yl]propanoate (25), and Ethyl α-(Benzyloximino)-β-[2-(ethylthio)-3-(1,1-dimethyl-2-propenyl)indolen-3-yl]-propanoate (26). Ethyl α-(Benzyloximino)-β-[2-(ethylthio)indol-3-yl]propanoate. A solution of benzyl bromide in dimethoxyethane (1 mL) was added dropwise to a stirred solution of **9b** (1.5 mmol, 0.46 g) in dimethoxyethane (10 mL) at room temperature. Stirring in an argon atmosphere was continued for 4 h at room temperature. Then the solvent was removed in vacuo. A solution of the residue in CH_2Cl_2 was washed with 1 N HCl and with brine and subsequently dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to flash column chromatography (CH_2Cl_2) to give the *O*-benzyl derivative of **9b** in 74% (0.44 g) yield. Spectroscopical data are identical with those reported previously.[6]

Dimethylallyl bromide (2.5 mmol, 0.350 g) was added portionwise to a solution of the *O*-benzyl derivative of **9b** (0.25 mmol, 0.099 g) and suspension of K_2CO_3 (0.25 mmol, 0.035 g) in dry acetone (10 mL). After 2 weeks the reaction mixture was filtered and the solvent evaporated. Flash column chromatography gave **25** (48%, 0.056 g) and a mixture of **23b** and **26** in a ratio of 3:2 (41%, 0.047 g). HPL-chromatography of the latter fraction gave **26** slightly contaminated with **23b** and pure **23b**.

Compound 23b: oil, homogeneous on TLC, R_f 0.53 ($MeOH/CH_2Cl_2$, 1/99, v/v); UV (MeOH) λ_{max} 304 (sh), 291 (sh), 282, 218 (sh), 202 nm, λ_{min} 258 nm; EIMS (70 eV), *m/e* (relative intensity) 464 ($[M]^+$, 61), 396 ($[C_{22}H_{24}N_2O_3S]^+$, 36), 357 ($[C_{20}H_{25}N_2O_2S]^+$, 10), 289 ($[C_{15}H_{17}N_2O_2S]^+$, 29), 190 ($[C_{11}H_{12}NS]^+$, 28), 215 (26), 91 ($[C_7H_7]^+$, 100); exact mass calcd for $C_{27}H_{32}N_2O_3S$ 464.2134, found 464.2128; ^1H NMR (90 MHz, $CDCl_3$) δ 7.49–6.91 (m, 4 H, indolenine C(4)–C(7)*H*), 7.33 (s, 5 H, C_6H_5), 5.18 (s, 2 H $OCH_2C_6H_5$), 4.40 (m, 1 H, ^3J = 6 Hz, indolenine C(3)CH_2CH=), 4.11 (q, 2 H, OCH_2CH_3), 3.23 (q, 2 H, S-CH_2CH_3), 3.26 and 2.94 (AB spectrum, $^2J_{AB}$ = 12.6 Hz, 2 H, indolenine C(3)CH_2), 2.53 (m, 2 H, indolenine C(3)CH_2CH=), 1.43 (s, 6 H, CH=C(CH_3)$_2$), 1.37 (t, 3 H, SCH_2CH_3), 1.18 (t, 3 H, OCH_2CH_3).

Compound 25: oil, homogeneous on TLC, R_f 0.75 ($MeOH/CH_2Cl_2$, 1/99, v/v); UV (MeOH) λ_{max} 293 (sh), 285, 224, 202 nm, λ_{min} 259, 213 nm; EIMS (70 eV), *m/e* (relative intensity) 464 ($[C_{27}H_{32}N_2O_3S]^+$, 56), 357 ($[C_{20}H_{25}N_2O_2S]^+$, 8), 258 ($[C_{16}H_{20}NS]^+$, 6), 190 ($[C_{11}H_{12}NS]^+$, 26), 149 (36), exact mass calcd for $C_{27}H_{32}N_2O_3S$ 464.2134, found 464.2129; ^1H NMR (90 MHz, $CDCl_3$) δ 7.49–6.84 (m, 4 H, indole C(4)–C(7)*H*), 7.22 (s, 5 H, C_6H_5), 5.24 (s, 2 H $OCH_2C_6H_5$), 5.09 (m, ^3J = 6 Hz, ^4J = 1 Hz, NCH_2CH=C), 4.89 (d, 2 H, ^3J = 6 Hz, NCH_2CH=), 4.20 (s, 2 H, indole C(3)CH_2), 4.12 (q, 2 H, OCH_2iCH_3), 2.62 (q, 2 H, SCH_2CH_3), 1.84 (d, ^4J = 1 Hz, 3 H, -CH=C(CH_3)CH_3), 1.66 (d, ^4J = 1 Hz, 3 H, -CH=C(CH_3)CH_3), 1.17 (t, 3 H, SCH_2CH_3), 1.11 (t, 3 H, OCH_2CH_3).

Compound 26: ^1H NMR (90 MHz, $CDCl_3$) δ 7.42–6.79 (m, 4 H, indolenine C(4)–C(7)*H*), 7.30 (s, 5 H, C_6H_5), 6.11 (X part of ABX spectrum, $^3J_{trans}$ = 16 Hz, $^3J_{cis}$ v 11 Hz, 1 H, $C(CH_3)_2CH_x$ = CH_AH_B), 5.09 (s, 2 H, $CH_2C_6H_5$), 5.09 and 5.01 (AB part of ABX spectrum, $^3J_{trans}$ = 16 Hz, $^3J_{cis}$ = 11 Hz, $C(CH_3)_2CH_x$=CH_{AHB}), 4.02 (q, 2 H, OCH_2CH_3), 3.76 and 3.52 (AB spectrum, $^2J_{AB}$ = 9 Hz, 2 H, indolenine C(3)CH_2), 3.20 (q, 2 H, SCH_2iCH_3), 1.32 (t, 3 H, SCH_2CH_3), 1.08 (t, 3 H, OCH_2CH_3), 1.04 and 0.99 (s, 6 H, indolenine C(3)C(CH_3)$_2$).

O-Acylation of α-Diazo Ketones. A Novel Route to Alkenediazonium and 1,3-Dioxolium Salts

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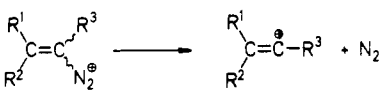
O-Acylation of α-diazo ketones with benzoyl triflate or diphenylacetyl triflate generates the corresponding β-(acyloxy)alkenediazonium salts **5** and **15**. These thermolabile compounds can be trapped with isopropylamine at low temperature to give triazoles **21**. Dediazoniation of **5** and **15** leads to 1,3-dioxolium salts **7** and **16** as well as small amounts of vinyl triflates **8** and **17** via intermediary vinyl cations. O-Benzoylation with benzoyl triflate has also been realized for the quinoid α-diazo ketone **9**; the resulting diazonium salt **10** gives triazole **13** on treatment with isopropylamine.

Introduction

Alkenediazonium salts **1** have been generated, either as reactive intermediates or as isolable compounds, by a



1 **2**

number of synthetic routes.[1] Starting from alkyl diazoacetates or α-diazoacetamides, stable ethenediazonium salts were obtained by O-alkylation with Meerwein salts.[1] α-Diazo ketones seem not to have been subjected to such a procedure, but the reaction product from ω-diazoacetophenone and $PCl_4^+SbCl_6^-$ clearly results from O-alkylation of the diazo ketone by an intermediarily generated alkyl cation.[2] We have recently found that triflic anhydride reacts with azibenzils to give vinylene bis(trifluoromethanesulfonates) via initial electrophilic attack of a CF_3SO_2 group on the carbonyl oxygen of the ambident α-diazo ketone; ethenediazonium salts are merely intermediates in the reaction sequence.[3] Successful O-alkylations and O-sulfonylations of α-diazo ketones suggest that acylation reactions will also be feasible, provided the acylating reagent has a sufficiently high electrophilicity. For our study, we chose acyl triflates which have already been introduced as superior electrophilic acyl transfer reagents.[4] They supersede by far the conventional acylating reagents such as acyl halides and carboxylic anhydrides in terms of efficiency and mildness of the reaction conditions. Their high acylation potential has been testified by Friedel–Crafts acylation of the aromatic nucleus in the absence of a Lewis acid catalyst,[4,5] by electrophilic

(1) (a) Bott, K. *Angew. Chem.* **1979**, *91*, 279; *Angew. Chem., Int. Ed. Engl.* **1979**, *19*, 259. (b) Bott, K. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Supplement C, Chapter 16.

