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LIGHT-INDUCED REACTIONS OF 1,1,1-TRIFLUORO-3-DECYN-2-ONE WITH OLEFINS

P. MARGARETHA *, C. SCHRÖDER

Institut für Organische Chemie, Universität Hamburg, M.L.King Platz 6
D-2000 Hamburg 13 (F.R.G.)

S. WOLFF and W.C. AGOSTA

Laboratories of the Rockefeller University, New York, NY 10021 (U.S.A.)

SUMMARY

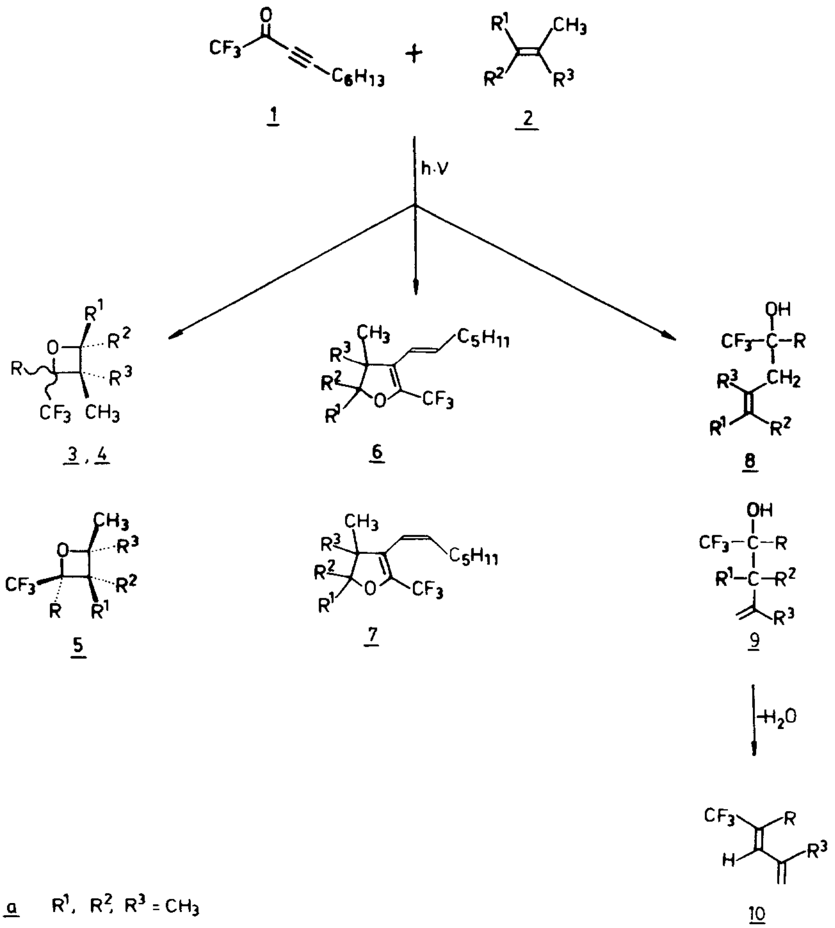
Irradiation (λ= 300 nm) of 1,1,1-trifluoro-3-decyn-2-one in the presence of olefins affords RH-reduction products (tertiary alcohols) in addition to [2+2] -(oxetans) and [3+2] -(dihydrofurans) cycloadducts.

INTRODUCTION

Irradiation of conjugated acetylenic ketones in the presence of alkenes, e.g. 3-pentyn-2-one and 2,3-dimethyl-2-butene, affords oxetans as well as 2,3-dihydrofurans, both products arising from a common 1,4-biradical intermediate which frequently differs in spin state for the two types of addition [1-3]. As we had already found a pronounced influence of an α-fluoro substituent on the photochemical behaviour of cycloalkanones [4] and 2-cycloalkenones [5,6] , we decided to investigate in what manner fluorine substituents would affect the above mentioned reactions of ynones. We now report results on the photochemical behaviour of 1,1,1-trifluoro-3-decyn-2-one (1) in the presence of various olefins.

