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THE DUALITY IN THE CYCLOADDITIONS OF F-DIMETHYLKETENE WITH CYCLOPROPENONES. A NOVEL SYNTHESIS OF UNSYMMETRICAL TRIAFULVENES[1]

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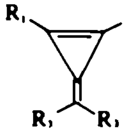
Abstract—The reaction of F-dimethylketene 3 and diphenylcyclopropenone 7 in benzene solution affords 4-fluorocarbonyl-4-trifluoromethyl-1,2-diphenyltriafulvene 10. A mechanism of the cycloaddition through the intermediates F-methacryloyl fluoride 11 and the oxetane 12 is suggested. A contribution of the dipolar structure 10a is indicated. The cycloaddition of 3 and cyclopropenones constitutes a synthetic route to both symmetrical and unsymmetrical triafulvenes.

The syntheses of triafulvenes 1 from cyclopropenones 2 are usually accomplished by condensation reactions of 2 with active methylene compounds.[2,3] The most serious limitation of this general scheme is the necessity to employ reagents and reaction conditions which do not cleave the three-menbered rings of 1 and 2. Basic condensation agents are therefore avoided and acetic anhydride or methanol are often the solvents of choice. Other methods include the use, instead of the carbonyl compound 2, of the corresponding 3,3-dichlorocyclopropene or 3-ethoxycyclopropenium salts.[4,5] We wish to report an alternative synthesis of trifulvene derivatives based on cyclopropenones-F-dimethylketene 3 cycloadditions. Starting from symmetrical cyclopropenones, the method may lead to symmetrical as well as to unsymmetrical triafulvenes. Syntheses of [n]fulvenes by cycloadditions of substituted ketenes to [n]annulenones were first reported by Staudinger in his classical studies of the chemistry of ketenes (e.g. the synthesis of 8,8 - diphenyl - 4,5 - benzoheptafulvene).[6-8] The method failed, however, with cyclopropenones 2.[9] Tropone, the higher homologue of 2, gave a heptafulvene derivative with dichloroketene[10] but not with diphenylketene.[11,12] The synthesis of ω,ω-bis(trifluoromethyl) [n]fulvenes by cycloadditions of 3 to [n]annulenones has hardly been attempted.

The reaction of di-p-tolylcyclopropenone 4 and 3 followed the normal course (as previously reported), affording 1,2 - di - p - tolyl - 4,4 - bis(trifluoromethyl) - triafulvene 5.[11] The reaction presumably involves a cycloaddition of the C=O bond of 4 across the C=C bond of 3, followed by an elimination of CO_2 from the α-spirolactone intermediate 6, to form the triafulvene 5. The reaction of 3 and diphenylcyclopropenone 7 followed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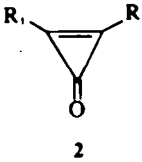
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$(CF_3)_2C{=}C{=}O$
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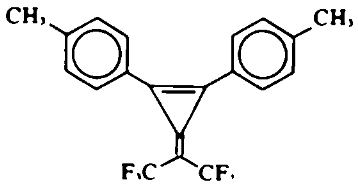
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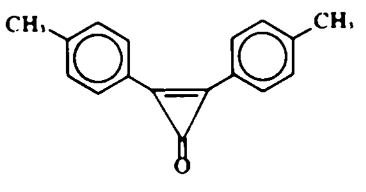
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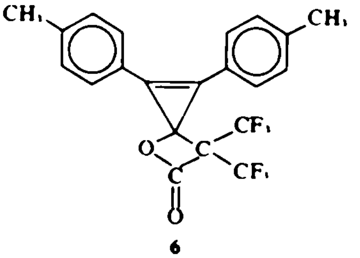
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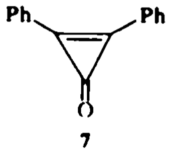
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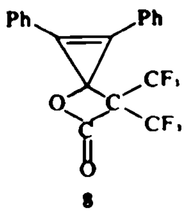
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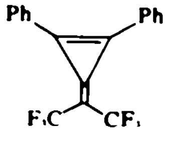
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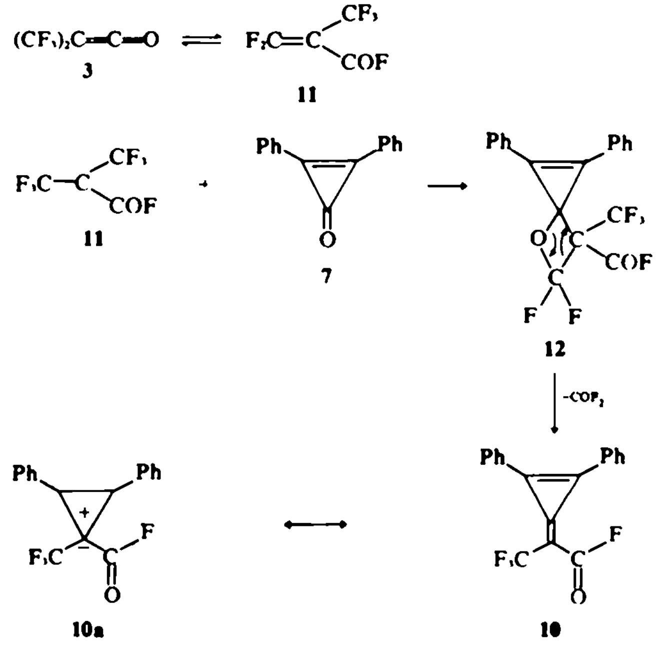
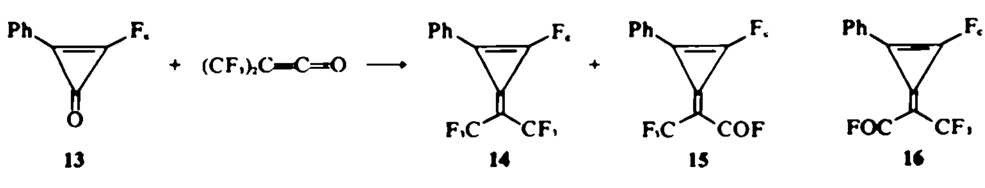
another route. The resulting product was neither the cycloadduct α-spirolactone **8** nor the expected 1,2-diphenyl-4,4-bis(trifluoromethyl)triafulvene **9** ($C_{18}H_{10}F_6$). The product analysed for $C_{18}H_{10}F_4O$, indicating a substitution of two fluorine atoms by an oxygen atom. The molecular ion in the mass spectrum appeared at *m/e* 318 and was by far the most abundant signal. The sharp infrared frequency at 1850 cm^{-1} indicated the presence of a 1,2-disubstituted triafulvene,[14-16] while the very strong absorption at 1780 cm^{-1} pointed to a carbonyl stretching vibration which could be ascribed to an acyl fluoride. Among the other prominent IR signals, those appearing at 1500 (1,2-disubstituted triafulvene) and 1330 cm^{-1} (C-F) may be noted.