(2) Bott, K. *Angew. Chem.* **1982**, *94*, 802; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 780; *Angew. Chem. Suppl.* **1982**, 1702.

(3) Maas, G.; Lorenz, W. *J. Org. Chem.* **1984**, *49*, 2273.

(4) Effenberger, F. *Angew. Chem.* **1980**, *92*, 147; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 151.

(5) (a) Effenberger, F.; Sohn, E.; Epple, G. *Chem. Ber.* **1983**, *116*, 1195. (b) Minato, H.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1977**, 609. (c) Forbus, T. R., Jr.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 313.

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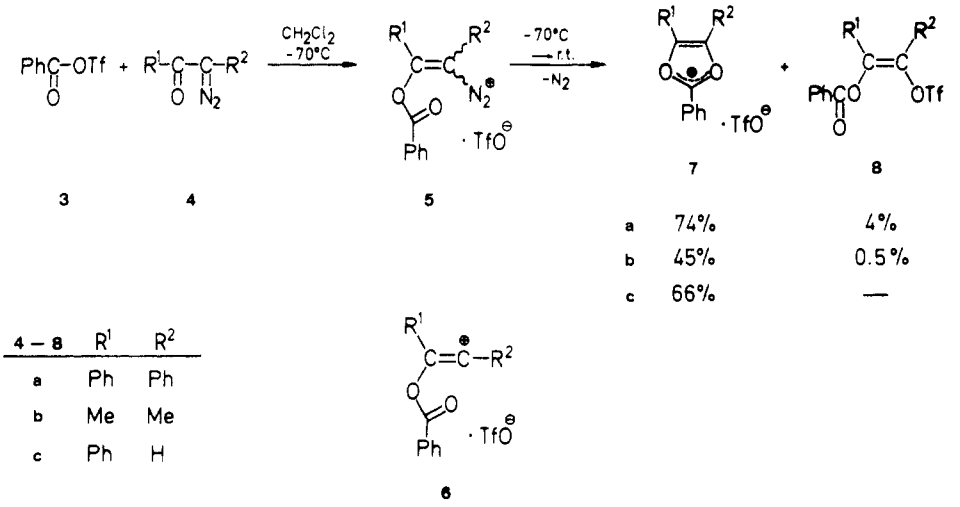
Scheme I



addition to acetylenes,[6] and benzoylation of alcohols, including sterically hindered secondary and tertiary ones, with benzoyl triflate.[7] The high reactivity of acyl triflates is due to the pronounced leaving group character of the trifluoromethanesulfonate group; some aroyl triflates even exist in a dissociation equilibrium with the corresponding aroylium triflates in 1,2-dichloroethane solution.[8]

One of the characteristic features of alkenediazonium salt chemistry is their eventual dediazoniation leading to vinyl cations (**1** → **2**).[9] Electron-releasing substituents in the β-position of **1** or incorporation of the C=C bond into an appropriate ring system tend to suppress this fragmentation reaction, however.[1] For example, neither thermal nor any other reaction of 2,2-diethoxyethenediazonium hexachloroantimonate leads to products which would require vinyl cation intermediates.[10]

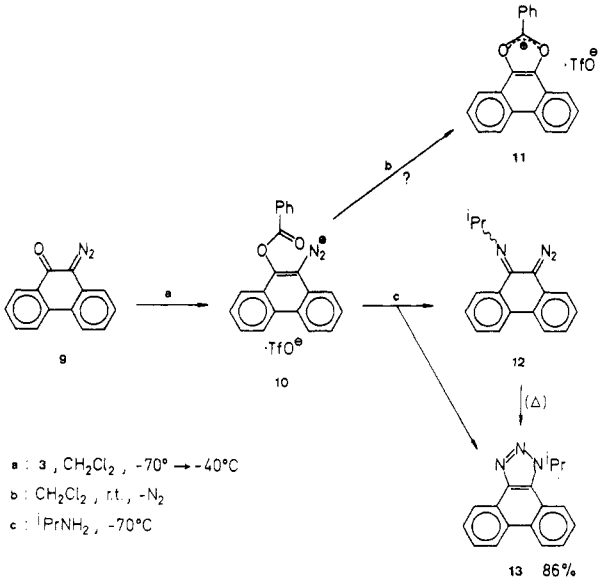
Even though an alkenediazonium salt bearing only one β-alkoxy substituent (**1**·$SbCl_6^-$, R^1 = Ph, R^2 = OCH_2COPh, R^3 = H) has proved isolable and thermally stable,[2] β-(acyloxy)alkenediazonium salts are expected to be less stabilized due to reduced electron donation from the acyloxy group. N_2 elimination should then lead to β-(acyloxy)vinyl cations.

Results and Discussion

Reaction of Acyl Triflates with α-Diazo Ketones. Benzoyl triflate (**3**), which is prepared conveniently from benzoyl chloride and triflic acid,[7,8] reacts with α-diazo ketones **4a–c** even below −70 °C to form β-(benzoyloxy)-alkenediazonium triflates **5a–c**. Salt **5b** was observed as a white precipitate at −70 °C which started to split off N_2 around −40 °C. Evidence for the generation of the other two salts is provided by intermolecular trapping (**5a**) and direct NMR observation (**5c**) (see below).

When the reaction mixtures were allowed to assume room temperature, the 1,3-dioxolium salts **7a–c** could be isolated as major products (Scheme I). Further products in the reaction of **4a** were benzil (7%), vinyl triflate **8a** (4%), and benzoin benzoate (8%, from partial hydrolysis of the dioxolium salt during workup). Similarly, 3-diazo-2-butanone (**4b**) furnished traces of **8b** as well as acetoin benzoate (4%), the product of partial hydrolysis of **7b**. Byproducts in the reaction of **4c** with **3** were phenacyl triflate and benzoic acid as well as a trace amount of ω-chloroacetophenone. The former two products could be attributed to partial hydrolysis of benzoyl triflate in the reaction mixture to give benzoic and triflic acids, the latter reacting with **4c** in the usual manner. However, neither careful exclusion of moisture nor a longer reaction time (to ensure quantitative consumption of **3** and **4c** before workup) led to a decreased yield of these byproducts, and their formation by hydrolysis of the dioxolium salt or some other unidentified reaction product during workup has to be considered.