RESULTS AND DISCUSSION

We first examined the reaction of 1 with 2,3-dimethyl-2-butene (2a), 2-methylpropene (2b) and 2-methoxypropene (2c). Irradiation (λ= 300 nm) of a benzene solution of these addends yields the oxetans 3 - 5, the 2,3-dihydrofurans 6 and 7, as well as the tertiary alcohols 8 and 9 (the spectral data of a mixture of 8a and 9a have already been reported [2]). The overall yield of these products, determined by measuring the conversion of 1 against an internal standard by GC, lies in the range of 25 - 45%. The relative product distribution is given in Table 1. Attempted gas chromatographic isolation of the RH-reduction products 9b and 9c led to formation of dienes 10b and 10c, respectively.



a R^1, R^2, R^3 = CH_3

b R^1, R^2 = H; R^3 = CH_3

c R^1, R^2 = H; R^3 = OCH_3

R = $-C{\equiv}C-C_6H_{13}$

TABLE 1

Product yields in reactions 1 + 2

Olefin	Product	3	4	5	6	7	8	9	Overall
		Relative yield							
2a		36 ^{a}			-	42	14	8	30%
2b		36 ^{b}		17	7	25	15 ^{c}		25%
2c		46	11	-	11	21	11 ^{d}		45%

^{a} 3a = 4a = 5a; ^{b} 3b = 4b; ^{c} 8b = 9b; ^{d} 8c = 9c .

The assignment of the structures of the photoproducts is based on their ^{1}H-NMR - (Table 2) and mass spectra (Table 3). The predominant orientation of addition of the alkenes 2b and 2c to excited 1 leading to products with the CH_2-group vicinal to oxygen is proven by the chemical shift and the magnitude of the geminal coupling constant of the methylene hydrogens (δ= 4.7 - 4.1 ppm, J = 6 Hz for oxetans 3 and 4, and J = 11 Hz for dihydrofurans 6 and 7, respectively). The corresponding AB-system for oxetan 5c appears at δ= 3.5 ppm with J = 10.6 Hz. Differentiation between E- and Z - dihydrofurans 6 and 7 is straightforward by analysis of the vicinal coupling constant of the olefinic protons, J = 17 and 10 Hz, respectively. As for the mass spectra, the oxetans are characterised by base peaks corresponding to the mass of the alkene radical cation formed via retro [2+2] cleavage.

Comparing the results obtained from 1 and 2 with those of similar methyl ketones (3-pentyn-2-one, 3-decyn-2-one, 5,5-dimethyl-3-hexyn-2-one) [1,2] with the same olefins shows that the relative amount of oxetans vs. 2,3-dihydrofurans increases for the trifluoroalkynone, and that a novel type of product (8 and 9) is formed from 1. The first effect is related to the influence of CF_3 vs. CH_3 on the behaviour of 1,4-biradical 11, path a) ostensibly being favoured for X = F.

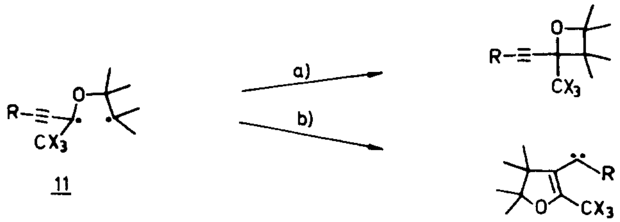


TABLE 2

^{1}H-NMR Spectroscopic Data of Photoproducts (in $\mathrm{CDCl_3}$)