The longest wavelength absorption maximum in the UV spectrum (representing the $N \rightarrow V_1$ transition) appeared at 335, 334, 328 and 322 nm in cyclohexane, benzene, ethanol and acetonitrile, respectively. This blue shift of 13 nm on change of solvent from cyclohexane to acetonitrile is characteristic of 1,2-diaryltriafulvenes.[17] Both the ^1H and the ^{19}F NMR spectra of the product were most useful for the determination of the structure of the product. The ^1H NMR spectrum contained three multiplets centered at 7·62 (6H), 8·00 (2H) and 8·26 ppm (2H). Such a pattern is consistent with the spectrum of two monosubstituted phenyl groups in which (a) the *ortho* protons absorb at a lower field than the *meta* and *para* protons, and (b) the two pairs of *ortho* protons of the two phenyl groups are not magnetically equivalent. The ^{19}F NMR spectrum consisted of a doublet at −52·5 ppm representing three fluorine nuclei coupled (J = 12·5 Hz) to a quartet at 19·6 ppm representing one fluorine nucleus. Such a pattern can only be explained by the presence of a single fluorine in close proximity to a CF_3 group. On the basis of this evidence, we submit that the reaction product of **3** and **7** is 4-fluorocarbonyl-4-trifluoromethyl-1,2-diphenyltriafulvene **10**. The following features of **10** should be noted. While the substituents at the three-membered ring of **10** are identical, the substituents at the exocyclic carbon atom of the triafulvene system are not identical. This is the origin of the magnetically non-equivalence of the two pairs of *ortho* protons. The downfield shift of all the four protons *ortho* to the triafulvene ring, relative to the corresponding *meta*- and *para*-protons, is ascribed primarily to the partial positive charge in the three-membered ring.[3,14,15] In the case of the unsymmetrical **10**, however, it appears that the downfield shift of the *ortho*-pair (Z) to the fluorocarbonyl group is more pronounced than that of the *ortho*-pair (Z) to the CF_3 group. This difference may be due to the effect of the diamagnetic anisotropy of the carbonyl group. The solvent shift in the UV spectra of **10** is consistent with the decrease in the dipolar character of **10** in the transition from the ground state to the first excited state.

The formation of **10** in the reaction of **3** and **7** may be rationalized on the basis of a prior rearrangement of F-dimethylketene **3** to F-methacryloyl fluoride **11** in the presence of diphenylcyclopropenone **7**. This rearrangement is known to occur under the catalytic influence of fluoride ion[18,19] or triethylamine.[20] Once **11** is formed, a cycloaddition of the C=O bond of **7** across the C=C bond of **11** takes place, giving the oxetane **12**. The intermediate **12** could easily eliminate carbonyl fluoride to form the triafulvene **10**. (Scheme 1). This mechanism is supported by the observations of England *et al.* who very recently reported a series of cycloadditions of **11** to carbonyl



Scheme 1.



compounds, to give the corresponding 1 - fluorocarbonyl - 1 - trifluoromethylethylene derivatives.[19] In one case, the reaction of **11** with benzaldehyde, the corresponding oxetane intermediate was isolated and characterized.[19] Furthermore, the reaction of **3** with dimethylformamide yielded both the unsaturated amine $(CF_3)_2C{=}CHN(CH_3)_2$ and the unsaturated acid fluoride $(CH_3)_2NCH{=}C(CF_3)COF$.[19,21]