Scheme II

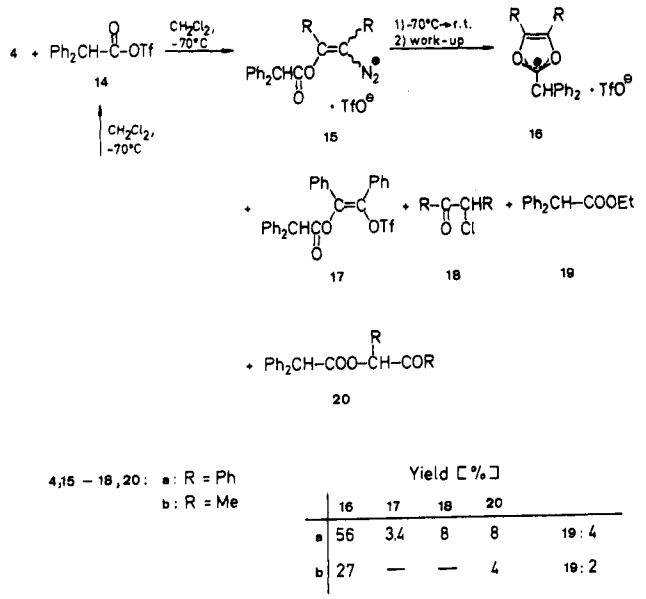


The configuration of (*Z*)-**8a** follows from UV data[3] (*cis*-stilbene chromophor), whereas that of **8b** remains undetermined. A hint to the *E* configuration in this case is furnished by the homoallylic ^5J coupling constant (1.5 Hz), which agrees with the value found in a similar compound[6] (**8b**, PhCO instead of PhCOO, ^5J = 1.1 Hz for the corresponding *Z* isomer).

In a further experiment, we have checked the ability of benzoyl triflate to O-benzoylate a quinoid α-diazo ketone. We have recently reported that triflic anhydride brings

(6) Martens, H.; Janssens, F.; Hoornaert, G. *Tetrahedron* **1975**, *31*, 177.
(7) Brown, L.; Koreeda, M. *J. Am. Chem. Soc.* **1984**, *49*, 3875.
(8) Effenberger, F.; Epple, G.; Eberhard, J. K.; Bühler, K.; Sohn, E. *Chem. Ber.* **1983**, *116*, 1183.
(9) (a) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979; pp 207–212. (b) Rappoport, Z. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, p 427.
(10) Szele, I.; Trencer, M.; Zollinger, H. *Helv. Chim. Acta* **1983**, *66*, 1691.
(11) Maas, G.; Tretter, A. *Liebigs Ann. Chem.* **1985**, 1866.

Scheme III



4,15 – 18,20: a: R = Ph
b: R = Me

Yield [%]

	16	17	18	20	
a	56	3.4	8	8	19 : 4
b	27	—	—	4	19 : 2

about O-sulfonylation of such compounds, providing access to stable *o*- and *p*-trifloxyarenediazonium salts.[9] Acetic anhydride was found not to be suited for the analogous acetylation reactions.[9] Benzoyl triflate smoothly transforms 10-diazo-9(10*H*)-phenanthrenone (**9**) into diazonium salt **15** (IR in Nujol: $\nu(CN_2)$ = 2260 cm^{-1}) (Scheme II). This aromatic diazonium salt is a yellow solid which gradually loses N_2 at room temperature to give an unseparable mixture of products which may or may not contain dioxolium salt **11**. Hydrolysis or aminolysis of the mixture did not furnish any products which would be expected to arise from such a dioxolium salt (see below).

Some acyl triflates which are generated at −30 to −50 °C are unstable at room temperature.[8] This is especially the case if a rather stable carbenium ion can be formed by decarbonylation of the acylium moiety.[8,12] The following example shows that such acyl triflates can be used for acylation of α-diazo ketones under in situ conditions at low temperature. Diphenylacetyl triflate (**14**), which we have generated by addition of triflic acid to diphenylketene at −70 °C,[13] decomposed on attempted workup at or above room temperature. However, in situ reaction with α-diazo ketones **4a,b** produced the alkenediazonium salts **15** which subsequently lost N_2 to furnish mainly the dioxolium salts **16a,b** (Scheme III). Among the byproducts, one finds vinyl triflate **17a** (analogous to **8**), ethyl diphenylacetate (**19**) (from reaction of **14** with ether added on workup), and the diphenylacetic esters **20a,b** (from partial hydrolysis of dioxolium salts **16a,b**). The appearance of the chloride **18a**, as well as of ω-chloroacetophenone in the reaction of **4c** with **3** (see above), should be attributed to the action of HCl on the respective diazo ketone; whereas it seems clear that hydrogen chloride comes from the solvent (CH_2Cl_2), its mode of formation has not been established.

Characterization of Alkenediazonium Salts 5 and 10. According to the known sensitivity of stable alkenediazonium salts toward nucleophilic β-attack,[1,10,14] the thermolabile salts **5a,b** could be trapped with isopropylamine to give the corresponding 3-isopropyl-1,2,3-triazoles **21a,b** (Scheme IV). Careful temperature control is mandatory in order to prevent vinyl cation formation from the alkenediazonium salts **5**. In the azibenzil reaction, this decomposition could not be suppressed completely even at −75 °C, as indicated by the formation of vinyl triflate **8a** and imidic ester **22**. The latter compound arises from ring cleavage of dioxolium salt **7a** by *i*-$PrNH_2$ (see below).

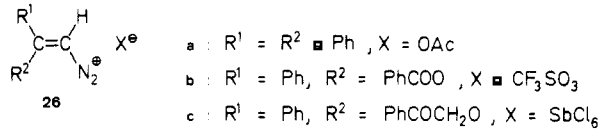
In mechanistic terms, reaction of the alkenediazonium salts **5** with a primary amine leads to a diazoalkane **23** which may split off benzoic acid before or after cyclization (**23** → **24** → **21** or **23** → **25** → **21**) (Scheme V).[15] Like its alkenediazonium relatives, salt **10** furnished a triazole (**13**) by reaction with isopropylamine. The diazoimine **12** was detected in very small quantities in the reaction mixture ($\nu(CN_2)$ = 2080, 2090 cm^{-1}); according to IR spectroscopy, triazole **13** after recrystallization from ether still contained traces of **12**.[16] Again, the experimental facts do not allow one to establish whether all or only part of triazole **13** was formed via the diazoimine.

The existence and transformation of alkenediazonium salt **5c** in the absence of a trapping reagent could be monitored by NMR spectroscopy. When **4c** and benzoyl triflate in dichloromethane were mixed at ca. −40 °C and when the ^{1}H NMR spectrum was recorded at this temperature, signals of only one alkenediazonium salt were found. We attribute these signals (a singlet at δ 8.91 for $=CH(N_2^+)$ and a multiplet at δ 8.30 for two aromatic protons) to (*Z*)-**5c**. This assignment correlates with the assumption, based on the temperature-invariance of ^{1}H NMR[17] and ^{13}C NMR[18] spectra, that the diazo ketone **4c** exists as only one conformer, namely *s-cis*, which is also predicted as the more stable conformer by Extended Hückel MO calculations.[19] At temperatures above −15 °C, a second set of signals appears (singlet at δ 9.08 and a two-proton multiplet at δ 8.50) at the expense of the first one;[20] these signals are attributed to (*E*)-**5c** (Scheme VI). After a few minutes at 0 °C, (*Z*)-**5c** has undergone complete isomerization to (*E*)-**5c**. Above ca. 10 °C, N_2 elimination indicates the formation of dioxolium ion **7c**. This experiment shows that the original conformation of the diazo ketone may be trapped in a kinetically controlled reaction but that geometrical isomerization of the alkenediazonium ion so formed may occur before thermally induced loss of N_2.[21]

Concerning the stability of alkenediazonium salts, a sequence **26a**[22] ~**26b** (≡**5c**) <**26c** (isolated as a stable $SbCl_6^-$ salt[2]) may be established.

