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## THE REACTIONS OF TRIFLUOROMETHYL AND TRICHLOROMETHYL RADICALS WITH CONJUGATED AND METHYLENE-INTERRUPTED DIENES AND ENYNES

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#### SUMMARY

The photochemical addition of  $CF_3I$  to buta-1,3-diene and vinylacetylene in the gas phase gave 1,4-adducts as the main products. In gas phase reactions only products derived from hydrogen abstraction were detected in the  $CF_3I/penta-1,3$ -diene system, but the 1,4-adducts again predominated in the liquid phase.  $CCl_3Br$  similarly gave a mixture of 1,2- and 1,4-adducts, the latter predominating, on photochemical reaction with penta-1,3-diene. The 1,2-adduct was the main product from the  $CCl_3Br/pent-1$ -en-4-yn reaction, but some hydrogen abstraction was observed. The preference shown by conjugated dienes to give 1,4-adducts in the <u>trans</u>- configuration is interpreted in terms of steric factors and the propensity of dienes to adopt the <u>s-trans</u> conformation.

#### INTRODUCTION

Relatively little is known about the orientation, stereochemistry or kinetics of radical addition to dienes and enynes, despite their importance in polymerization processes. Cvetanović and Irwin observed that methyl radicals add to buta-1, 3-diene approximately an order of magnitude faster than to ethylene [1]. Szwarc and co-workers [2] found that trifluoromethyl radicals also add to conjugated dienes more rapidly than to ethylene. Brace investigated the addition of perfluoro-n-butyl iodide to the 'skipped' penta-1,4-diene (and a series of longer chain dienes) finding the main product to be the 1,2-adduct at high diene ratios ; the rate of addition, per double bond, was virtually identical to that for a mono-alkene such as hept-1-ene [3].

The importance of hydrogen abstraction from allylic sites is apparent in the reactions of trichloromethyl [4] and trifluoromethyl [5] radicals with propene. The ease of hydrogen abstraction is usually attributed to the resonance stabilisation of the allyl radical. In the pentadienyl radical the unpaired electron is delocalised over five carbon atoms. It was anticipated, therefore, that hydrogen abstraction from 1,3-pentadiene (and 1,4-pentadiene) would be easier than hydrogen abstraction from propene, i.e. <u>both</u> addition and abstraction would occur more readily. Hydrogen abstraction has not been reported for this type of diene and the present study was undertaken to probe the mechanism of radical interaction with such systems.

Product studies do not seem to have been undertaken for conjugated dienes or enynes reacting with carbon-centred radicals. However, Vasil'eva found that thiols give both 1,2and 1,4-adducts with conjugated dienes [6]. Poutsma and Ibarbia found that trimethyltin radicals add to both the double and triple bonds of conjugated enynes and in each case 1,2- and 1,4-adducts were isolated [7].

### RESULTS

<u>Buta-1,3-diene</u>. The photochemical addition of trifluoromethyl iodide to buta-1,3-diene in the gas phase gave rise to two isomeric products which were shown to be the <u>trans</u>- and <u>cis</u>-1,4-adducts ( $CF_3CH_2CH=CHCH_2I$ ). No 1,2-adducts or diadducts were detectable. The <u>trans</u> isomer predominated, the <u>trans</u> to <u>cis</u> ratio being ca. 4.0 to 1 and virtually independent of

temperature. Competitive experiments were carried out with ethylene and it was established that the overall rate of  $CF_3$ . addition to butadiene is ca. 10 times that for addition to ethylene at 450 K. Our results were not of sufficiently good quality for use in the calculation of Arrhenius parameters.

<u>Vinylacetylene</u>. The main products from the photochemical addition of trifluoromethyl iodide to vinylacetylene were the 1,4-adduct from addition to the double bond  $(CF_3CH_2CH=C=CHI)$ , and the <u>trans</u>- and <u>cis</u>-1,2-adducts from addition to the triple bond  $(CF_3CH=CICH=CH_2)$ . There were also several minor components which could not be identified. Addition to the double bond predominated over addition to the triple, and for the latter the <u>trans</u> to <u>cis</u> ratio was ca. 2.5 to 1. Although addition to the double bond predominated, the proportion of this addition relative to addition to the triple bond depended on the concentrations of the reactants. It seems probable that at high vinylacetylene concentrations the adduct radicals are <u>selectively</u> removed in telomerization reactions, and the product chromatograms did show evidence of telomers in the form of broad, long retention time, peaks which were not identified.

