Push-Pull Triafulvenes from 1,1'-Oxy-di[2,3-bis(dimethylamino)cyclopropenylium] and 1-[Bis(dimethylamino)cyclopropenylio]pyridinium Salts

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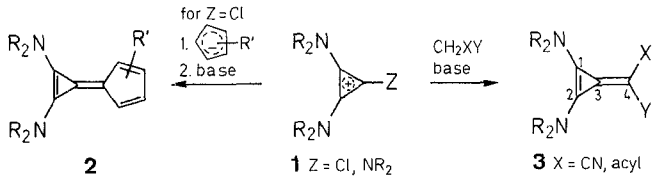
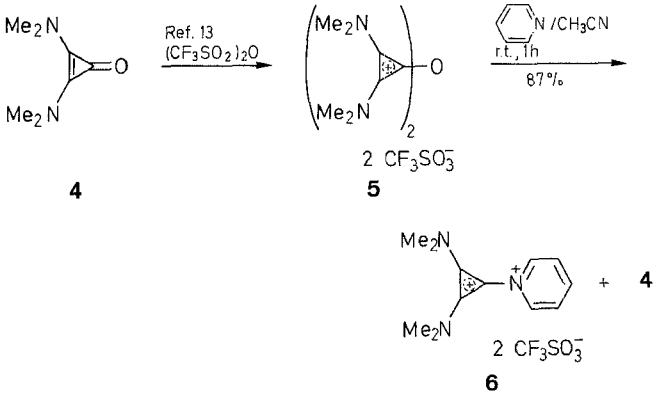
1-[Bis(dimethylamino)cyclopropenylio]pyridinium salt **6** reacts with activated methylene compounds **7** in the presence of pyridine to give triafulvenes **8**. The use of 1,1'-oxy-di[2,3-bis(dimethylamino)cyclopropenylium] salt **5** for the same purpose is limited: with the ambident anions of 1,3-diketones, enol ether salts **9** are formed in some cases at the complete expense of triafulvenes **8**. Compound **8n**, however, can be obtained only from **5**.

Triafulvenes have attracted much interest since they represent the simplest cross-conjugated, cyclic hydrocarbons.[1-3] A variety of triafulvenes have been obtained, mainly by several classical olefin-forming reactions, e.g. the Wittig olefination of cyclopropenones[4] and the condensation of oxy-substituted cyclopropenylium salts with anions of activated methylene compounds[5-7] or with silyl-substituted anions.[8] However, only a few 1,2-diamino-triafulvenes have been prepared so far.[2,3,9-11] A rather general synthesis of push-pull triafulvenes **2** and **3** combines 1-chloro-2,3-diaminocyclopropenylium salts **1** (Z = Cl) with cyclopentadienides[9] and anions of activated methylene compounds.[2,10] With 1,3-diketonates, however, C–O and C–C bond formation may compete with each other.[10] The use of triaminocyclopropenylium salts (**1**, Z=[NR_2]) for the synthesis of **3** meets with serious limitations.[12]



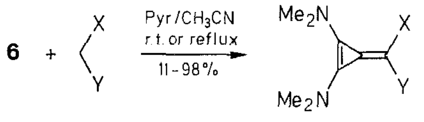
In this paper, we show that the cyclopropenylium salts **5** and **6** may be used as precursors to a variety of push-pull triafulvenes of type **3**. 1,1'-Oxy-di[2,3-bis(dimethylamino)cyclopropenylium] bis(trifluoromethanesulfonate) **5** is readily obtained from cyclopropenone **4** and trifluoromethanesulfonic anhydride.[13] Reaction of **5** with pyridine yields the 1-(diaminocyclopropenylio)pyridinium salt **6** as a crystalline, stable, though somewhat moisture-sensitive compound.