3a	X ; 1.38, 1.19, 1.05, 0.81 (s, $\mathrm{C\underline{H}_3}$).
3b	4.50 and 4.11 (AB, J = 5.2); X); 1.00, 0.86 (s, $\mathrm{C\underline{H}_3}$).
3c	4.55 and 4.38 (AB, J = 6.4); 3.32 (s, $\mathrm{OC\underline{H}_3}$); X); 1.26 (s, $\mathrm{CH_3}$).
4c	4.73 and 4.20 (AB, J = 6.0); 3.32 (s, $\mathrm{OC\underline{H}_3}$); X); 1.47 (s, $\mathrm{C\underline{H}_3}$).
5b	3.62 and 3.47 (AB, J = 10.6); x); 1.30 (s, 6H, $\mathrm{C\underline{H}_3}$).
6b	6.11 (dq, J = 17.0, 1.5) and 5.87 (dt, J = 17.0, 7.2), olefinic; 4.05 (s, 2H, $\mathrm{OC\underline{H}_2}$); Y); 1.12 (s, 6H, $\mathrm{C\underline{H}_3}$).
6c	6.16 (dq, J = 16.0, 1.6) and 6.12 (dt, J = 16.0, 7.1), olefinic; 4.47 and 4.09 (AB, J = 11.2); 3.22 (s, $\mathrm{OC\underline{H}_3}$); Y); 1.44 (s, $\mathrm{C\underline{H}_3}$).
7a	5.63 (dt, J = 9.0, 6.5) and 5.46 (dq, J = 9.0, 1.5), olefinic; Y ; 1.31 (s, 6H, $\mathrm{C\underline{H}_3}$); 0.98 (s, 6H, $\mathrm{C\underline{H}_3}$).
7b	5.76 (dt, J = 11.0, 7.0) and 5.60 (dq, J = 11.0, 2.0), olefinic; 4.11 (s, 2H, $\mathrm{OC\underline{H}_2}$); Y); 1.31 (s, 6H, $\mathrm{C\underline{H}_3}$).
7c	5.79 (dt, J = 11.5, 7.2) and 5.62 (dq, J = 11.5, 1.6), olefinic; 4.53 and 4.11 (AB, J = 11.3); 3.22 (s, $\mathrm{OC\underline{H}_3}$); Y); 1.37 (s, $\mathrm{C\underline{H}_3}$).
8a	2.75 and 2.55 (AB, J = 14.0); X); 1.86 (s, $\mathrm{C\underline{H}_3}$); 1.76 (s, 6H).
9a	5.03 (s, 1H); 5.00 (s, 1H); X); 1.94 (s, $\mathrm{C\underline{H}_3}$); 1.35 (s, 6H, $\mathrm{C\underline{H}_3}$).
10b	5.04 (s, 1H); 5.00 (s, 1H); 4.47 (m, 1H); X); 1.77 (s, $\mathrm{C\underline{H}_3}$).
10c	4.59 (m, 1H); 4.07 (s, 1H); 4.04 (s, 1H); 3.42 (s, $\mathrm{OC\underline{H}_3}$); X);
13a	4.70 (m, 1H), 4.52 (m, 2H), 3.69 (m, 1H), 3.42 (m, 1H), $\mathrm{OC\underline{H}}$; X ; 1.23 (t, $\mathrm{C\underline{H}_3}$).
13b	4.95 (m, 1H), 4.65 (m, 2H), $\mathrm{OC\underline{H}}$; X); 1.31 (s, 9H, $\mathrm{C\underline{H}_3}$).
14a	4.64 (m, 3H), 3.68 (m, 1H), 3.54 (m, 1H), $\mathrm{OC\underline{H}}$; X); 1.18 (t, $\mathrm{C\underline{H}_3}$).
14b	4.75 (m, 2H), 4.50 (m, 1H), $\mathrm{OC\underline{H}}$; X); 1.19 (s, 9H, $\mathrm{C\underline{H}_3}$).
17	6.27 and 5.40 (d , J = 3.6, $\mathrm{C\underline{H}}$); X).

X 2.30 (t, 2H); 1.60–1.20 (m, 8H); 0.90 (t, 3H).

Y 2.08 (m, 2H); 1.55–1.20 (m, 6H); 0.90 (t, 3H).

TABLE 3

Mass Spectroscopic Data of Photoproducts [a]

Monocyclic Oxetans	M^+	$M^+ - C_{10}H_{13}F_3O$ [b]	Other
3a	290 (4%)	84 (100%)	
3b	262 (0.5%)	56 (100%)	
3c	278 (5.3%)	72 (100%)	
4c	278 (0.5%)	72 (100%)	
5b	262 (0.5%)	56 (100%)	
13a	278 (0.9%)	72 (100%)	
13b	306 (0.1%)	100 (6%)	57 ($C_4H_9^+$, 100%)
14a	278 (0.8%)	72 (100%)	
14b	306 (0.2%)	100 (4%)	57 ($C_4H_9^+$, 100%)
Dihydrofurans	M^+	$M^+ - CH_3$	base peak
7a	290 (40%)	275 (48%)	41
7b	262 (59%)	247 (30%)	43
7c	278 (26%)	263 (30%)	43