Mechanism of Dioxolium Salt Formation. The formation of **7** and **8** (Scheme I) as well as of **16** and **17**

(12) Effenberger, F.; Epple, G. *Angew. Chem.* **1972**, *84*, 294; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200.
(13) The analogous synthesis of acetyl triflate from ketene and triflic acid has been published: Germain, A.; Commeyras, A.; Casadevall, A. *Bull. Soc. Chim. Fr.* **1973**, *7–8*, 2527.
(14) Saalfrank, R. W.; Weiss, B.; Peters, K.; v. Schnering, H. G. *Chem. Ber.* **1985**, *118*, 4026; see also earlier papers cited therein.
(15) For mechanistic considerations, see: Saalfrank, R. W.; Ackermann, E. *Chem. Ber.* **1981**, *114*, 3456. Weiss, B. *Ibid.* **1985**, *118*, 2626.
(16) For α-diazo imine → 1,2,3-triazole cyclizations, see: Regitz, M. *Tetrahedron Lett.* **1965**, 3287. Regitz, M.; Schwall, H. *Liebigs Ann. Chem.* **1969**, *728*, 99.
(17) (a) Wentrup, C.; Dahn, H. *Helv. Chim. Acta* **1970**, *53*, 1637. (b) Kessler, H.; Rosenthal, D. *Tetrahedron Lett.* **1973**, 393.
(18) Zellhofer, T. Ph.D. Thesis, Frankfurt, West Germany 1980.
(19) Csizmadia, G.; Houlden, S. A.; Meresz, O.; Yates, P. *Tetrahedron* **1969**, *25*, 2121. Only for a coplanar arrangement of phenyl ring and α-diazo carbonyl unit, stabilization of the *s*-cis conformer at the expense of the *s*-trans form is predicted.
(20) The chemical shifts of the olefinic protons in both isomers are temperature-dependent. On lowering the temperature from 0 to −50 °C, the following changes are observed: Δδ = −0.03 ppm for (*Z*)-**5c**, +0.07 ppm for (*E*)-**5c**.
(21) For the related salt 1·$SbCl_6^-$ (R^1 = Ph, R^2 = $PhCOCH_2O$, R^3 = H), the isolation of the mixture of diastereomers has been reported: ref 2.
(22) Jones, W.M.; Miller, F. W. *J. Am. Chem. Soc.* **1967**, 89, 1960. Diazonium ion **26a** generated in situ from a vinyl triazene and HOAc, splits off N_2 "in a matter of seconds" at room temperature.



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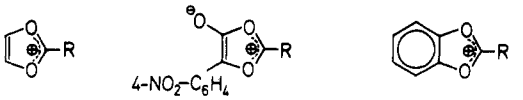
(Scheme III) is rationalized by the intervention of vinyl cations such as **6** which arise from the alkenediazonium salts **5** and **15**, respectively, by loss of dinitrogen. The vinyl cations can either be trapped by an external nucleophile ($TfO^- \rightarrow$ **8**, **16**) or by an internal one (>C=O → **7**, **17**). The latter possibility was obviously not viable in the reaction of azibenzil (**4a**) with triflic anhydride, where only the collapse of a vinyl cation/triflate anion ion pair occured.[3]

Instead of the participation of a free vinyl cation **6** in the formation of dioxolium salts **7**, one could also think of nucleophilic assistance of the β-benzoyloxy group of **5** in the dediazoniation step. This would require *E* configuration of the diazonium salt **5**, and hence *s*-trans conformation of the –C(O)–C(N_2)– fragment in the α-diazo ketones **4**. This prerequisite holds for **4a** and **4b** which exist exclusively (**4a**[18]) or predominantly (**4b**[18,23]) as *s*-trans conformers at the temperatures of our reactions. Diazo ketone **4c** most likely has the *s*-cis conformation,[17-19] but our NMR study shows that the alkenediazonium salt **5c** undergoes *Z* → *E* isomerization prior to the dediazoniation step (see above). Thus, the configurational requirements for nucleophilic assistance of the β-benzoyloxy group of **5** in the dediazoniation step are fullfilled in all three cases. The fact that we have been unable to obtain a dioxolium salt from the arenediazonium salt **10** (Scheme II), which is confined to the *Z* configuration, seems to corroborate further the idea of this neighboring group participation.[24] In contrast, the 2-trifloxyvinyl benzoates **8** and acetate **17a** certainly arise from trapping of vinyl cations such as **6** by the weakly nucleophilic[25] triflate anion. ^{19}F NMR scrutiny excludes the possibility of an interconversion **7** ⇌ **8** in $CDCl_3$ solution. The stereoselective formation of (*Z*)-**8a** and (*Z*)-**17a** is likely to result from steric factors which govern the orientation of triflate anion attack on the linear vinyl cation.[3]

Characterization of 1,3-Dioxolium Salts 7. The 1,3-dioxolium ion is a rather little known heterocyclic system because of its marked lability. The 2-hydroxy- and methoxy-substituted 1,3-dioxolium salts **27** (R = OH, OMe) were generated only in solution by protonation[26,27] and methylation[26] of vinylene carbonate. Several 2-thio-substituted 1,3-dioxolium salts have been isolated, but proved to be extremely moisture-sensitive.[28,29] The electroneutral mesoionic compounds **28** (R = Ph, Me), which may be represented by 1,3-dioxolium-type resonance structures, withstood isolation and had to be trapped by cycloaddition reaction.[30] It appears that the salts **7** and **16** reported in this paper are the first isolable 1,3-dioxolium salts which do not carry a charge-stabilizing hetero atom at C-2.

1,3-Benzodioxolium ions **29** are somewhat more stable than their monocyclic relatives: Derivatives bearing aryl,[31] methoxy,[31] and chloro[32] substituents at C-2 were isolated as their BF_4^- or $SbCl_6^-$ salts, and the NMR spectra of the parent[26,32] and the 2-hydroxy-1,3-benzodioxolium[26] ions have been recorded in superacid media. Opposite views exist as to whether 1,3-dioxolium ions represent oxygen-substituted carbenium ions or true 6π heteroaromatic compounds.[26,27]



27 28 29

^{13}C NMR data of dioxolium salts **7a,b** reveal a high-field shift of C-2 by some 7 ppm as compared to the dioxolenium salt **30**[33] (Scheme VII). Obviously, delocalization of the positive charge into the olefinic bond of **7** is responsible for the shielding of C-2. The following changes were observed between δ(C2) in 2-hydroxy-1,3-dioxolenium and 2-hydroxy-1,3-dioxolium ions: 158.9 → 155.9 ppm in $CF_6COOH/CDCl_3$[27] and 156.7 → 164.3 in $FSO_3H/SbF_5/SO_2$.[26] Delocalization of positive charge over all ring atoms of **7** should also result in a deshielding of C(4,5). Since we have no comparison with a neutral 1,3-dioxole bearing the same substituents, this issue cannot be answered with certainty. For **7b**, δ(C4,5) is ca. $9^{26} - 14^{27}$ ppm downfield from the corresponding signal in the 2-hydroxy-1,3-dioxolium ion. Provided that the influence of the two methyl groups on the chemical shift of δ(C4,5) is negligible, (compare: ethylene, δ = 123.5, and *cis*-2-butene, δ(C2,3) = 124.2[34]), the deshielding must be attributed indeed to the delocalization of positive charge. Altogether, these data support the view that some sort of aromatic delocalization is present in 1,3-dioxolium salts, the extent of which depends on the presence or absence of ring substituents which can effectively stabilize the positive charge.

All dioxolium salts **7** and **16** are extremely moisture-sensitive solids. Nucleophilic attack of water probably occurs at C-2 followed by ring opening to give carboxylic esters such as **20** and **31**. The analogous reaction of **7a** with a primary amine (isopropylamine) furnished imidic ester **22**. With a secondary amine, the product of nucleophilic addition at C-2 can be isolated, as has been demonstrated by the synthesis of 2-(diisopropylamino)-1,3-dioxole **32** from **7a** and diisopropylamine. On prolonged exposure to air-moisture, **32** is cleaved into benzoin and *N,N*-diisopropylbenzamide.

