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THE BIMOLECULAR REACTIONS OF TRIMETHYLENEMETHANE DIRADICALS WITH ACRYLONITRILE AND MOLECULAR OXYGEN

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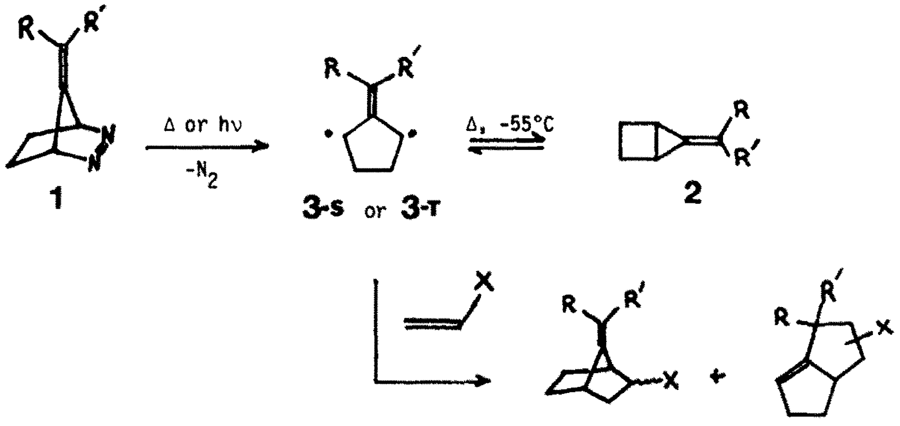
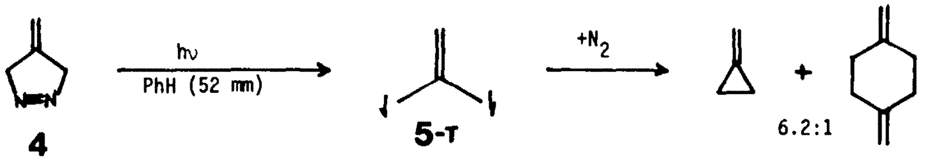
Abstract - The interception and trapping by molecular oxygen and acrylonitrile of trimethylenemethane diradicals during their reversible thermal formation from stable methylenecyclopropane precursors is reported. The regiochemistry of acrylonitrile cycloaddition to a trimethylenemethane is also unequivocally demonstrated and provides insight into the trapping process.

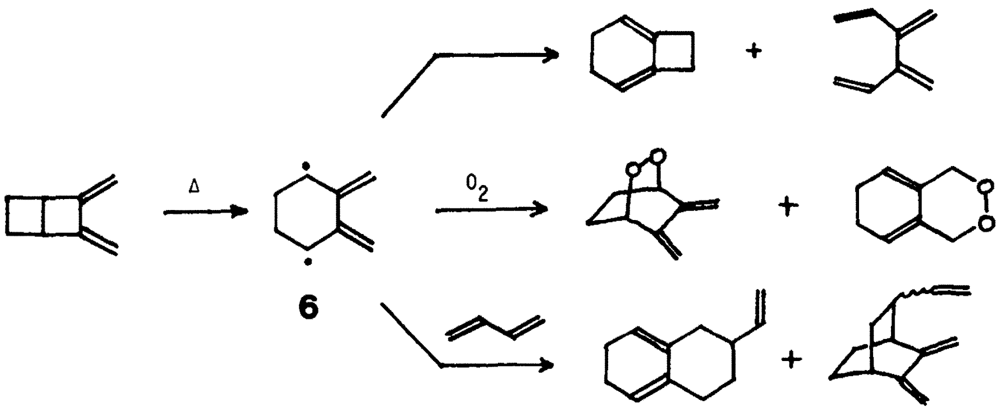
The interception of diradicals in bimolecular trapping reactions has only been rarely observed. In general, intramolecular cyclization processes compete too favorably with any intermolecular reactions. Berson, in a series of elegant papers, has described conditions wherein the trapping of both the singlet and triplet forms of 2-alkylidenecyclopentane-1,3-diyl, **3-S** and **3-T**, formed during the thermal or photochemical deazetations of **1**, or from the thermolysis (-56°C) of the strained and very reactive 5-alkylidenebicyclopentane (**2**), is able to be distinctly observed.[1] Berson has accumulated convincing kinetic evidence for the reversible formation of singlet trimethylenemethane species **3-S** which can itself undergo cycloadditions with diylophiles such as acrylonitrile or maleic anhydride.[2] It should be noted that in the absence of trapping diylophiles, at temperatures >-56°C, **2** is not stable and undergoes dimerization, presumably via **3-T**.



Indeed triplet diradicals, including parent trimethylene methane, 5-T, have often been trapped bimolecularly. Gajewski noted, for example, the dimerization of 5-T during his study of the deazetation of pyrazoline 4.[3] Wilson and Geiser have been successful in trapping 3-T as well