It is noteworthy that **10**, being an acid fluoride, is not esterified in boiling methanol. This unusual stability may be due to contribution of the dipolar "aromatic" structure **10a** in the ground state. The partial negative charge in **10a** renders the carbon atom of the acyl fluoride less reactive towards nucleophilic reagents (methanol) as compared with ordinary acyl fluorides. In fact, preparation of F-acrylic acids or esters from F-acryloyl fluorides ($CF_2{=}CFCOF$ and **11**) is not practical because nucleophilic attack on these compounds proceeds on the terminal CF_2 groups in preference to the acid fluoride groups.[19]

The reaction of **3** with an unsymmetrical cyclopropenone (**2**, $R_1 \neq R_2$), may lead to three triafulvenes, a 4,4-bis(trifluoromethyl)triafulvene (**1**, $R_1 \neq R_2$, $R_3 = R_4 = CF_3$) and two geometrical isomers of 4 - fluorocarbonyl - 4 -trifluoromethyltriafulvene (**1**, $R_1 \neq R_2$, $R_3 = CF_3$, $R_4 =$ COF). Indeed, preliminary results of the reaction of 1 - ferrocenyl - 2 - phenylcyclopropenone **13**[22] and **3** indicated the formation of 1 - ferrocenyl - 2 - phenyl - 4,4 - bis(trifluoromethyl)triafulvene **14** and a mixture of (Z)- and (E) - ferrocenyl - 4 - fluorocarbonyl - 2 - phenyl - 4 - trifluoromethyltriafulvene, **15** and **16** respectively.[22]

Thus, the reaction of **3** and cyclopropenones may serve as a synthetic route to both symmetrical and unsymmetrical triafulvenes.

EXPERIMENTAL

M.ps were taken on a Unimelt Thomas and Hoover capillary mp apparatus and were uncorrected. IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer, UV spectra on a Unicam SP 800 spectrophotometer and ^{1}H NMR spectra at 100 MHz on a Varian HA-100 spectrometer. ^{1}H chemical shifts are reported in parts per million, downfield from Me_4Si as internal standard. ^{19}F NMR spectra were recorded at 94·1 MHz on a Varian HA-100 spectrometer. ^{19}F chemical shifts are reported in parts per million, downfield from CCl_3F as external standard or from C_6H_5F as internal standard, with the downfield direction taken as positive. Mass spectra were recorded on a Varian MAT 311 spectrometer.

4 - Fluorocarbonyl - 4 - trifluoromethyl - 1,2 - diphenyltriafulvene **10**

A solution of diphenylcyclopropenone **7** (2·06 g) in dry benzene (60 ml) was treated under anhydrous conditions in a round bottom flask at −78°C with bis(trifluoromethyl)ketene **3** (2·0 ml). The flask was corked and left at room temperature for 5 days. The solvent was evaporated, and the remaining crude product (2·5 g, 79% yield) was recrystallised, twice from cyclohexane. The product **10** was obtained as colourless cottonlike crystals, m.p. 134–135°. UV: $\lambda_{max}^{cyclohexane}$ 230 nm (log ϵ 4·34), 237 (4·34), 251s (4·41), 266 (4·51), 280 (4·53), and 335 (4·22); $\lambda_{max}^{C_6H_6}$ 283 nm (log ϵ 4·52) and 334 (4·18); $\lambda_{max}^{CH_3CN}$ 223s nm (log ϵ 4·16), 231*s* (4·12), 250*s* (4·24), 278 (4·51), and 322 (4·19); λ_{max}^{EtOH} 226 nm (log ϵ 4·13), 231 (4·10), 253*s* (4·24), 280 (4·46), and 328 (4·13). IR ν max (nujol) 3050 (w), 1850 (m), 1780 (vs), 1600 (w), 1575 (w), 1500 (s), 1330 (vs), 1275 (s), 1140 (m), 1100 (s), 1070 (m), 1030 (m), 970 (s), 765 (s), 722 (m), and 685 cm^{-1} (s). ^{1}H NMR ($CDCl_3$) δ 7·73–7·42 ppm (m, 6H, Ar *meta* and *para* to triafulvene), 7·88–8·10 (m, 2H, Ar *ortho* to triafulvene, (Z) to CF_3), and 8·10–8·34 (m, 2H, Ar *ortho* to triafulvene, (Z) to COF). ^{19}F NMR (CH_2Cl_2, external CCl_3F) δ −52·5 ppm (d, J = 12·5 Hz, 3F, CF_3) and +19·6 (quartet, J = 12·5 Hz, 1F, COF: (CH_2Cl_2, internal C_6H_5F) δ + 53·7 ppm. (quartet, J = 12·5 Hz, 3F, CF_3) and 125·9 (d, J = 12·5 Hz, 1F, COF). (Found: C, 68·06; H, 3·25; F, 24·10. $C_{18}H_{10}F_4O$ requires: C, 67·92; H, 3·14; F, 23·90%).

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