Treatment of the 2-diphenylmethyl-substituted dioxolium salt **16a** with diisopropylethylamine produced the yellow 2-(diphenylmethylene)-1,3-dioxole **33**. In contrast to the corresponding 2-methylene-1,3-dithioles[35] and -diselenoles,[36] this cyclic ketene acetal is an extremely moisture-sensitive compound which could not be isolated in a pure form. The formation of **33** follows, however, from

(23) Curci, R.; DiFuria, F.; Lucchini, V. *Spectrosc. Lett.* **1974**, *7*, 211.
(24) Vinyl cation formation from *trans*-α-acetoxy-β-bromo-4,4'-dimethoxystilbene during acetolysis (AcOH, NaOAc, 140 °C) is considered to occur without β-acetoxy participation. This is not fully pertinent to the transformation **5a** → **6a**, however, since the 4-anisyl function in the α-position stabilizes the incipient positive charge better than does the acetoxy group: Rappoport, Z.; Atidia, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2316.
(25) For the surprisingly high nucleophilicity of highly nucleofugal anions in reactions involving carbocations, see: Zefirov, N. S.; Koz'min, A. S. *Acc. Chem. Res.* **1985**, *18*, 154.
(26) Olah, G. A.; Grant, J. L. *J. Org. Chem.* **1977**, *42*, 2237.
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(28) (a) Moses, P. R.; Chambers, J. Q.; Sutherland, J. O.; Williams, D. R. *J. Electrochem. Soc.* **1975**, *122*, 608. (b) Braun, R. D.; Green, D. C. *J. Electroanal. Chem.* **1977**, *79*, 381.
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(30) Hamaguchi, M.; Nagai, T. *J. Chem. Soc., Chem. Commun.* **1985**, 190, 1319.
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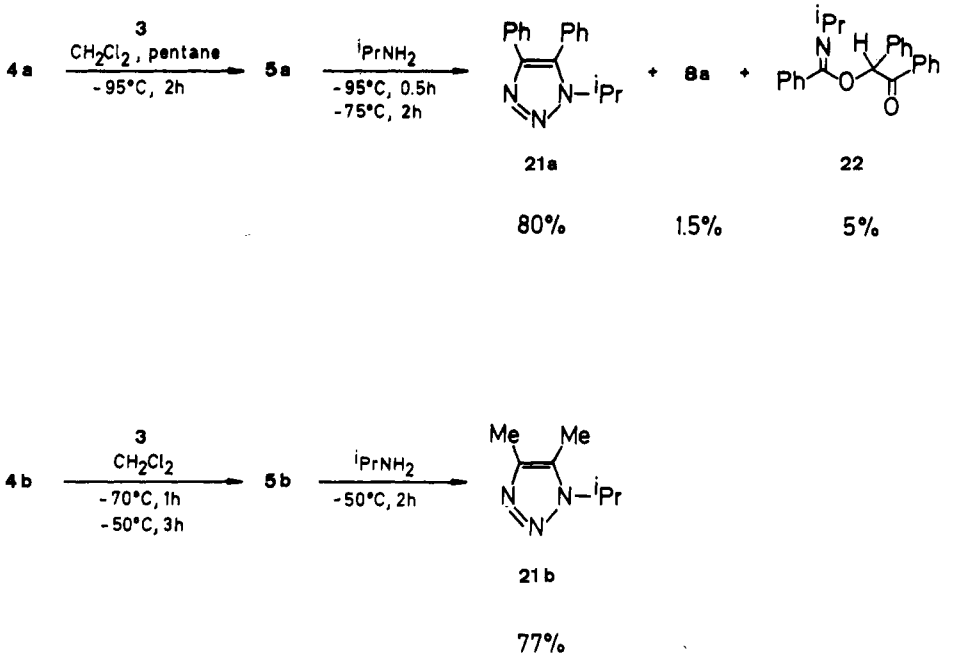
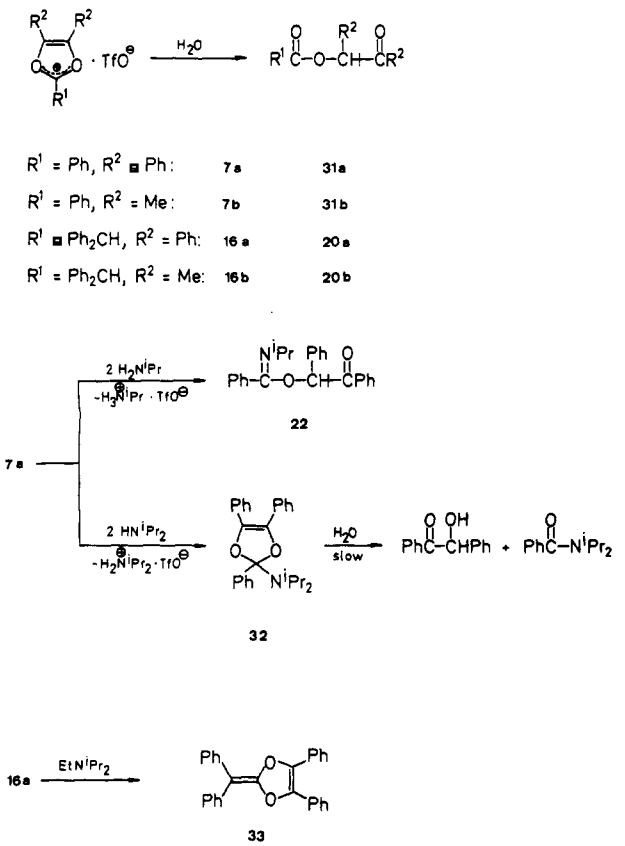
(33) Łukaszczyk, J. *Polish J. Chem.* **1981**, *55*, 2497.
(34) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}-C-NMR-Spektroskopie*; Thieme: Stuttgart, 1984; p 115.
(35) Hirai, K.; Sugimoto, H.; Ishiba, T. *Sulfur Rep.* **1983**, *3*, 1.
(36) Meier, H.; Menzel, I. *Tetrahedron Lett.* **1972**, 445.

Scheme IV



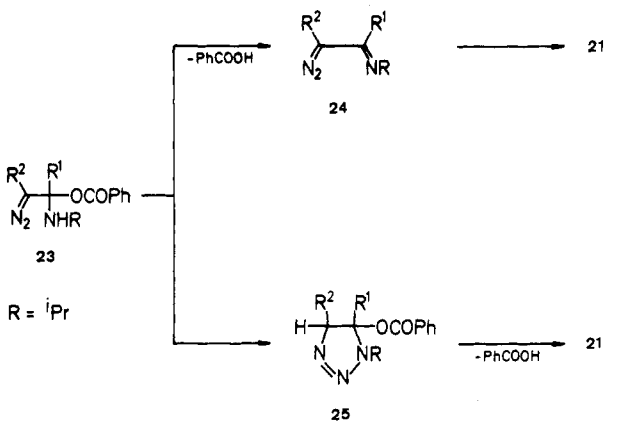
the nearly quantitative isolation of diisopropylethylammonium triflate and the disappearance of the methine signal of **16a** in the ^1H NMR spectrum.



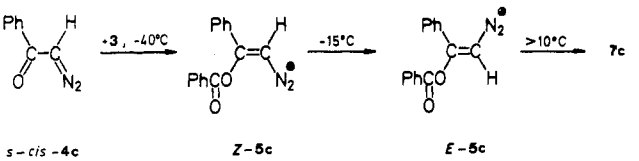
Experimental Section

For instrumentation, see ref 3. Melting points were determined in a heat block (sealed and argon-filled capillaries for dioxolium salts). ^1H and ^{13}C NMR data: δ values in ppm relative to Me_4Si. ^{19}F NMR data: chemical shifts in ppm relative to hexafluorobenzene. All reactions except the hydrolyses of dioxolium salts were carried out in an argon atmosphere; solvents had been dried and distilled. Column chromatography was done on Merck Lobar columns (silica gel LiChroprep Si 60, 40–63 μm, dried and distilled solvents) and by the flash chromatography method[37] (50–100 g of silica gel Woelm, 0.063–0.2 mm, elution time 5–10 min).