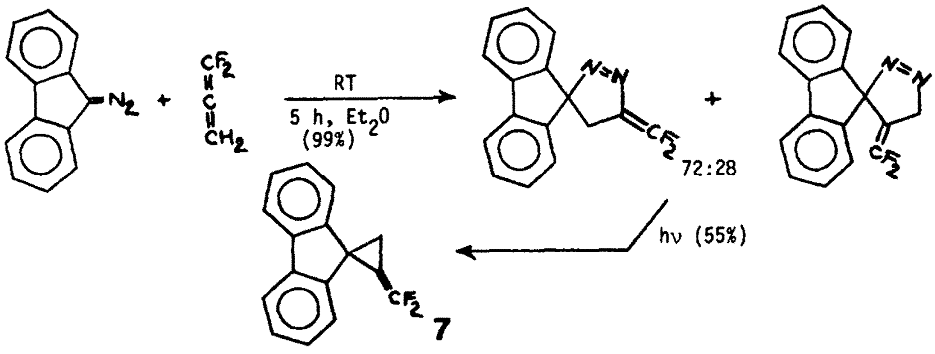
as triplet cyclopentane-1,3-diyl with molecular oxygen, forming cyclic peroxides in good yield.[4] In such trapping experiments, it has commonly been assumed that any diradical species successfully trapped by molecular oxygen are in their triplet states.[1,4,5] Consistent with this assumption is the very interesting report of the trapping of a thermally-generated diradical by Roth whereby the trapping of singlet and triplet 2,3-dimethylene-1,4-cyclohexadiyl 6 by 1,3-butadiene and molecular oxygen respectively, is elegantly demonstrated.[6]



We wish to report at this time a similar interception and trapping of trimethylenemethane diradicals by acrylonitrile and molecular oxygen during their reversible thermal generation from methylenecyclopropane precursors.

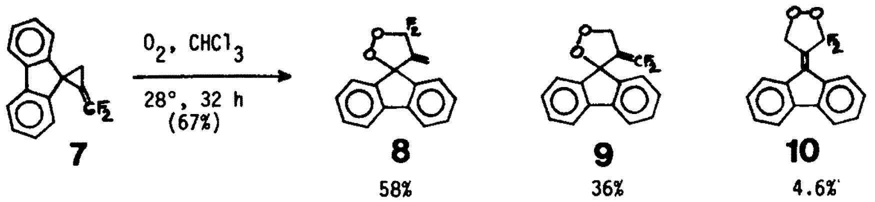
Results

2-(Difluoromethylene)spiro[cyclopropane-1,9'-[9H]-fluorene], 7, was synthesized by addition of diazofluorene to 1,1-difluoroallene,[7] followed by photolysis of the product mixture. Attempts to purify 7 by recrystallization or column chromatography led to the isolation of



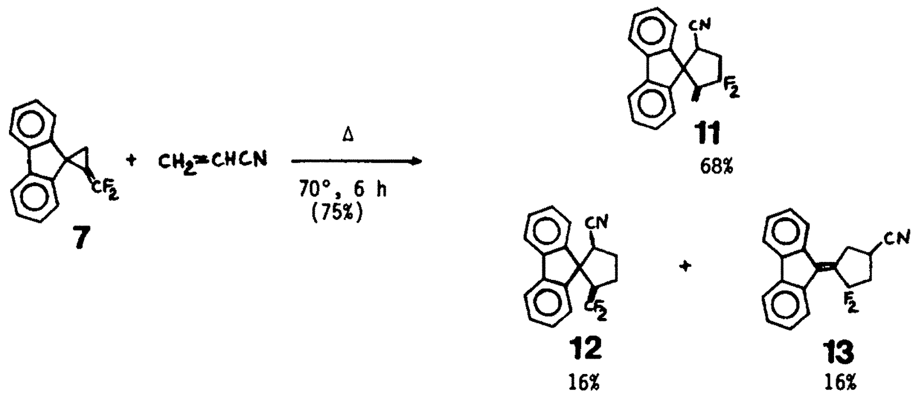
impurities with masses of 272 (i.e. mass of **7** + 32) and the realization that **7** was apparently reactive with O_2.

Indeed, bubbling O_2 into a $CHCl_3$ solution of **7** led to its clean conversion to the three dioxolanes **8**, **9** and **10**.



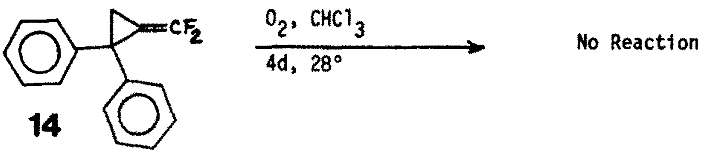
The three adducts, **8**, **9** and **10**, were isolated by silica gel flash chromatography and characterized by $^1H_1$, ^{19}F and ^{13}C NMR and IR-spectroscopy. Distinctive spectroscpic characteristics included for **8**, vinyl protons at δ 5.72 (d of t) and 5.10 ppm (d of t), a single ^{19}F absorption at ϕ 77.7 (triplet), and a triplet with J_{CF} = 266 Hz at δ 127.6 ppm in the ^{13}C spectrum; for **9**, a two proton triplet at δ 5.16, two ^{19}F absorptions at ϕ 85.4 (d of t) and 87.8 (d of t) and a doublet of doublets at δ 148.1 in the ^{13}C spectrum with J_{CF} = 285.6 and 290.5 Hz (the characteristic strong IR absorption due to $=CF_2$ at 1789 cm^{-1} was also present); for **10**, a two proton triplet at δ 5.55 and a single ^{19}F absorption at ϕ 78.0.

When **7** was heated at 70°C in acrylonitrile a surprisingly regioselective formation of three adducts was observed in 75% yield. The products were isolated by flash chromatography and characterized by NMR and IR spectroscopy. Distinctive spectroscopic characteristics included for **11**, vinyl protons at δ 5.68 and 4.90 ppm (d of d of d), two ^{19}F absorptions at ϕ 88.3 and 98.5 ppm (AB), and a triplet in ^{13}C (J_{CF} = 247.7 Hz) at δ 123.9 ppm; for **12**, no vinyl protons, a ^{19}F AB system at ϕ 85.7 and 86.2 ppm, a ^{13}C doublet of doublets (J_{FF} = 287.5 and 291.1 Hz) at δ 150.5 ppm, and the expected strong IR absorption at 1765 cm^{-1}; for **13**, no vinyl protons, an AB pattern in ^{19}F at ϕ 89.5 and 92.4 ppm and a triplet in the ^{13}C spectrum at δ 128.4 (J_{CF} = 248.2 Hz). In the characterization of **11**, **12** and **13** the $^1J_{CF}$, $^2J_{CF}$ and $^3J_{CF}$ couplings were particularly informative structure indicators.

