_x = 1.419 g cm^{-3}. **Data collection**: CAD4 automated diffractometer, monochromatized Mo Kα radiation, crystal size 0.70 × 0.25 × 0.23 mm. Two asymmetric units were measured in the range $2 \leq \theta \leq 22°$, which after averaging gave 2907 unique reflections. Scan width (0.70 + 0.35 tan θ)°, scan speed 1.33–4.0 deg min^{-1}. The average intensity loss of three monitoring reflections was 1.6% which was corrected linearly. No absorption correction was applied. **Structure solution and refinement**: The phase problem was solved with MULTAN82. Missing heavy atoms and hydrogen atoms were located in ΔF maps. The heavy atoms were refined anisotropically, the H atoms isotropically with the fixed B value of their bond neighbors. Full matrix refinement (2326 reflections with $I > 2(I)$, unit weights) converged at R = 0.045, R_W = 0.041. The largest shift/error ratio was 0.30 for heavy atoms and 0.68 for H atoms at this point. Final coordinates, temperature factors, and bond geometry tables are found in the supplementary material. All calculations were done with the Enraf Nonius SDP package on a PDP 11/23 plus computer.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. We thank Prof. Zvi Rappoport for a discussion.

Registry No. 2b, 3493-18-3; **2c**, 3580-75-4; (*Z*)-**4a**, 89849-96-7; (*E*)-**4a**, 89849-97-8; (*E*)-**4b**, 89849-98-9; (*Z*)-**4b**, 89849-99-0; (*E*)-**4c**, 89850-00-0; (*Z*)-**4c**, 89850-01-1; **5a**, 134-81-6; **5b**, 22711-23-5; **5c**, 22711-21-3; **6**, 4254-17-5; **7**, 89850-02-2; **8**, 7509-44-6; **9**, 89850-04-4; **14**, 89850-05-5; PhC≡CPh, 501-65-5; *p*-ClC_6H_4C≡CPh, 5172-02-1; azibenzil, 3469-17-8; triflic anhydride, 358-23-6; benzoin methyl ether, 3524-62-7.

Supplementary Material Available: Tables of postional and thermal parameters of **7**, bond distances and angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Notes

Activated Alkynes as Partners in Pictet–Spengler Condensations

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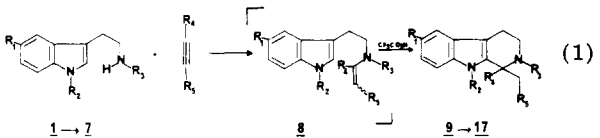
Received January 4, 1984

One of the most useful syntheses of tetrahydro-β-carbolines is the Pictet–Spengler condensation of tryptamines with ketones or aldehydes.[2] Its generally accepted mechanism involves a cationic cyclization of an iminium ion on the indole nucleus and, in principle, any enamine preparation ought to be applicable to a tetrahydro-β-carboline synthesis. The purpose of this paper is to propose an alternative to the Pictet–Spengler reaction on the basis of the condensation of tryptamines with suitable alkynes.

Reaction of tryptamines **1** → **7** with dimethyl acetylenedicarboxylate (DMAD) and of **7** with methyl propiolate or butynone yields enamines **8** as shown by ^1H NMR of the crude reaction mixtures. Protonation of these enamines brought about by an excess of trifluoroacetic acid leads directly to 1,2,3,4-tetrahydro-β-carbolines **9** → **17** (eq 1, Table I) in yields ranging from 76% to 99.5%. The overall sequence can be accomplished in ca. 30 min.



(1)

Starting materials are either commercially available (**1**, **5**) or prepared according to the literature (**2**,[4] **3**,[5] **4**,[6] **7**[7]). Methyl *N*-(2-(3-indolyl)ethyl)glycinate (**6**) is prepared by reductive condensation of tryptamine with methyl glyoxylate after thermal depolymerization of the reagent.[8]

The structure of compounds **9** → **17** are supported by their spectral properties as well as by combustion analysis or by high-resolution mass spectroscopy. Usual preparations of the corresponding monoester compounds involve the tedious use of the mono ethyl ester of oxaloacetic acid;[9] the diethyl ester corresponding to **9** has previously been prepared from tryptamine and diethyl oxaloacetate.[9] It is worth noting that, in our hands, Pictet–Spengler reactions between N_a-methyltryptamines **3** and **4** and carbonyl partners gave poor and irreproducible yields.

Experimental Section

General Procedures. All melting points were determined on a Koffler apparatus and are corrected; IR spectra were recorded on a Beckmann Acculab 2 spectrometer and UV spectra on a LERES-SPILA S28 photometer; ^1H NMR spectra were measured on a Perkin-Elmer R12B spectrometer (60 MHz) or on a IEF 400 instrument, a prototype built at the University of Orsay (401 MHz). Mass spectra were recorded on a JEOL D300 spectrometer. Elemental analysis were performed by the Microanalysis Department of the Faculty of Sciences of Reims.

Typical Procedure for Pictet–Spengler Reactions. Preparation of 15. To a solution of N_b-benzyltryptamine (**7**;

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