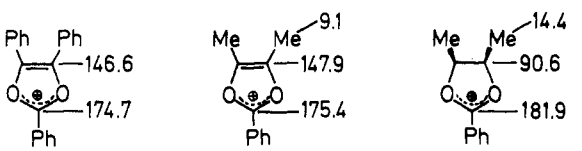
Scheme V



Scheme VI



Scheme VII. ^{13}C NMR Values (δ Relative to Me_4Si, 7a in CD_3CN, 7b and 30 in CD_3NO_2 Solution)



Reaction of Azibenzil (4a) with Benzoyl Triflate (3). The solution of **3**[7] (1.71 g, 6.8 mmol) in 5 mL of CH_2Cl_2 is cooled to −70 °C. With magnetic stirring, a solution of 1.50 g (6.8 mmol) of azibenzil (**4a**)[38] in 10 mL of CH_2Cl_2 is added dropwise. After addition, stirring is continued for 30 min. The solution is allowed

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(38) Morrison, H.; Danishefsky, S.; Yates, P. *J. Org. Chem.* **1961**, *26*, 2617.

to warm to room temperature, pentane (100 mL) is added, and the mixture is cooled again to −70 °C. The yellow precipitate is filtered off under argon and dried at 0.01 torr; one obtains 2.26 g (74%) of yellow 2,4,5-triphenyl-1,3-dioxolium trifluoromethanesulfonate (**7a**): mp 171 °C; IR (CH_3CN) 1671, 1592, 1579 (all w), 1243 (vs), 1232–1213 (vs, br), 1171, 1156, 1095–1020 cm^{-1} (all m); ^1H NMR (CD_3CN) δ 7.50–8.73; ^{13}C NMR (CD_3CN) δ 118.0 (s), 122.7 (s), 128.7 (d), 130.7 (d), 131.6 (d), 132.6 (d), 133.6 (d), 141.0 (d), 146.6 (C-4,5), 174.7 (C-2). Anal. Calcd for $C_{22}H_{15}F_3O_5S$ (448.4): C, 58.93; H, 3.37. Found: C, 58.7; H, 3.34.

The filtrate of the reaction mixture is concentrated and the residue is separated from polymeric material by flash chromatography (80 g of silica gel, 400 mL of chloroform). Further fractionation by Lobar column chromatography (petroleum ether–chloroform, 1:1) gives (a) 0.11 g (4%) of (*Z*)-2-[[(trifluoromethyl)sulfonyl]oxy]-1,2-diphenylvinyl benzoate (**8a**) [131–132 °C (from ether–pentane); IR (KBr) 1738 (C=O), 1426 (—SO_2OC), 1239, 1212, 1138, 1089 (all s), 1051, 1021 (m) cm^{-1}; UV (ethanol) λ_{max} (log ϵ) 229.5 (5.49), 270.3 nm (4.13); ^1H NMR ($CDCl_3$) δ 7.10–8.37; ^{19}F NMR ($CDCl_3$) δ 87.2. Anal. Calcd for $C_{22}H_{15}F_3O_5S$ (448.4); C, 58.93; H, 3.37. Found: C, 59.0; H 3.46.], (b) 94 mg (7%) of benzil, and (c) 0.16 g (8%) of α-benzoylbenzyl benzoate [mp 122–124 °C (from ether–pentane), lit.[39] mp 122.5–124 °C].

Reaction of 3-Diazo-2-butanone (4b) with Benzoyl Triflate (3). A solution of **3**[7] (5.20 g, 20.4 mmol) in 20 mL of CH_2Cl_2 is cooled to −70 °C and **4b**[38] (2.00 g, 20.4 mmol) in CH_2Cl_2 (20 mL) is added dropwise. After 1.5 h, the temperature is raised to −50 °C and the suspension is stirred at this temperature for 3 h. The mixture is allowed to assume room temperature (evolution of N_2) and then is recooled to −70 °C after addition of 150 mL of pentane. The mixture is filtered under argon, yielding 2.99 g (45%) of colorless 4,5-dimethyl-2-phenyl-1,3-dioxolium trifluoromethanesulfonate (**7b**): mp 138–140 °C; IR (CH_3CN) 1673 (w), 1593 (w), 1252 (vs, br), 1231–1211 (vs, br), 1152 (s), 1108–1014 (m, br); ^1H NMR (CD_3CN) δ 2.46 (s, 6 H), 7.61–8.40 (m, 5 H); ^{13}C NMR (CD_3NO_2) δ 9.1 (CH_3), 118.3 (ipso-C), 131.7 (β-C), 132.3 (α-C), 140.9 (γ-C), 147.9 (C-4,5), 175.4 (C-2). Anal. Calcd for $C_{12}H_{11}F_3O_5S$ (324.3): C, 44.44; H, 3.42. Found C, 44.2; H, 3.38.

The filtrate of the reaction mixture is freed of polymeric material by flash chromatography on silica gel (400 mL of chloroform and 200 mL of ether as eluents). The last 100 mL of eluent contain 0.34 g (13%) of benzoic acid. Further separation of the eluated solution by Lobar column chromatography yields (a) 30 mg (0.5%) of 3-[[(trifluoromethyl)sulfonyl]oxy]-2-buten-2-yl benzoate (**8b**) (propably *Z* isomer) as a colorless oil [IR (film) 1739 (C=O), 1416 (—SO_2OC), 1211, 1144, 1109, 1061 (all s), 1024 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.02 (q, ^5J = 1.6 Hz, 3 H), 2.14 (q, ^5J = 1.6 Hz, 3 H), 7.36–8.31 (5 H); ^{19}F NMR ($CDCl_3$) δ 87.6. Anal. Calcd for $C_{12}H_{11}F_3O_5S$ (324.3): C, 44.44; H, 3.42. Found: C, 44.7; H 3,50.], (b) 52 mg (2%) of ethyl benzoate, and (c) 0.84 g (4%) of 3-oxo-2-butyl benzoate, identified by spectral comparison with an authentic sample.

Reaction of ω-Diazoacetophenone (4c) with Benzoyl Triflate (3). To a solution of **3**[7] (2.60 g, 10.3 mmol) in CH_2Cl_2 (15 mL), cooled to −70 °C is added 1.50 g (10.3 mmol) of **4c**[40] in CH_2Cl_2 (5 mL) dropwise. The solution is allowed to assume room temperature and is then stirred for another 2 h. With pentane, 2.43 g (66%) of 2,4-diphenyl-1,3-dioxolium trifluoromethanesulfonate (**7c**) are precipitated as a colorless, extremely moisture-sensitive crystalline powder: mp 149–150 °C dec; IR (CH_3CN) 1679–1623 (br, w), 1214 (m), 1241 (vs, br), 1202 (vs, br), 1144 (s), 1047 (m), 1009 cm^{-1} (m); ^1H NMR (CD_3CN) δ 7.60–8.26 (8 H), 8.45–8.64 (2 H), 9.01 (s, 1 H). Anal. Calcd for $C_{16}H_{11}F_3O_5S$ (372.4): C, 51.62; H, 2.98. Found: C, 51.4; H, 2.98.

The filtrate is separated from polymeric material by flash chromatography on silica gel ($CHCl_3$ as eluent). The solvent is replaced by pentane; on cooling, phenacyl trifluoromethanesulfonate (0.62 g, 22%, mp 55 °C (lit.[41] mp 55.5–56 °C) crystallizes. The remaining product mixture is fractionated by Lobar column chromatography (eluent ether–petroleum ether (1:10)): (a) 24 mg (1.5%) of ω-chloroacetophenone, mp 57 °C; (b) 20 mg (1%) of phenacyl trifluoromethanesulfonate (23% totally); (c) 0.18 g (15%) of benzoic acid.