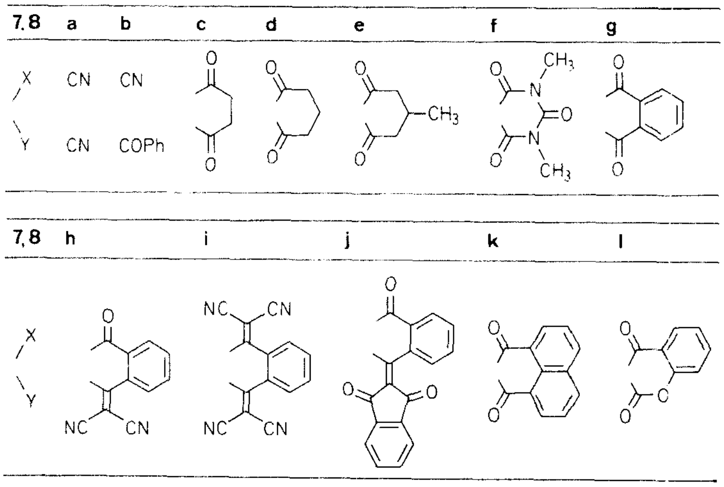
Reaction of **6** with activated methylene compounds **7a–m** in the presence of pyridine yields triafulvenes **8a–m** (Table 1).[14] The transformations proceed at room temperature, except for **8a, m**, where heating is required in order to avoid products from reversible nucleophilic attack at the pyridine ring of **6**. With the Meldrum's acid (**7n**) this reaction mode is irreversible,[15] and a triafulvene cannot be obtained (but see below). Electrophilic attack of **6** at the anion of **7m** occurs at both carbon (→ triafulvene **8m**, 21%) and oxygen (→ **9m**, ca. 50%). The enol ether salt **9m** hydrolyzes on work up, but its presence in the reaction solution is indicated by characteristic NMR signals [e.g. δ (CH=) = 5.70], which are identical with those of an independently prepared sample (see below). One might assume that the low yields of triafulvenes **8c–e** are also due to concomitant electrophilic *O*-attack at the anions of **7c–e**, but the corresponding products were absent from the reaction solutions according to ^{1}H-NMR analysis.

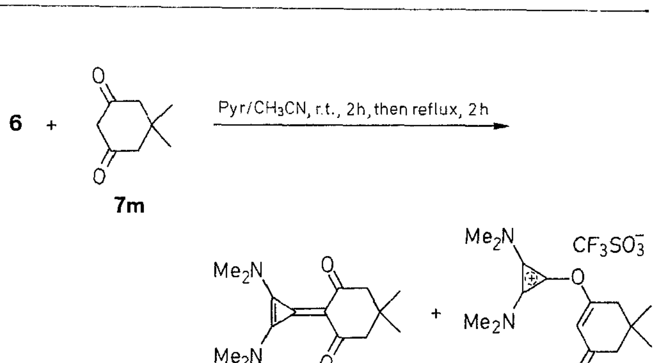
The precursor of **6**, 1,1'-oxy-di[2,3-bis(dimethylamino)cyclopropenylium] salt **5**, can also be used to synthesize triafulvenes **8** directly (Scheme **A**), but only in some cases are the yields better than those of the two-step procedure **5** → **6** → **8**.

With pyridine as a base, the sequence **5** → **6** → **8** can be carried out as a one-pot procedure, i.e. without isolation of **6**. The synthesis of **8g** may serve as an example (see Experimental Part), but in other cases, the presence of the cyclopropenone **4** also formed may render the isolation of the triafulvene more difficult than in the two-step procedure.