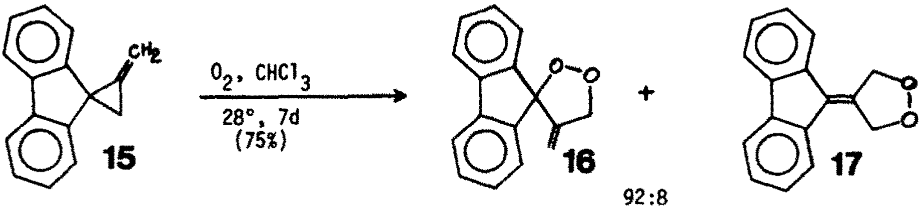


It was also found in preliminary experiments that **7** underwent similar reactions with dimethyl fumarate and tetracyanoethylene, although these adducts were not fully characterized.

Interestingly, 2,2-diphenyl-1-(difluoromethylene)cyclopropane (**14**), prepared similarly to **7**,[7] did not react similarly, while the fluorenyl system **15**, without fluorine substituents, did

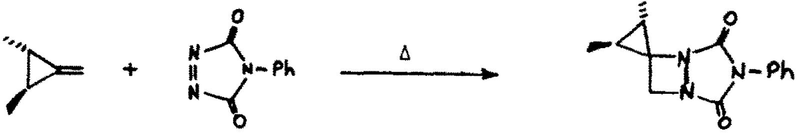


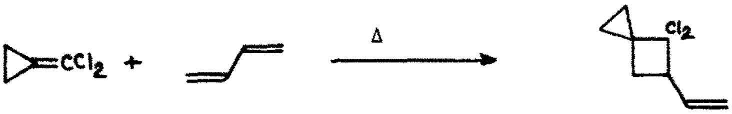
react with oxygen albeit more slowly to form the expected two adducts (**16** and **17**) which were easily characterized spectroscopically.

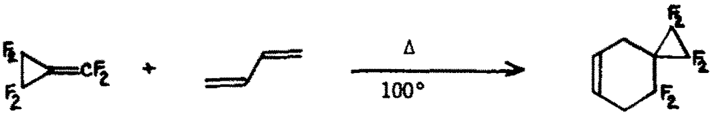


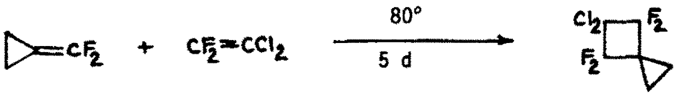
Discussion

Methylenecyclopropanes are generally unreactive addends in cycloadditions. When especially reactive ones such as (difluoromethylene)cyclopropanes and (dichloromethylene)cyclopropanes do react they've generally been shown to form the normal (2+2) adducts or (2+4) adducts as shown below.[8-11]