Others

8a + 9a : 290 (M^+, 1%), 83 ($C_6H_{11}^+$, 100%)

10c : 260 (M^+, 4%), 190 ($M^+ - C_5H_9$, 33%), 72 (100%)

17 : 292 (M^+, 0.2%), 179 ($M^+ - [CF_3 + CO_2]$, 100%), 86 ($C_3H_2O_3^+$, 37%)

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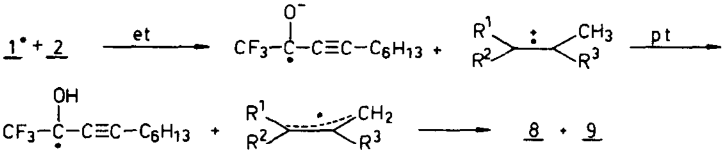
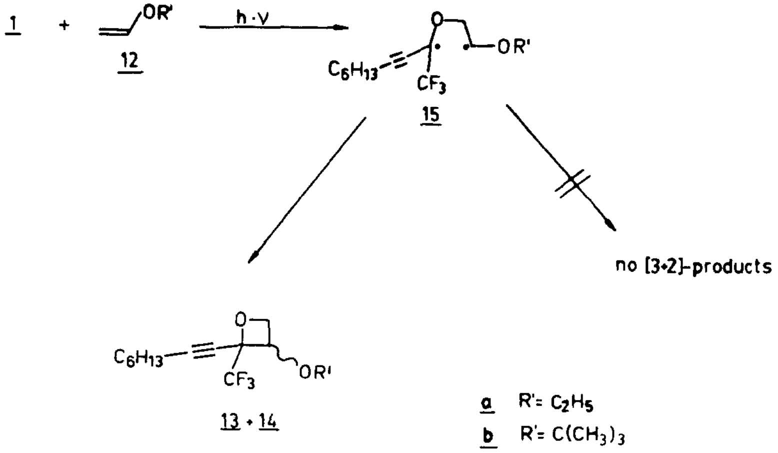
[a] Mass spectra recorded at 70 eV

[b] $C_{10}H_{13}F_3O$ = ketone 1

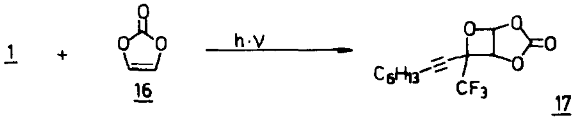
The second effect is connected to the fact that 1 is more easily reduced than the corresponding methyl ketone ($E_{1/2}$ *vs.* SCE, Pt-cathode, in CH_3CN with 10^{-1}M Bu_4NClO_4: 1 = - 1.39 V, 3-decyn-2-one = -2.11 V) and therefore excited 1 becomes more susceptible to electron transfer (et) from the olefin; proton transfer (pt) in the radical ion pair and coupling of the resulting radicals then leads to 8 and 9, respectively.



We next studied the reaction of 1 with ethoxyethylene (12a) and t-butoxyethylene (12b). For both vinyl ethers 1:1 mixtures of diastereomeric oxetans 13 and 14 were obtained selectively and in very good yields (90%), the ^{1}H NMR spectra indicating that the orientation of addition of 12 to excited 1 is the same as that for alkenes 2. A similar preference for [2+2] addition was noted in the cycloaddition of 3-pentyn-2-one and ketene diethyl acetal [3]. The reasons for this different behaviour of 1,4-biradical 15 from alkoxyalkenes, giving only [2+2] products is not yet fully understood.



Further, irradiation of 1 and 1,3-dioxol-2-one (16) gave one bicyclic oxetan product 17 selectively, albeit in low yield (20%). Again, as for the diastereomeric oxetans 3c and 4c, 13 and 14, and oxetan 5c, the assignment of the configuration of 17, based on ^{1}H-NMR- and mass spectroscopic data alone, is not possible.