7a-l **8a-l**



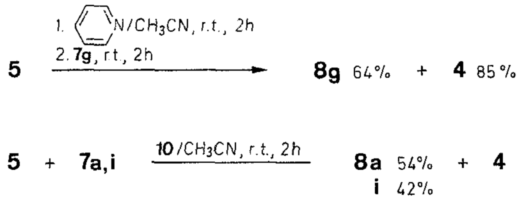


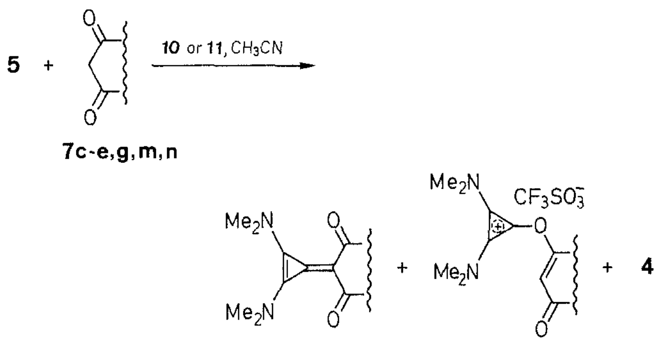
7m

8m 21% **9m**

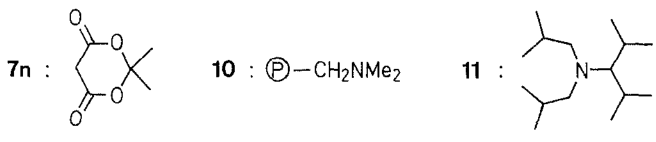
The synthesis of 4,4-diacyltriafulvenes from 1,3-diketonates will be limited if electrophilic *O*-attack at the ambident anion becomes a competing process, which leads to enol ether salts **9** (compare Refs. 10, 16). When the anions of **7c–e, m** are generated with the tertiary amine base **11**, the latter reaction mode occurs at the complete expense of triafulvenes. Only with the polymer-supported amine **10** are triafulvenes **8c, d** formed[17] along with the enol ether salts **9c, d**; with the anions of **7e, m**, triafulvene formation fails even under these conditions.[18] No enol ether salts are formed from 1,3-dicarbonyl compounds with a very low tendency to enolize (**7g, n**). In the case of **7a, i** no competing enol formation is possible; nevertheless, the yields of **8a, i** from **5** with polymer base **10** were inferior to those obtained by the two-step process (**5** → **6** → **8**).

The triafulvenes **8** are characterized by strong IR absorptions at 1909–1937 and 1380–1429 cm^{-1} (Table 1). These bands may be attributed to coupled vibrations of the methylenecyclopropene skeleton[1] with high contributions of the ring vibration in the former case, and presumably of the exocyclic (partial) double bond in the latter.





8c-e,g,m,n **9c-e,g,m,n**



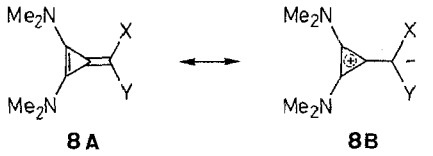
7–9	Base	Yield (%) 8	9	7–9	Base	Yield (%) 8	9
c	10	33	66[a]	g	10	24	–
	11	–	–[b]		11	42	–
d	10	24	55[a]	m	10	–	61
	11	–	–[b]		11	–	54
e	10	–	–[b]	n	11	42	–
	11	–	–[b]				

[a] Not isolated, yield determined by ^{1}H-NMR spectroscopy of the reaction mixture.
[b] Detected by ^{1}H-NMR spectroscopy, but not isolated (see Experimental Part).

The push-pull substitution of **8** allows a description of their ground-state electronic structure by the resonance **8A** ↔ **8B**. The high contribution of **8B** is documented in the ^{1}H-NMR spectra, where the NCH_3 peak appears at values (δ = 3.27–3.42, except for **8a, j**) that are typical for dimethylaminocyclopropenylium ions such as **1**, **5**, and **6**.[19] Moreover, the carbonyl absorptions in the IR spectrum of acylated triafulvenes **8c–h, i–m** are at considerably lower frequencies than those in the dicarbonyl compounds **7**, and even distinctly lower (ca. 30–70 cm^{-1}) than in analogous triafulvenes[20] having phenyl instead of dimethylamino groups.

The UV/VIS absorptions of the triafulvenes reported here display diverging behavior in differing solvents. (Table 2). Negative solvatochromism is observed for **8a–f, l, m, n**, where polar and hydrogen-donating solvents stabilize structure **8B** in the electronic ground state, which is more polar than the excited state. Positive solvatochromism is found for **8g, h** and, on the whole, for **8k**. For **8i** and **8j**, the longest-wavelength absorption does not change significantly with the solvent polarity, except for alcohols. No detailed rationalization for the diverging features of the indanedione derivatives **8g–j** will be attempted here.[21] We suggest, however, that the pseudo 8π perimeter of the 1,3-indanedione anion may be responsible for a destabilizing (anti-

aromatic) contribution of the dipolar structure **8B** to the electronic ground state of **8g** (compare Ref. 10). Furthermore, we want to point out, that the longest-wavelength absorption of **8i** is a structured band that is similar, but not identical, in position and shape to that of the anion of 1,3-bis(dicyanomethylene)indane.[22]



8A **8B**

Table 1. Triafulvenes **8** from Salts **5** or **6**[a]