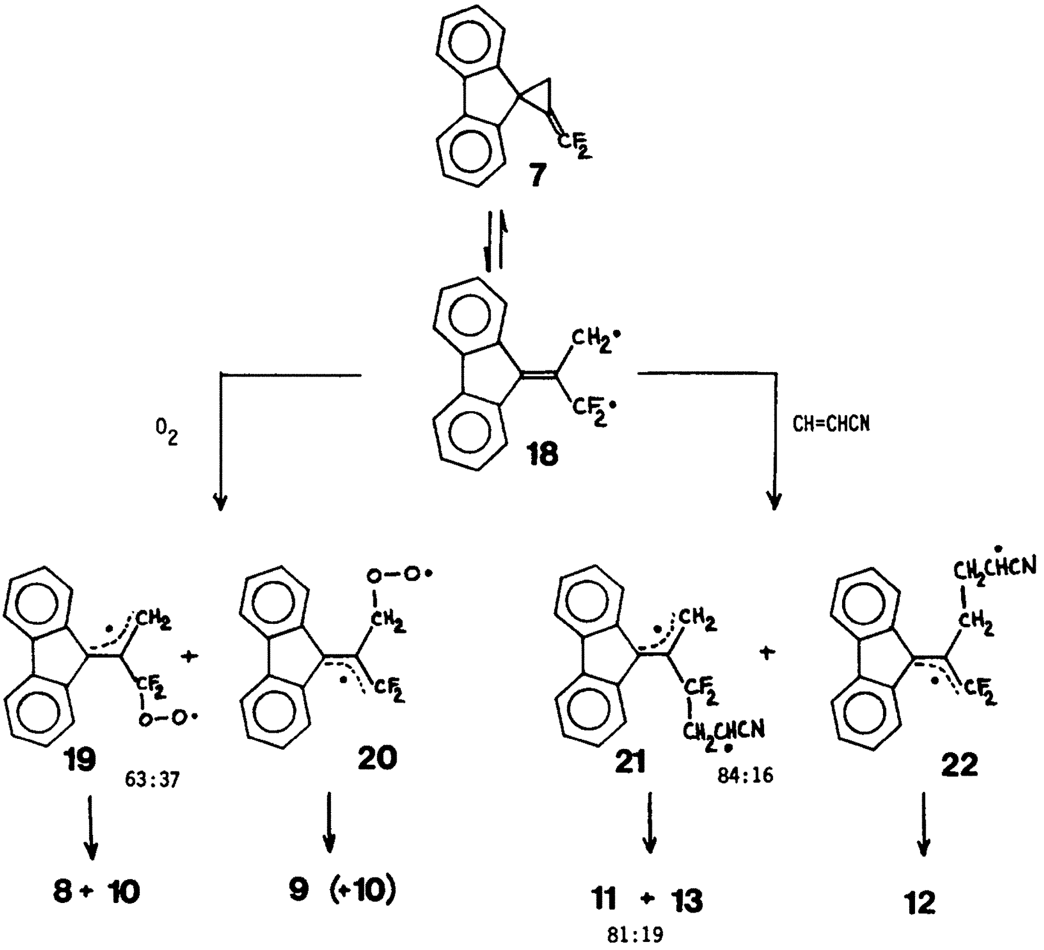




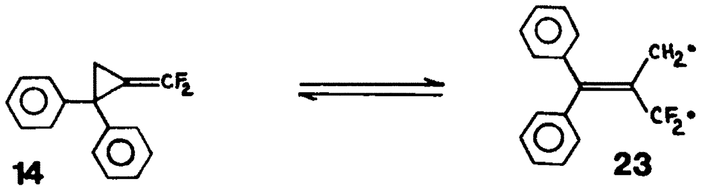


The reactions of **7** and **15** are most simply interpreted as deriving from a trapping of their respective, reversibly-formed trimethylenemethanes. For example, **7** would be expected to be in slow thermal equilibrium with trimethylenemethane **18** at room temperature. The fluorenyl group should lower the activation energy for homolysis to trimethylenemethane **18** by ~17 kcal/mole.[12]

With the activation energy for isomerization of (difluoromethylene)cyclopropane being 40.2 kcal/mole[13] this would give rise to an E_a for formation of **18** of ~25 kcal/mole. Assuming a log A of 13.2,[13] this would generate a rate constant of $k = 1.15 \times 10^{-5}$ at 28°C. If trapping were to occur with each cleavage of **7** to **18**, which is unlikely, the expected half-life for formation of peroxides **8**, **9** and **10** would be 16 hours, a value not inconsistent with the observed reactivity of **7**.

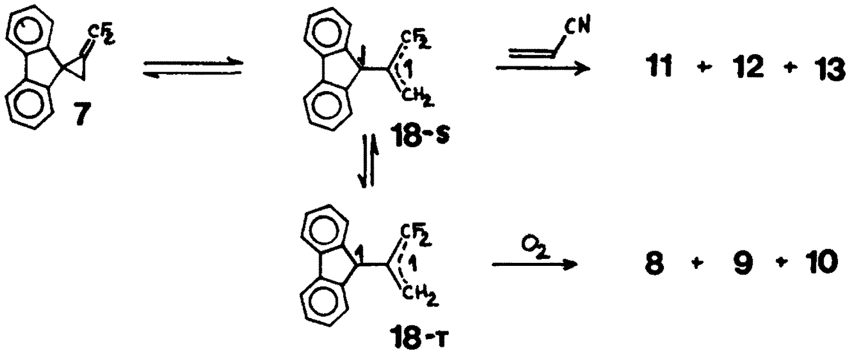


While the benzhydryl-radical-stabilized trimethylenemethane species **23** should be similarly stabilized[14], the preexponential factor for **14** → **23** conversion should be significantly

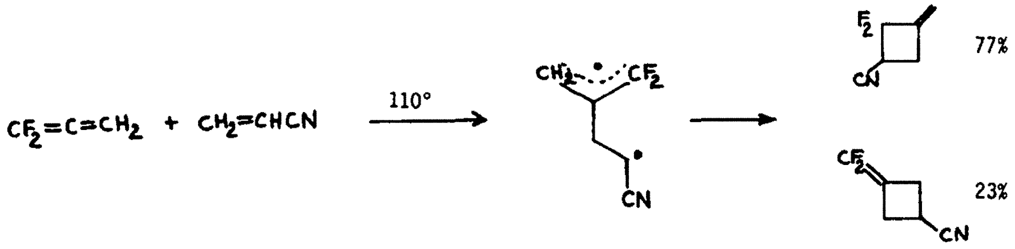


lower because of the entropy loss associated with stabilization by the two phenyls (Log A ≈ 10.8 for **14** vs ~13.2 for **7**)[14]. In contrast to the situation with the two phenyl substituents, the fluorenyl group should require virtually no loss of entropy to act as a radical stabilizer since it is perfectly aligned in **7** for delocalization of the incipient radical resulting from homolysis to **20**. The difference in log A alone would lead to a sufficient diminishment in rate for **14** to account nicely for the observed relative lack of reactivity of **14**.

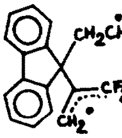
A mechanistic scheme similar to that proposed by Roth[6] for trapping of diradical **6**, wherein acrylonitrile and oxygen trap singlet and triplet **18**, respectively, is consistent with our results. The fact that **7** is stable indefinitely in solution in the absence of trapping agent would require **18-S** and **18-T** to be in equilibrium, as was found in Roth's case. While the above scheme is consistent with our results, there is no direct evidence for it. While the oxygen trapping is likely of the triplet, one cannot yet be certain as to the multiplicity of the species trapped by acrylonitrile.