Finally we undertook quenching studies on the reactions between 1 and 2a as well as 1 and 12a. In the first series of experiments (λ= 350 nm), naphthalene quenched the appearance of all three products at about the same rate, thus indicating that they could all be formed from the same triplet state of 1. Stern-Volmer kinetics from both experiments indicate that the lifetime of this quenchable triplet species from 1 is of the same order of magnitude as that of triplet 3-pentyn-2-one, i.e. about 0.5 ns .

EXPERIMENTAL

General

Absorptions in the IR spectra are given in cm^{-1}. The chemical shifts in the 400-MHz ^{1}H-NMR spectra are given in ppm relative to TMS (coupling constants J in Hz). Mass spectra were recorded at 70 eV. Analytical GC was performed on a SE 30 capillary column. Preparative GC separations were run on 8m 2.5% SE 30 (column A), 4m 5% SE 30 (column B) or 8m 10% OV 17 (column C).

Starting Materials

Trifluorodecynone 1 [7], t-butoxyethylene (12b) [8] and 1,3-dioxol-2-one [9] were synthesized according to the literature. Alkenes 2a, 2b, 2c and 12a were purchased from FLUKA AG.

Photolyses

These were performed in a Rayonet RPR-100 photoreactor using 300 nm lamps. Thus argon-degassed solutions of 206 mg (10^{-3} mol) 1 and 2.5 .10^{-2} mol alkene in 50 ml benzene were irradiated for 50 - 80 h. Products were isolated by preparative gas chromatography, all being liquids or oils.

Quenching Studies

The same photoreactor equipped with a merry-go-round set up and 350 nm lamps was used. The quencher (naphthalene) concentration varied from 0 - 2M.

Irradiation of 1 with alkenes

With 2,3-dimethyl-2-butene (2a)

Separation on column B (135°, isotherm.) afforded three fractions, first 4-(Z-1-heptenyl)-2,2,3,3,-tetramethyl-5-trifluoromethyl-2,3-dihydrofuran (7a) , second 2-(1-octinyl)-2-trifluoromethyl-3,3,4,4-tetramethyloxetan (3a), and third a 2:1 mixture of 2,3-dimethyl-5-trifluoromethyl-2-tridecen-6-in-5-ol (8a) and 2,3,3-trimethyl-4-trifluoromethyl-1-dodecen-5-in-4-ol (9a), IR (CCl_4): 3600, 3550-3300, 2240.

With 2-methylpropene (2b)

Separation on column C (160°, isotherm.) afforded two fractions, first a 4:2:1 mixture of 4-(Z-1-heptenyl)-3,3-dimethyl-5-trifluoromethyl-2,3-dihydrofuran (7b), 2-methyl-4-trifluoromethyl-1,3-dodecadien-5-in (10b) and 4-(E-1-heptenyl)-dihydrofuran 6b; second a 2:1 mixture of the regioisomeric 3,3- and 4,4-dimethyl - 2-(1-octinyl)-2-trifluoromethyloxetans 3b and 5b.

With 2-methoxypropene (2c)

Separation on column B (100 - 200°, 2°/min) afforded three fractions, first a 2:1 mixture of the diastereomeric E and Z - 4-(1-heptenyl)-5-trifluoromethyl-3-methoxy-3-methyl-2,3-dihydrofurans 6c and 7c, second a 1:1 mixture of cis 3-methoxy-3-methyl-2-(1-octinyl)-2-trifluoromethyloxetan (3c) and 2-methoxy-4-trifluoromethyl-1,3-dodecadien-5-in (10c), and third pure trans-3-methoxy-3-methyl-2-(1-octinyl)-2-trifluoromethyloxetan (4c).

With ethyl vinyl ether (12a)

Separation on column B (100 - 200°, 2°/min) afforded two fractions, each one containing one diastereomeric 2-(1-octinyl)-2-trifluoromethyl-3-ethoxyoxetan (13a & 14a).

With t-butoxyethylene (12b)

Separation (conditions as for ethyl vinyl ether) afforded pure diastereomeric 2-(1-octinyl)-2-trifluoromethyl-3-t.butoxyoxetans 13b & 14b.

With 1,3-dioxol-2-one (16)

The main product, 7-(1-octinyl)-7-trifluoromethyl-2,4,6-trioxabicyclo[3.2.0]heptan-3-one was isolated on column A (180°, isotherm.), IR (CCl_4): 2280, 1865.

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