Compound	Yield from **6**[b] (%)	mp (°C) (solvent)	Molecular Formula[c]	IR (KBr) ν (cm^{-1})	UV/VIS (CH_3CN) λ_{max} (nm) (lg ε)	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
8a	60 (54)	287–289 (MeOH)	$C_{10}H_{12}N_4$ (188.2)	2180, 2155, 1953, 1420, 1391	218 (4.06), 279 (4.34)	3.13 (s)
8b	64	200 (acetone)	$C_{16}H_{17}N_3O$ (267.3)	2170, 1937, 1588, 1559, 1404	223 (4.31), 336 (4.25)	3.28 (s, 12H); 7.27–7.53 (m, 3H); 7.70–7.97 (m, 2H)
8c	27 (33)	298–300 (EtOAc)	$C_{12}H_{16}N_2O_2$ (220.3)	1932, 1584, 1429	255 (4.17), 302 (4.37), 312 (4.37)	2.43 (s, 4H); 3.42 (s, broadened, 12H)
8d	11 (24)	180 (EtOAc)	$C_{13}H_{18}N_2O_2$ (234.3)	1909, 1569, 1380	231 (3.87), 303 (4.23)	1.99 (q, 2H, ^3J = 6.1); 2.38 (t, 4H); 3.33 (s, 12H)
8e	19 (–)	206–207 (EtOAc)	$C_{14}H_{20}N_2O_2$ (248.3)	1911, 1568, 1387	231 (3.90), 303 (4.26)	1.03 (d, broadened, 3H); 1.93–2.46 (m, 5H); 3.30 (s, 12H)
8f	96	316 (CH_3CN)	$C_{13}H_{18}N_4O_3$ (278.3)	1923, 1680, 1620, 1387	207 (4.06), 303 (4.38)	3.34 (s, 6H); 3.40 (s, 12H)
8g	76 (42)	324 (MeOH)	$C_{16}H_{16}N_2O_2$ (268.3)	1929, 1628, 1581, 1421	219 (4.46), 280 (4.13), 290 (4.36), 341 (4.41), 355 (4.40)[d]	3.38 (s, 12H); 7.30–7.64 (m, 4H)
8h	78	271 (MeOH)	$C_{19}H_{16}N_4O$ (316.4)	2098, 1929, 1642, 1579, 1420	248 (4.39), 253 (4.38), 312 (4.34), 325 (4.38), 499 (3.88)	3.23 (s, 6H); 3.37 (s, 6H); 7.30–7.60 (m, 3H); 8.20–8.37 (m, 1H)
8i	92 (42)	297 (MeOH)	$C_{22}H_{16}N_6$ (364.4)	2096, 1929, 1405	255 (4.67), 367 (4.37), 572 (4.33)	3.27 (s, 6H); 3.33 (s, 6H); 7.33–7.53 (m, 2H); 8.28–8.42 (m, 2H)
8j	98	308 (MeOH)	$C_{25}H_{20}N_2O_3$ (396.4)	1922, 1669, 1632, 1578, 1428	253 (4.66), 329 (4.39), 423 (3.80), 555 (4.19), ~610 (sh)	3.16 (s, 12H); 7.30–7.78 (m, 7H); 8.25–8.42 (m, 1H)
8k	67	307–308 (EtOAc)	$C_{20}H_{18}N_2O_2$ (318.4)	1914, 1623, 1560, 1390	229 (4.75), 330 (4.55), 343 (4.47), 436 (3.35)	3.40 (s, 12H); 7.63 (dd, 2H); 8.03 (dd, 2H); 8.53 (dd, 2H)
8l	69	256 (EtOAc)	$C_{16}H_{16}N_2O_3$ (284.3)	1916, 1610, 1518, 1405	217 (4.26), 270 (3.89), 342 (4.19)	3.40 (s, 12H); 7.10–7.60 (m, 3H); 8.03–8.23 (m, 1H)
8m	21 (–)	209 (MeOH)	$C_{15}H_{22}N_2O_2$ (262.3)	1923, 1573, 1552, 1400	232 (3.89), 303 (4.31)	1.04 (s, 6H); 2.27 (s, 4H); 3.33 (s, 12H)
8n	– (42)	202 (CH_3CN)	$C_{13}H_{18}N_2O_4$ (266.3)	1927, 1652, 1559, 1404	231 (4.07), 288 (4.34)	1.67 (s, 6H); 3.33 (s, 12H)

[a] Melting points (uncorrected): heat block. UV/VIS spectra: GCA/Mc Pherson EU-700-32. IR spectra: Perkin-Elmer Infrared Spectrometer 397. ^{1}H-NMR spectra: Varian EM 390 (90 MHz, TMS as standard). ^{13}C-NMR spectra: Bruker WP 200 (TMS as standard).