The regiochemical results are also consistent with the proposed mechanism. It is reasonable that intermediates **19** and **21** should be kinetically favored over **20** and **22** respectively. The strong thermodynamic preference for sp^3-hybridized versus sp^2-hybridized CF_2[15] apparently influences the regiochemistry of O_2 and CH_2=CHCN trapping substantially, not unlike the kind of preferences shown in cyclization of difluoroallene (2+2) cycloaddition intermediate diradicals.[16] Note, moreover, that O_2 trapping is less regioselective (63:37) than that of CH_2=CHCN (84:16), as one might have expected on the basis of the usual reactivity-selectivity inverse relationship.



The regiochemistry of acrylonitrile addition provides additional important information about the trapping process. While Berson demonstrated that his trimethylenemethane species **3** could be trapped by acrylonitrile, the regiochemistry of the addition with respect to the acrylonitrile was not reported. Our observation of adducts **11**, **12** and **13** would seem to exclude the possibility



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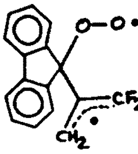

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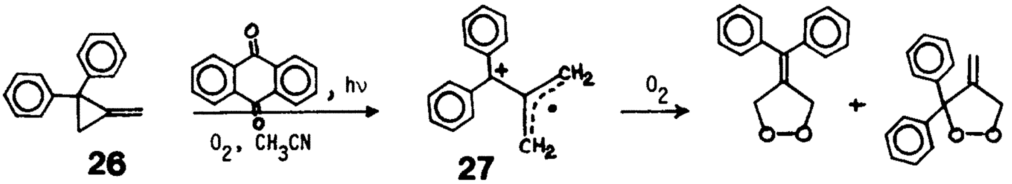
of intermediate **24** and, by analogy, **25**, playing significant roles in the trapping processes.

The fluorenyl group, not the geminal fluorine substituents, of **7** would appear to give rise to its special reactivity. The diminished but real reactivity of unfluorinated analog **15** indicates the fluorine substituents to be salutory but not required for cycloaddition to occur.

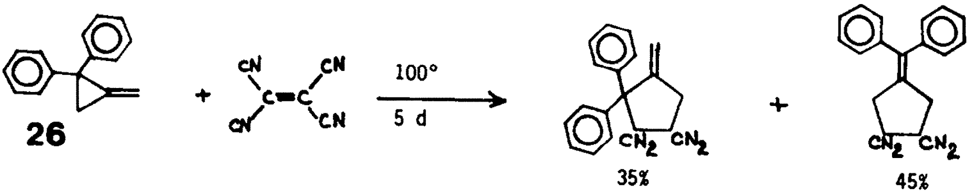
The nature and regiochemistry of the addition products would appear to require a mechanism involving trapping of trimethylenemethane diradicals. Concerted mechanisms of **7** and **15**, or processes involving charge-transfer or electron transfer seem unlikely.

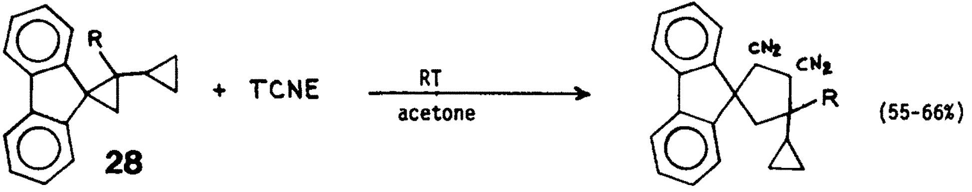
Takehashi and coworkers have recently reported[18] the photosensitized trapping of a trimethylenemethane radical cation **27** by molecular O_2. However there is no chance that our



reactions could have been photoinitiated. All reagents were colorless; hence the chance of inadvertant photolysis is remote.

In this connection, two cases of related reactions which likely involve non-photoinduced electron-transfer should be mentioned. One, a 1971 report of the reaction of TCNE (and apparently only TCNE) with 2,2-diphenylmethylenecyclopropane, **26**,[19a] was at that time interpreted in terms of a standard diradical mechanism, while the other, a very recent report of the reactions of TCNE with various fluorene-activated cyclopropanes, **28**,[19b] proposes electron





transfer as the initial mechanistic step. With neither acrylonitrile nor O_2 being effective thermal electron acceptors, especially when compared to TCNE, it seems unlikely that electron transfer is involved in our observed reactions. However, this possibility has not yet been explicitly excluded.

CONCLUSIONS

While there is yet a significant amount of mechanistic ambiguity regarding the formations of these 1:1 adducts of methylenecyclopropane **7** and **15** with molecular oxygen and acrylonitrile, the structures of the products clearly point to the reactions involving intermolecular interception and resultant cycloaddition of trimethylenemethane intermediates. Additional kinetic, stereochemical and regiochemical studies, likely with simpler species that can be studied in the gas phase, will be required to elucidate ambiguities as to the details of the mechanism.

EXPERIMENTAL

Infrared spectra were determined either as films between KBr plates or in solution with matched liquid cells (0.1 mm). NMR chemical shifts for ^1H spectra are reported in ppm downfield from internal TMS in $CDCl_3$ solution. Chemical shifts for ^{19}F spectra are reported in ppm upfield from internal $CFCl_3$ in $CDCl_3$ solution. Chemical shifts for ^{13}C spectra are reported in ppm downfield from internal TMS in $CDCl_3$ solution. All assignments of ^{13}C NMR resonances are made with the aid of off-resonance spectra or pulse-sequence spectra.

1,1-Diphenyl-2-(difluoromethylene)cyclopropane, (15).