Trapping of Alkenediazonium Salt 5a with Isopropylamine. To a suspension of **3**[7] (2.23 g, 9 mmol) in 40 mL of CH_2Cl_2–pentane (1:1), cooled to −100 °C, is added a solution of **4a**[38] (2.00 g, 9 mmol) in 20 mL of CH_2Cl_2 dropwise. The mixture is then kept with stirring at −100 to −95 °C for 2 h. Then, isopropylamine (2.70 g, 45 mmol) in CH_2Cl_2 (20 mL) is added dropwise at this temperature. After 30 min, the temperature is raised to −75 °C, and after 2 h the mixture is brought to room temperature. Extraction with water and separation of the organic phase by Lobar column chromatography (eluent $CHCl_3$–petroleum ether, 1:1) yields (a) 60 mg (1.5%) of **8a** (see above), (b) 0.17 g (5%) of α-benzoylbenzyl *N*-isopropylbenzimidate (**22**) [mp 89–91 °C; IR (KBr) 1673 (s, C=O), 1592 cm^{-1} (m, C=N); ^1H NMR ($CDCl_3$) δ 0.75 (d, 3 H), 1.05 (d, 3 H), 3.48 (sept, 1 H), 6.95 (s, 1 H), 7.23–8.13 (15 H); ^{13}C NMR ($CDCl_3$) δ 24.4 (CH_3), 24.8 (CH_3), 49.7 (N-*C*H), 78.1 (Ph-*C*H), 128.2, 128.6, 128.8, 128.9, 129.8, 132.0, 132.9, 135.2, 136.7 (Ar C), 157.5 (*C*=N), 197.2 (*C*=O); MS (70 eV), *m/e* (relative intensity) 357 (M^+, 0.6). Anal. Calcd for $C_{24}H_{23}NO_2$ (357.4); C, 80.64; H, 6.49; N, 3.92. Found: C, 80.4; H, 6.59; N, 3.8], and (c) 1.90 g (80%) of 1-isopropyl-4,5-diphenyl-1,2,3-triazole (**21a**) [mp 126 °C, lit.[42] mp 126–128 °C].

Trapping of Alkenediazonium Salt 5b with Isopropylamine. A solution of 5.20 g (20.4 mmol) of **3**[7] in CH_2Cl_2 (50 mL) is cooled to −70 °C, and a solution of **4b**[38] (2.00 g, 20.4 mmol) in CH_2Cl_2 (50 mL) is added dropwise. After addition, the suspension is stirred at −70 °C for 1 h and at −50 °C for 3 h. Isopropylamine (6.00 g, 102 mmol) is gradually added after recooling to −70 °C. A homogeneous solution forms which after 2 h is warmed to room temperature and extracted four times with water. The organic layer is dried ($MgSO_4$) and the solvent is removed at 15 torr. Kugelrohr distillation at 90 °C (0.05 torr) gives 2.19 g (77%) of 1-isopropyl-4,5-dimethyl-1,2,3-triazole (**21b**): IR (film) 1579 (s), 1442 (s, br), 1380 (s), 1365 (m), 1328 (s), 1246 (s), 1232 (s), 1179 (m), 1159 (s), 1133 (m), 1102 (s), 1055 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.53 (d, 6 H), 2.19 (s, 3 H), 2.22 (s, 3 H), 4.48 (sept, 1 H); ^{13}C NMR ($CDCl_3$) δ 7.9 (CH_3), 10.2 (CH_3), 23.0 ($CHCH_3$), 50.3 ($CHMe_2$), 128.2 (C-5), 140.7 (C-4). Anal. Calcd for $C_7H_{13}N_3$ (139.2): C, 60.4; H, 9.41; N, 30.2. Found: C, 60.3; H, 9.50; N, 30.0.

Reactions with 10-Diazo-9(10*H*)-phenanthrenone (9). (a) To a solution of **3**[7] (1.15 g, 4.5 mmol) in CH_2Cl_2 (20 mL), cooled to −70 °C, is added a solution of **9**[43] (1.00 g, 4.5 mmol) in CH_2Cl_2 (10 mL) dropwise. The yellow suspension is warmed to 0 °C, and ether is added to complete the crystallization. The yellow precipitate is filtered off under argon and dried at 0.01 torr. One obtains 1.84 g (86%) of yellow 10-(benzoyloxy)-9-phenanthrenediazonium trifluoromethanesulfonate (**10**), which gradually loses N_2 at room temperature: IR (Nujol) 2260 (CN_2), 1779 cm^{-1} (C=O).

(b) To a solution of 1.55 g (6.1 mmol) of **3**[7] in CH_2Cl_2 (50 mL), cooled to −70 °C, is added a solution of **9**[43] (1.34 g, 6.1 mmol) in CH_2Cl_2 (50 mL) dropwise. One hour after addition, the yellow suspension is stirred at −40 °C for 2 h and then recooled to −70 °C. Isopropylamine (1.80 g, 30.5 mmol) in CH_2Cl_2 (20 mL) is added dropwise, whereupon a homogeneous red solution forms. After 5 h, the solution is allowed to assume room temperature, extracted with water, and dried ($MgSO_4$). The solvent is replaced by ethyl acetate and crystallization is induced by addition of ether to yield 1.38 g (86%) of 3-isopropylphenanthro[9,10-*d*]-1,2,3-triazole (**13**): amber-colored crystals, mp 150–154 °C; ^1H NMR ($CDCl_3$) δ 1.86 (d, 6 H), 5.43 (sept, 1 H), 7.52–7.88 (4 H), 8.20–8.96 (4 H). Anal. Calcd for $C_{17}H_{15}N_3$ (261.3): C, 78.13; H, 5.79; N, 16.08. Found: C, 78.0; H, 5.80; N, 16.0.

Reaction of 4a with Diphenylacetyl Triflate (14). Diphenylacetyl triflate is generated by adding diphenylketene[44] (1.00 g, 5.1 mmol) in CH_2Cl_2 (10 mL) to a suspension of 0.77 g (5.1 mmol) of triflic acid in CH_2Cl_2 (20 mL), cooled to −70 °C. Azi-

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(40) Regitz, M; Menz, F. *Chem. Ber.* **1968**, *101*, 2622.
(41) Vedejs, E.; Engler, D. A.; Mullins, M. J. *J. Org. Chem.* **1977**, *42*, 3109.
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(43) Süs, O.; Steppan, H.; Dietrich, R. *Liebigs Ann. Chem.* **1958**, *617*, 20.
(44) Simth, L. I.; Hoehn, H. H. *Organic Syntheses*; Wiley: New York, 1967; Collect. Vol. III, p 356.

benzil (**4a**)[38] (1.13 g, 5.1 mmol) in CH_2Cl_2 (20 mL) is added dropwise to this mixture, and the light-green suspension thus formed is warmed to room temperature after 45 min. To complete the precipitation, pentane is added, yielding 1.53 g (56%) of colorless 2-(diphenylmethyl)-4,5-diphenyl-1,3-dioxolium trifluoromethanesulfonate (**16**): mp 101 °C dec; ^1H NMR ($CDCl_3$) δ 6.28 (s, 1 H), 7.27–7.77 (m, 20 H); ^{19}F NMR (CD_3CN) δ 85.7. Anal. Calcd for $C_{29}H_{21}F_3O_5S$ (538.5): C, 64.68; H, 3.93. Found C, 64.10; H, 3.87.