[b] In parentheses: Yields from **5** in the presence of base **10** or **11** (only highest value given, compare Scheme **A**).

[c] Satisfactory microanalyses obtained: C ±0.4 (**8c**: −0.5; **8f**: −0.5; **8k**: −0.4); H ±0.20; N ±0.2 (**8g**: −0.4).

[d] Shoulder on long-wavelength side.

Table 2. UV/VIS Absorption Spectra of Triafulvenes **8** in Different Solvents[a]

Compound	Solvent[b] Benzene	Dioxane	CH_2Cl_2	Acetone	EtOH	CH_3OH
8a	289 (4.30)	287 (4.38)	284 (4.34)		279 (4.38)	277 (4.31)
8b	343 (4.26)	340 (4.18)	340 (4.21)	340 (4.22)	336 (4.24)	335 (4.24)
8c	318 (4.05)	314 (4.28)	313 (4.32)		298 (4.33)	296 (4.33)
8d	317 (4.32)	314 (4.27)	306 (4.25)		290 (4.28)	289 (4.32)
8m	316 (4.33)	312 (4.69)	305 (4.32)		292 (4.32)	291 (4.38)
8f	317 (4.73)	314 (4.42)	306 (4.45)		303 (4.34)	302 (4.32)
8n	295 (4.39)	291 (4.39)	291 (4.34)		284 (4.35)	282 (4.38)
8l	346 (4.30)	345 (4.26)	345 (4.25)	344 (4.27)	336 (4.25)	336 (4.23)
8g	[c]	[c]	[c]	[c]	416 (3.21)	416 (3.17)
8h	493 (3.91)	497 (3.90)	498 (3.89)	497 (3.93)	500 (3.84)	502 (3.87)
8i	568 (4.33)	570 (4.28)	572 (4.39)	569 (4.30)	571 (4.22)	561 (4.24)
8j	556 (4.18)	553 (4.16)	558 (4.19)	555 (4.15)	550 (4.02)	544 (3.95)
8k	430 (3.36)	435 (3.41)	433 (3.39)	434 (3.33)	434 (3.40)	434 (3.43)

[a] Long-wavelength absorption, λ_{max} (nm), lg ε in parentheses.

[b] Solvents in the order of increasing E_T^N values; see Table 1 for values in CH_3CN.

[c] Shoulder that cannot be located precisely ("λ_{max}" < 416 nm).

Anhydrous acetonitrile was used. Compounds **7b**,[23] **7e**[24] **7h**,[25,26] **7i**[25,27], and **7k**[28] were prepared according to published methods.

1-[2,3-Bis(dimethylamino)-1-cyclopropenylio]pyridinium Bis(trifluoromethanesulfonate) (6):
Pyridine (0.158 g, 2.0 mmol) is added to a solution of **5**[13] (1.12 g, 2.0 mmol) in acetonitrile (20 mL). After stirring at room temperature for 1 h, **6** is precipitated by addition of ether. The solid is redissolved in acetonitrile and precipitated again with ether; yield: 0.87 g (87%); mp 184°C.

$C_{14}H_{17}F_6N_3O_6S_2$	calc.	C 33.54	H 3.42	N 8.38
(501.4)	found	33.4	3.51	8.5

IR (KBr): ν = 1949 (s), 1658 (vs), 1471 (s), 1415 (s), 1289 (vs), 1257 (vs), 1223 (s), 1162 (s), 1139 (s), 1029 (vs) cm^{-1}.

^{1}H-NMR (CD_3CN): δ = 3.40 (s, 6H, NCH_3); 3.46 (s, 6H, NCH_3); 8.37 (dd, 2H, J = 7.7, 1.4 Hz, H-3, 5); 8.90 (tt, 1H, J = 7.7, 6.3 Hz, H-4); 9.15 (dd, 2H, J = 6.3, 1.4 Hz, H-2, 6).

^{13}C-NMR (CD_3CN): δ = 44.2 (NCH_3), 44.5 (NCH_3), 125.6 (s, C-1'), 130.5 (d, C-3, 5), 131.7 (s, C-2', 3'), 146.0 (d, C-2, 6), 151.2 (d, C-4).