A 60-mL glass tube containing 100 mg (0.370 mmole) 5-(Difluoromethylene)-4,5-dihydro-3,3-diphenyl-3,H-pyrazole and 40 mL pentane was sealed under vacuum and irradiated in a Rayonet Photoreactor (350 nm) for 15 hours. The cloudy mixture was concentrated by rotary evaporation at reduced pressure to give 89 mg (99%) yellow oil which was **15** (purification by flash chromatography using silica gel and hexane): $R_f = 0.39$; IR(CCl_4) 3095, 3070, 3036, 1845 (s), 1690 (w), 1602 (w), 1498, 1231, 1166 cm^{-1}; ^1H NMR δ 7.3-7.1 (complex m, 10H), 1.98 (t, 2H, $J_{HF} = 4.5$ Hz); ^{19}F NMR ϕ 84.3 (d of t, 1F, $J_{FF} = 64.7$ and $J_{HF} = 4.5$ Hz), 90.0 (d of t, 1F, $J_{FF} = 64.7$ and $J_{HF} = 4.5$ Hz); ^{13}C NMR δ 151.6 (d of d, $J_{CF} = 281.4$ and 276.5 Hz, $=CF_2$), 141.8 (d, $J_{CF} = 2.4$ Hz, subst aromatic), 128.6, 128.1, 127.1 (aromatic), 78.1 (t, $J_{CF} = 35.4$ Hz, C_2), 36.1 (d, $J_{CF} = 6.1$ Hz, C_1), 20.8 (d, $J_{CF} = 3.7$ Hz, CH_2); mass spectrum gave M^+ 242.0895 ± 0.0021 (9 ppm), calcd for $C_{16}H_{12}F_2$ 242.0907 dev -0.00116 (5 ppm). Anal. C, H.

In a similar experiment, 4-(difluoromethylene)-4,5-dihydro-3,3-diphenyl-3H-pyrazole[7] was irradiated for 5 hours to give 85% **15**.

2-(Difluoromethylene)spiro[cyclopropane-1,9'-[9H]-fluorene], (7).

Into a 700-mL gas sample bulb with teflon Rotoflo stopcock containing 5.00 g (26.0 mmoles) diazofluorene[20] and 200 mL ether was condensed 2.37 g (31.2 mmoles) difluoroallene.[21] The tube was kept at room temperature for 5.5 hours, then connected to a vacuum line and 50 mL ether were transferred off in order to remove excess difluoroallene.

The tube was irradiated in a Rayonet Photoreactor (350 nm) for 8 hours. The nitrogen evolved was removed on the vacuum line and irradiation was continued for a total of 28 additional hours.

After 36 hours irradiation, the solvent was rapidly removed by rotary evaporation at reduced pressure to give a yellow solid, which was immediately and rapidly purified by flash chromatography using silica gel and 95% hexane/5% EtOAc to give 3.4 g (54%) yellow solid **7**.[7] Solutions of **7** must be kept cold and the procedure followed rapidly in order to minimize reaction with oxygen.

5,5-Difluoro-4-methylenespiro[1,2-dioxolane-3,9'-[9H]fluorene], (8), 4-(Difluoromethylene)spiro-[1,2-dioxolane-3,9'-[9H]fluorene], (9), and 3,3-Difluoro-4-fluorenylidene-1,2-dioxolane, (10).

A solution of 338 mg (1.41 mmoles) **7** in 10 mL $CHCl_3$ was exposed to a slow flow of oxygen which was bubbled through the solution. Analysis by TLC after 32 hours indicated the starting material was gone. The solution was concentrated by rotary evaporation at reduced pressure to give an oily yellow solid. Flash chromatography using silica gel and hexane gave 172 mg (45%) pale yellow solid **8**: R_f = 0.18; mp 75-78.5°; IR (CCl_4) 3074, 1831 (w), 1690 (vw), 1612 (w), 1453, 1334, 1134, 1110 (s), 1089 cm^{-1}; ^1H NMR δ 7.58 (d, 2H, J = 7.5 Hz), 7.51 (d, 2H, J = 7.5 Hz), 7.39 (t, 2H, J = 7.5 Hz), 7.27 (t, 2H, J = 7.5 Hz), 5.72 (d of t, 1H, J_{HH} = 1.5 and J_{HF} = 2.4 Hz), 5.10 (d of t, 1H, J_{HH} = 1.8 and J_{HF} = 2.4 Hz); ^{19}F NMR ϕ 77.7 (t, J_{HF} = 2.4 Hz); ^{13}C NMR δ 146.4 (t, J_{CF} = 27.2 Hz, C_4), 142.2, 140.7 (subst aromatic), 130.9, 128.7, 125.6, 120.4 (aromatic), 127.6 (t, J_{CF} = 266.5 Hz, CF_2), 115.0 (=CH_2), 94.8 (t, J_{CF} = 3 Hz, quat C); mass spectrum gave M^+ 272.06549 ± 0.00531 (20 ppm), calcd for $C_{10}H_{16}O_2F_2$ 272.06489 dev 0.00060 (2 ppm); Anal. C, H.

It also gave 70 mg (18%) of **9**: R_f = 0.07; mp 136-138°; IR (CCl_4) 3075, 2925, 2870, 1789 (s), 1453, 1305, 1291, 1120 cm^{-1}; ^1H NMR δ 7.64-7.20 (complex m, 8H), 5.16 (t, 2H, J_{HF} = 3.4 Hz); ^{19}F NMR ϕ 85.4 (d of t, 1F, J_{FF} = 48.6 and J_{HF} = 3.4 Hz), 87.8 (d of t, 1F, J_{FF} = 48.6 and J_{HF} = 3.4 Hz); ^{13}C NMR δ 148.1 (d of d, J_{CF} = 285.6 and 290.5 Hz, =CF_2), 142.1, 140.6 (subst aromatic), 130.4, 128.4, 125.0, 120.3 (aromatic), 99.6 (d of d, J_{CF} = 23.2 and 19.5 Hz, C_4), 90.3 (quat C), 70.5 (d, J_{CF} = 2.4 Hz, CH_2); mass spectrum gave M^+ 272.06604 ± 0.00196 (7 ppm), calcd for $C_{16}H_{10}O_2F_2$ 272.06489 dev 0.00116 (4 ppm).