The filtrate of the reaction mixture is concentrated and the residue is fractionated by Lobar column chromatography (2000 mL ether–petroleum ether (1:4), 1500 mL chloroform–petroleum ether (1:1), 400 mL of chloroform); one obtains (a) 94 mg (3.4%) of (*Z*)-2-[[(trifluoromethyl)sulfonyl]oxy]-1,2-diphenylvinyl diphenylacetate (**17a**) [mp 122 °C (from pentane–ether); IR (KBr) 1759 (s, C=O), 1419 (vs, $-SO_2OC-$), 1241 (s), 1229 (vs), 1203 (vs), 1145 (vs), 1100 (vs), 1081 (s), 1031 cm^{-1} (m); UV (cyclohexane) λ_{max} (log ε) 214 (4.51), 271 (4.11); ^1H NMR ($CDCl_3$) δ 5.33 (s, 1 H), 6.77–7.60 (20 H); ^{19}F NMR ($CDCl_3$) δ 87.7. Anal. Calcd for $C_{29}H_{21}F_3O_5S$ (538.5): C, 64.68; H, 3.93. Found: C, 64.90; H, 4.06.], (b) 94 mg (8%) of 2-chloro-1,2-diphenylethanone [mp 63–64 °C, lit.[45] mp 65–66 °C], (c) 46 mg (4%) of ethyl diphenylacetate [mp 58 °C, lit.[46] mp 58 °C], and (d) 0.26 g (8%) of α-benzoylbenzyl diphenylacetate [mp 157–158 °C, lit.[47] mp 157.5–158.5].

Reaction of 4b with Diphenylacetyl Triflate (14). Diphenylacetyl triflate is generated in situ by adding at −70 °C a solution of diphenylketene[44] (1.00 g, 5.1 mmol) to a suspension of 0.77 g (5.1 mmol) of triflic acid in CH_2Cl_2 (20 mL). After 15 min, **4b**[38] (0.50 g, 5.1 mmol) in CH_2Cl_2 (20 mL) is added dropwise and the mixture is stirred for 1.5 h at −70 °C. It is then allowed to assume room temperature; nitrogen evolution starts around 15 °C. After addition of pentane and cooling to −70 °C, one obtains a colorless precipitate of 4,5-dimethyl-2-(diphenylmethyl)-1,3-dioxolium trifluoromethanesulfonate (**16b**) (0.57 g, 27%) which is very moisture-sensitive and melts with decomposition between 85 and 95 °C: IR (CD_3CN) 1238, 1209, 1148 (all vs), 1052, 1020 cm^{-1} (both s); ^1H NMR (CD_3CN) δ 2.40 (s, 6 H), 6.28 (s, 1 H), 7.48 (10 H); ^{19}F NMR (CD_3CN) δ 85.3. Anal. Calcd for $C_{19}H_{17}F_3O_5S$ (414.4): C, 55.07; H, 4.13. Found: C, 56.7; H, 4.18.

The filtrate was concentrated and the residue was separated by Lobar column chromatography with petroleum ether–ether (20:1) to give (a) 23 mg (2%) of ethyl diphenylacetate (mp 57 °C, lit.[46] mp 58 °C) and (b) 53 mg (4%) of 3-oxo-2-butyl diphenylacetate (**20b**) which was compared with a sample independently prepared as follows.

To a solution of **4b**[38] (1.50 g, 15.3 mmol) and diphenylacetic acid (3.24 g, 15.3 mmol) in CH_2Cl_2 (30 mL) is added triflic acid dropwise until gas evolution has ceased. Stirring is continued for 1 h, and the solution is neutralized with triethylamine. In order to remove polymeric material as well as triethylammonium triflate, the solution is subjected to flash chromatography (50 g silica gel, 400 mL of chloroform). The solvent is removed and the residue is recrystallized from ether–pentane, yielding 2.97 g (69%) of colorless **20b**: mp 45 °C; IR (KBr) 1721 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.36 (s, 3 H), 2.00 (s, 3 H), 5.12 (s, 1 H), 5.14 (q, 1 H), 7.33 (m, 10 H). Anal. Calcd for $C_{18}H_{18}O_3$ (282.3): C, 76.57; H, 6.42. Found: C, 76.6; H, 6.41.

Hydrolysis of Dioxolium Salts. A solution of 1 g of dioxolium salt in CH_2Cl_2 (100 mL) containing 1 mL of water is stirred at room temperature for 10 h. Evaporation of the solvent and (usually) recrystallization yields the following: (a) α-benzoylbenzyl benzoate (**31a**) (quantitatively) from **7a**, mp 122–124 °C (from ether–pentane), (b) 3-oxo-2-butyl benzoate (**31b**) (quantitatively) from **7b** as a liquid, NMR comparison with literature data,[48] (c) α-benzoylbenzyl diphenylacetate (**20a**) (92%) from **16a**, mp 157–158 °C (from CH_2Cl_2–pentane), and (d) 3-oxo-2-butyl diphenylacetate (**20b**) (quantitatively by NMR) from **16b**.

Reaction of Dioxolium Salt 7a with Isopropylamine. Isopropylamine (0.47 g, 8.0 mmol) in CH_2Cl_2 (20 mL) is added at −70 °C to a suspension of dioxolium salt **7a** (1.80 g, 4.0 mmol) in CH_2Cl_2 (30 mL). A homogeneous solution forms which after warming to room temperature is extracted with water. Workup of the organic layer yields 1.29 g (90%) of imidic ester **22**, mp 89–91 °C (from pentane); see above for spectral data.

Reaction of Dioxolium Salt 7a with Diisopropylamine. Diisopropylamine (0.90 g, 8.9 mmol) in CH_2Cl_2 (20 mL) is added dropwise at −70 °C to a suspension of 2.00 g (4.5 mmol) of **7a** in CH_2Cl_2 (20 mL). A homogeneous solution forms which is warmed to room temperature, combined with pentane (100 mL), and recooled to −70 °C. The precipitate of diisopropylammonium triflate is filtered off and the filtrate is dried ($MgSO_4$). The solvent is evaporated and the residue is fractionated by crystallization from ether–pentane, yielding (a) 0.07 g (5%) of α-benzoylbenzyl benzoate (**31a**) (by partial hydrolysis of **7a**) and (b) after 3 months at −30 °C 1.35 g (78%) of 2-(diisopropylamino)-2,4,5-triphenyl-1,3-dioxole (**32**) [mp 98–99 °C; IR (KBr) 1662 (m), 1598 (m), 1278 (s), 1214 (s), 1064 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.23 (d, 12 H), 3.27 (sept, 2 H), 7.17–7.83 (15 H). Anal. Calcd for $C_{26}H_{29}NO$ (387.5): C, 80.58; H, 7.54; N, 3.61. Found: C, 80.8; H, 7.30; N, 3.30.] On standing, **32** slowly hydrolyzes to give benzoin and *N,N*-diisopropylbenzamide.

Deprotonation of Dioxolium Salt 16a. The mixture of **16a** (1.54 g, 2.9 mmol) and 0.37 g (2.9 mmol) of diisopropylethylamine in pentane (30 mL) is stirred under argon for 2 h. Still under argon, diisopropylethylammonium triflate (0.72 g, 91%) is filtered off and washed with pentane (30 mL) and ether (30 mL). The yellow filtrate, which has a yellow-green fluorescence, is concentrated in an oil pump vacuum, yielding a bright-yellow solid which consists mostly of 4,5-diphenyl-2-(diphenylmethylene)-1,3-dioxole (**33**), according to ^1H NMR. The compound is extremely sensitive to moisture and probably air oxidation; among its decomposition products, one finds α-benzoylbenzyl diphenylacetate (**26a**) and benzil. A sample which was recrystallized from ether–pentane did not analyze correctly for $C_{28}H_{20}O_2$ (388.4): calcd C, 86.57; H, 5.19. Found: C, 83.3; H, 5.34.

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