Triafulvenes 8a–m from Salt 6; General Procedure:
Salt **6** (1.50 g, 3.0 mmol) in CH_3CN (10 mL) is added to a solution of **7a–m** (3.0 mmol) and pyridine (0.475 g, 6.0 mmol) in CH_3CN (20 mL). The mixture is stirred at room temperature for 1 h (**7a**: reflux, 24 h; **7b**: r.t., 7 d, or reflux, 24 h; **7m**: r.t., 2 h, then reflux, 2 h). Work up is done by one of the following procedures:

Procedure A (**8f**): The solution is concentrated to ca. 10 mL, and the product is crystallized at −35°C.

Procedure B (**8h–j**): The solvent is replaced by $CHCl_3$ (200 mL). After extraction with aqueous ammonia (10%; 20 mL) and water (3 × 20 mL), the organic layer is dried ($MgSO_4$). The solvent is evaporated, and the residue is recrystallized from methanol.

Procedure C (**8a–e, g, k–m**): After work up according to Procedure B, the residue is subjected to column chromatography on silica gel (100 g) with methanol (600 mL) as eluent.

Reaction of Salt 5 with Pyridine and 1,3-Indanedione (7g):
A solution of salt **5** (0.563 g, 1.0 mmol) and pyridine (0.237 g, 3.0 mmol) in CH_3CN (30 mL) is stirred for 2 h. After addition of **7g** (0.146 g, 1.0 mmol), stirring is continued for 2 h. Work up as in Procedure C (see above) gives:

2,3-bis(dimethylamino)cyclopropenone (**4**); yield: 0.119 g (85%); mp and spectroscopic data agree with literature values[29]; and

2-[*2,3-bis(dimethylamino)-2-cyclopropen-1-ylidene*]-*1,3-indanedione* (**8g**); yield 0.173 g (64%).

Reaction of Salt 5 with Methylene Compounds 7 in the Presence of Dimethylaminomethylpolystyrene (10):
A solution of **5**[13] (1.12 g, 2.0 mmol) in CH_3CN (10 mL) is added dropwise to the mixture of methylene compound **7** (2.0 mmol) and amine **10** (1.43 g, 4.0 m-equiv) in CH_3CN (20 mL). After stirring at room temperature for 2 h, the polymer is filtered off and rinsed with $CHCl_3$ (30 mL). The filtrates are combined, and the solvent is removed at 30°C/12 Torr. Further work up is done individually:

3-Dicyanomethylene-1,2-bis(dimethylamino)cyclopropene (**8a**) from malononitrile (**7a**): Recrystallization from CH_3CN gives colorless needles; yield: 0.203 g (54%); see Table 1.

2-[*2,3-Bis(dimethylamino-2-cyclopropen-1-ylidene*]-*1,3-cyclopentanedione* (**8c**) from 1,3-cyclopentanedione (**7c**): Chromatography over silica gel (100 g) with methanol (400 mL) affords cyclopropenone **4** (0.335 g, 120% and triafulvene **8c** (0.145 g, 33%); see Table 1. Enol ether salt **9c** is present in the crude reaction mixture [^{1}H-NMR ($CDCl_3$): δ = 3.25 (s, $N-CH_3$); 5.99 (t, ^4J = 1.3 Hz, =CH); yield: 66%], but is hydrolyzed to **4** and **7c** on chromatographic work up.

2-[*2,3-Bis(dimethylamino)-2-cyclopropen-1-ylidene*]-*1,3-cyclohexanedione* (**8d**) from 1,3-cyclohexanedione (**7d**): Chromatography over silica gel (100 g) with methanol (400 mL) affords cyclopropenone **4** (0.390 g, 140%) and triafulvene **8d** (0.113 g, 24%); see Table 1. Enol ether salt **9d** is found in the crude reaction mixture [^{1}H-NMR data identical with an independently prepared sample (see below); yield: 55%], but is hydrolyzed on chromatographic work up.

1-[(5-Methyl-3-oxo-1-cyclohexen-1-yl)oxy]-2,3-bis(dimethylamino)cyclopropenylium trifluoromethanesulfonate (**9**) from 5-methyl-1,3-cyclohexanedione (**7e**): In the reaction solution, **9e** and cyclopropenone **4** are present practically exclusively according to ^{1}H-NMR analysis; separation, however, proved impossible.

^{1}H-NMR (CD_3CN): δ = 3.16 (s, 12H); 5.72 (t, 1H, ^4J = 1.1 Hz).

2-[*2,3-Bis(dimethylamino-1-cyclopropen-1-ylidene*]-*1,3-indanedione* (**8g**) from 1,3-indanedione (**7g**): Chromatography over silica gel (100 g) with methanol (400 mL) yields **8g** as orange needles; yield: 0.128 g (24%); see Table 1.