Finally it gave 15 mg (4%) of **10**: R_f = 0.09; mp 130.5-131.5°; IR (CCl_4) 3070, 1840 (w), 1670, 1607, 1454, 1278, 1140, 1117, 1096, 1083 cm^{-1}; ^1H NMR δ 7.97 (m, 1H), 7.64 (m, 2H), 7.48-7.08 (m, 5H), 5.55 (t, 2H, J_{HF} = 1.9 Hz); ^{19}F NMR ϕ 78.0 (quartet, J_{HF} = 1.9 Hz); ^{13}C NMR δ 141.5, 141.2, 136.7, 136.0, 133.8 (subst aromatic and olefinic), 130.3, 130.2, 128.1, 127.8, 124.3, 120.3, 119.8, 126.2 (t, J_{CF} = 8 Hz) (aromatic), 75.5 (t, J_{CF} = 2.7 Hz, CH_2) (no peak for the CF_2 carbon was observed); mass spectrum gave M^+ 272.06561 ± 0.00161 (6 ppm), calcd for $C_{16}H_{10}O_2F_2$ 272.06489 dev 0.00072 (3 ppm).

The relative yields determined by ^1H NMR integration were 58.6% for **8**, 36.8% for **9**, and 4.6% for **10**. The combined yield of isolated products was 67%.

4,4-Difluoro-5-methylenespiro[cyclopentane-1,9'-[9H]-fluorene]-2-carbonitrile (11), 5-(Difluoromethylene)-spiro[cyclopentane-1,9'-[9H]-fluorene]-2-carbonitrile, (12), and 3,3-Difluoro-4-fluorenylidenecyclopentanecarbonitrile, (13).

Into a 30-mL glass tube containing 1.00 g (4.16 mmoles) **7** under nitrogen, was condensed 6.0 mL (4.8 g, 91 mmoles) acrylonitrile. The tube was sealed under vacuum and heated at 70° for 6 hours. The tube was opened and the cloudy, amber mixture was concentrated by rotary evaporation at reduced pressure to give an amber oil. Flash chromatography using silica gel and 90% hexane/10% EtOAc gave 491 mg (49%) recovered starting material, R_f = 0.70, 390 mg (32%) white solid **11**: R_f = 0.43; mp 124.5-125.5°; IR (CCl_4) 3075, 2248 (w), 1670 (w), 1453, 1124, 933 cm^{-1}; ^1H NMR δ 7.7 (m, 2H), 7.3 (m, 6H), 5.68 (d of d of d, 1H, J_{HF} = 2.0 and 4.3, J_{gem} = 0.85 Hz), 4.90 (d of d of d, 1H, J_{HF} = 2.0 and 3.9, J_{gem} = 0.85 Hz), 3.63 (d of d of d, 1H, J_{HF} = 1.5, J_{HH} = 8.3 and 11.4 Hz), 3.1-2.8 (m, 2H); ^{19}F NMR ϕ 88.3 and 98.5 (AB pattern, J_{FF} = 249.8, downfield F has t of t fine structure with J_{HF} = 17.0 and 4.1 Hz, upfield F has m fine structure); ^{13}C NMR δ 147.5, 147.3, 140.7, 140.1 (subst aromatics), 129.1, 129.0, 128.4, 128.2, 124.0, 123.4, 120.5, 120.3 (aromatics), 147.1 (t, J_{CF} = 21.9 Hz, subs olefinic), 123.9 (t, J_{CF} = 247.7 Hz, CF_2), 117.0 (CN), 116.9 (d, J_{CF} = 5 Hz, =CH_2), 60.6 (d, J_{CF} = 2.2 Hz, quat C), 38.8 (t, J_{CF} = 26.3 Hz, CH_2), 36.9 (d, J_{CF} = 6.6 Hz, CH); mass spectrum gave M^+ 293.10121 ± 0.00151 (5 ppm), calcd for $C_{19}H_{13}NF_2$ 293.10161 dev -0.00040 (1 ppm). Anal. C, H, N.

It also gave 162 mg of **12** and **13**, R_f = 0.18-0.23 which was further separated by flash chromatography using silica gel and 80% hexane/20% ether to give 64 mg (5%) white solid **12**: R_f = 0.28; mp 178.2-180.3°; IR (CCl_4) 3075, 2975, 2246 (vw), 1765 (s), 1453, 1274 cm^{-1}; ^1H NMR δ 7.68 (m, 2H), 7.3 (m, 6H), 3.33 (d of d, 1H, J = 7.4 and 10.5 Hz), 2.8 (m, 2H), 2.47 (m, 2H); ^{19}F NMR ϕ 85.7 (d of t, 1F, J_{FF} = 42.3 and J_{HF} = 3.7 Hz), 86.2 (d of m, 1F, J_{FF} = 42.3 Hz); ^{13}C NMR

δ 146.9, 146.2 (t, J_{CF} = 2.4 Hz), 140.3, 140.1 (subst aromatics), 128.9, 128.6, 128.0, 127.9, 124.0, 122.7, 120.3 (aromatic), 150.5 (dd, J_{CF} = 287.5 and 291.1 Hz, =CF_2), 117.9 (CN), 93.5 (dd, J_{CF} = 23.2 and 17.1 Hz, olefinic), 59.2 (quat C), 43.2 (d, J_{CF} = 2.4 Hz, CH), 29.9 (CH_2), 26.2 (CH_2); mass spectrum gave M^+ 293.10189 ± 0.00069 (2 ppm), calcd for $C_{19}H_{13}NF_2$ 293.10160 dev 0.00029 (1 ppm).