1,3-Bis(dicyanomethylene)-2-[2,3-bis(dimethylamino-1-cyclopropen-1-ylidene]indane (**8i**) from 1,3-bis(dicyanomethylene)indane (**7i**): Recrystallization from methanol gives violet crystals; yield: 0.307 g (42%); see Table 1.

2,3-Bis(dimethylamino)-1-[(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)oxy]-cyclopropenylium trifluoromethanesulfonate (**9m**) from dimedone (**7m**): The residue is concentrated to ca. 10 mL, and ether (10 mL) is added to give **9m** as colorless crystals; yield: 0.500 g (61%); mp 157–158°C.

$C_{16}H_{23}F_3N_2O_5S$	calc.	C 46.60	H 5.62	N 6.79
(412.4)	found	46.3	5.55	7.0

IR (KBr): ν = 1968 (C_3-ring); 1628 (C=O); 1270, 1150, 1029 (CF_3SO_3) cm^{-1}.

^{1}H-NMR (CD_3CN): δ = 1.06 (s, 6H, CH_3); 2.22 (s, 2H, CH_2); 2.53 (d, 2H, ^4J = 1.1 Hz, CH_2); 3.13 (s, 12H, $N-CH_3$); 5.70 (t, 1H, ^4J = 1.1 Hz, =CH).

^{13}C-NMR (CD_3CN): δ = 27.8 [$C(CH_3)_2$]; 33.0 (C-5); 40.9, 50.7 (C-4, C-6); 42.3 ($N-CH_3$); 109.7 (C-2); 110.0 (C-1'); 127.2 (C-2', 3'); 198.7 (C=O).

Reaction of Salt 5 with Methylene Compounds 7 in the Presence of 3-(2-Methylpropylamino)-2,4-dimethylpentane (11):
The solution of **5**[13] (1.12 g, 2.0 mmol) in CH_3CN (10 mL) is added dropwise to a solution of **7** (2.0 mmol) and **11** (0.91 g, 4.0 mmol) in CH_3CN (20 mL). After stirring for 2 h at room temperature, the solvent is evaporated at 30°C/12 Torr. The residue is worked up individually.

Enol ether salts **9c, e** from diketones **7c, e**: Separation of **9c, e** from also formed cyclopropenone **4** proved impossible. According to ^{1}H-NMR spectroscopy, **9** and **4** were the only products.

^{1}H-NMR (CD_3CN): **9c**: δ = 3.20 (s, 12H, $N-CH_3$); 5.90 (t, 1H, ^4J = 1.3 Hz, =CH); **9e**: δ = 3.16 (s, 12H, $N-CH_3$), 5.72 (broad s, 1H, =CH).

2,3-Bis(dimethylamino)-1-[3-oxo-1-cyclohexen-1-yl)oxy]cyclopropenylium trifluoromethanesulfonate (**9d**) from 1,3-cyclohexanedione (**7d**): The reaction solution is concentrated to ca. 10 mL. Salt **9d** is separated with ether (10 mL) as a viscous colorless oil (0.436 g, 57%), which cannot be purified further.

^{1}H-NMR (CD_3CN): δ = 1.90–2.23 (m, 2H, CH_2), 2.40 (br t, 2H, ^3J = 6.0 Hz, CH_2); 2.67 (t, 2H, ^3J = 6.0 Hz, CH_2); 3.16 (s, 12H, NCH_3); 5.72 (t, 1H, ^4J = 0.9 Hz, =CH).

Enol ether Salt **9m** from dimedone (**7m**): The reaction solution is concentrated to ca. 10 mL. After addition of ether, **9m** is obtained as colorless crystals; yield: 54%. Physical and spectroscopic data, see above.

Triafulvene **8g** from 1,3-indanedione (**7g**): Recrystallization from methanol affords orange needles; yield: 0.226 g (42%); see Table 1 for physical and spectroscopic data.

2,2-Dimethyl-5-[2,3-bis(dimethylamino)-2-cyclopropen-1-ylidene]-1,3-dioxane-4,6-dione (**8n**) from Meldrum's acid (**7n**): Chromatography on silica gel (100 g) with acetone (400 mL) gives **8n**; yield: 0.224 g (42%); mp 202°C (colorless needles from acetonitrile); see Table 1.

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