Finally it gave 67 mg (5%) of **13**: R_f = 0.20; mp 164.5-167°; ^1H NMR δ 8.1 (m, 1H), 7.6 (m, 2H), 7.3 (m, 5H), 3.4-2.3 (complex m, 5H); ^{19}F NMR ϕ 89.5 and 92.4 (AB pattern, J_{FF} = 251.2 Hz); ^{13}C NMR (acetone-d_6) δ 142.0, 141.8, 138.7, 138.5, 135.8 (subst aromatics and olefinic), 130.4, 130.2, 128.6, 128.3, 127.0, 120.7, 120.4 (aromatics), 132.6 (t, J_{CF} = 21.9 Hz, C_4 olefinic), 127.5 (t, J_{CF} = 9.9 Hz, aromatic), 128.4 (t, J_{CF} = 248.2 Hz, CF_2), 121.0 (CN), 41.3 (t, J_{CF} = 27.4 Hz, C_2), 37.6 (t, J_{CF} = 4.2 Hz, C_5), 25.0 (dd, J_{CF} = 3.4 and 5.5 Hz, CH); mass spectrum gave M^+ 293.10129 ± 0.00104 (4 ppm), calcd for $C_{19}H_{13}NF_2$ 293.01060 dev -0.00032 (1 ppm).

The total combined yield of isolated products was 42% with 49% recovered starting material. On a smaller scale, an isolated yield of 75% products and 15% starting material was obtained. The relative yields of products determined by integration of the ^{19}F NMR spectrum of the reaction mixture were 68.2% for **11**, 15.6% for **12**, and 16.1% for **13**.

2-Methylenespiro[cyclopropane-1,9'-[9H]fluorene], (15).

Into a 150-mL glass tube containing 2.00 g (10.4 mmoles) diazofluorene[20] and 50 mL CCl_4 was condensed 2.00 g (52 mmoles) allene. The tube was sealed under vacuum and irradiated in a Rayonet Photoreactor for 6 hours. The tube was cooled and opened. The dark red-brown solution was concentrated to give an oil which was purified by flash chromatogrphy using silica gel and hexane. A total of 0.764 g crude solid, R_f = 0.32, were obtained. Further purification by fractional crystallization from hexane gave white needles (mp 149.5-150.5) of an undesired by-product and colorless rhombohedral crystals of **15** which were separated by hand to give 90 mg (4.2%) pure **15**: mp 104-111°; IR (CCl_4) 3075, 3022, 2975, 1450, 1120, 893 cm^{-1}; ^1H NMR δ 7.9 (m, 2H), 7.4-7.1 (m, 6H), 5.75 (t, 1H, J = 2.3 Hz), 5.52 (t, 1H, J = 3.0 Hz), 2.30 (t, 2H, J = 2.8 Hz); ^{13}C NMR δ 147.4, 140.1, 138.6 (subst aromatic and olefinic), 126.9, 126.2, 119.9 (aromatics), 104.7 (=CH_2), 34.1 (quat), 21.2 (CH_2); mass spectrum gave M^+ 204.09302 ± 0.00188 (9 ppm), calcd for $C_{16}H_{12}$ 204.0939 dev -0.00088 (4 ppm). Anal. C, H.

4-Methylenespiro[1,2-dioxolane-3,9'-[9H]fluorene], (16) and 4-Fluorenylidene-1,2-dioxolane, (17).

A solution of 63 mg (0.308 mmole) **15** in 5 mL $CHCl_3$ was exposed to a slow flow of oxygen which was bubbled through the solution. Analysis by ^1H NMR after 43 hours indicated 57% completion by integration. The reaction was continued. After 7 days, the solution was concentrated by rotary evaporation at reduced pressure to give a yellow solid. Flash chromatography using silica gel and 96% hexane/4% EtOAc gave 7 mg (11%) recovered starting material and 55 mg (75%) crude product mixture. Recrystallization from hexane/$CHCl_3$ gave 24 mg (33%) pure major isomer **16**: R_f = 0.24 mp 148.0-149.6°; IR (CCl_4) 3072, 2908, 2853, 1678 (vw), 1452 (s), 900 cm^{-1}; ^1H NMR δ 7.6-7.2 (complex m, 8H), 5.08 (t, 2H, J = 2.0 Hz), 5.03 (d of t, 1H, J = 1.9 and 1.0 Hz), 4.64 (d of t, 1H, J = 2.2 and 1.0 Hz); ^{13}C NMR δ 155.5 (subst olefinic), 144.6, 140.7 (subst aromatics), 129.8, 128.3, 125.3, 120.1 (aromatics), 105.6 (=CH_2), 93.0 (quat), 74.3 (CH_2); mass spectrum gave M^+ 236.08347 ± 0.00193 (8 ppm), calcd for $C_{16}H_{12}O_2$ 236.08373 dev -0.00026 (1 ppm). Anal. C, H.

Characterization of the minor product **17** relies on the ^1H NMR spectrum of the reaction mixture which showed a singlet at 5.17 ppm for the CH_2 protons of **17**. Integration of the ^1H NMR spectrum of the product mixture indicated relative yields of 90.8% for **16** and 9.2% for **17**.

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