<u>Trans- and cis-penta-1,3-diene</u>. The photochemical reaction of  $CF_3I$  with <u>cis</u>-piperylene in the gas phase led to isomerization of the diene into a mixture of both stereoisomers. In addition, the presence of deca-1,3,7,9-tetraene and 1,1,1-trifluorohex-3-ene, suggested that hydrogen abstraction was occurring, but no adducts were detectable. When the reaction was carried out at ambient temperature, in a sealed tube, where the majority of the reactants are in the liquid phase, the volatile products were accompanied by the <u>trans-</u> and <u>cis-1,4-adducts</u> (ratio 10 to 1),  $CF_3CH_2CH=CHCHICH_3$  (80%) together with the 1,2-adduct.  $CF_3CH_2CHICH=CHCH_3$  (20%). This was probably mainly the <u>trans-</u>isomer, but the stereochemistry could not be deduced with certainty from the n.m.r. spectra. Photochemical reaction of  $CCl_3Br$  with <u>cis-penta-1,3-diene</u> in the liquid phase gave a mixture trans- and cis-1,4-adducts (<u>trans</u> to <u>cis</u> ratio 18 to 1)  $CCl_3CH_2CH=CHCHBrCH_3$  (80%) and some 1,2-adduct  $CCl_3CH_2CHBrCH=CHCH_3$  (20%). Hydrogen abstraction appeared to be minor in this system.

<u>Pent-1-en-4-yn</u>. The photochemical reaction of  $CCl_3Br$  with pent-1-en-4-yn in the liquid phase at ambient temperature produced both the 1,2-dibromide BrCH=CBrCH<sub>2</sub>CH=CH<sub>2</sub> from bromine atom addition to the triple bond, but the 1,2-adduct  $CCl_3CH_2CHBrCH_2CECH$  from addition of  $CCl_3$ · radicals to the double bond was by far the main product. No adducts from  $CCl_3$ · radical attack on the triple bond were detected. The presence of CHCl<sub>3</sub> indicated that some hydrogen abstraction had taken place.

#### DISCUSSION

The products from the addition of  $CF_3I$  and  $CCl_3Br$  to the dienes and engnes are collected in the table. Their nature strongly suggests that reaction takes place by a radical chain process:

where X = F or Cl, Z = I or Br and D = diene or enyne. The bromine atoms from CCl<sub>3</sub>Br photolysis can also add to D and a dibromide is formed when the resulting radical abstracts from CCl<sub>3</sub>Br. This is a non-chain process, and the dibromide was only detected as a minor component in the pent-1-en-4-yn reaction. Iodine atoms also add to D, but the reaction is reversible and diiodides are not usually detected. Hydrogen abstraction was significant with penta-1,3-diene, penta-1,4diene and pent-1-en-4-yn, but addition appeared to be the major process for both CF<sub>3</sub> and CCl<sub>3</sub> radicals in solution.

The competitive addition of  $CF_3$  radicals to buta-1,3-diene and ethylene showed that addition to the diene is faster ( $k_d/k_e \approx 10$  at 450 K). This is in agreement with the earlier results of Szwarc and co-workers [2]. The enhanced reactivity of butadiene can be attributed to the production of a delocalised allyl-type of radical in the addition step (see scheme) with a corresponding lowering of the activation barrier.

The table shows that the main products from  $CX_3$  radical addition to the conjugated dienes (and vinylacetylene) were 1,4-adducts. The substituted allyl radicals (1) and (2) formed on addition to the dienes can abstract iodine (or bromine) from the reactant to give either the 1,2-adduct or the 1,4-adduct depending on whether (1) or (2) react at the substituted end or at the methylene terminus. It is most probable that steric factors govern the relative proportions



of the two types of adduct. With buta-1,3-diene the terminus is a methylene group, so steric hindrance to halogen abstraction is less than at the substituted end, and only 1,4-adducts were observed. In the penta-1,3-diene case both ends of the allyl radical are substituted and the proportion of 1,2-addition becomes appreciable. Poutsma and Ibarbia in their study of  $Me_3SnH$  addition to conjugated engues reported a preponderance of 1,2-addition to pent-1-en-3-yn [7]; probably because steric hindrance would be much less for hydrogen abstraction from  $Me_3SnH$  by the intermediate propargyl-type of radical. We found predominantly 1,4-addition of  $CF_3I$  to vinylacetylene; which is consistent with iodine abstraction by the intermediate propargyl radicals being less hindered at the methine terminus.

For both  $CF_3I$  and  $CCl_3Br$  addition to conjugated dienes a mixture of <u>trans</u>- and <u>cis</u>- 1,4-adducts was produced and in each case the <u>trans</u>-isomer predominated. Radical addition to the diene in its <u>s-trans</u> and <u>s-cis</u> conformation will produce a substituted allyl radical in two different conformations (see scheme). For allyl itself and simple alkyl substituted derivatives the two conformations do not interconvert in the accessible temperature range [8]. Halogen abstraction by (1) leads to the <u>trans</u>-1,4-adduct whereas (2) leads to the <u>cis</u>-1,4-adduct. The preponderance of the <u>trans</u>-adducts is therefore a direct consequence of the well established fact that conjugated dienes exist predominantly in the <u>s-trans</u> conformation.

There is a possibility that the products might be under thermodynamic control; some, such as the 1,2 adduct of  $CF_3I$  and buta-1,3-diene, not being stable under the reaction conditions. Trifluoromethyl radical addition to conjugated dienes is more exothermic than addition to alkenes [11], therefore the process is not likely to be reversible under our experimental conditions. The adducts might however decompose by dehydroiodination, e.g.

# $CF_3CH_2CHICH=CH_2 \longrightarrow CF_3CH=CHCH=CH_2 + HI$

We did not observe products of this type under our experimental conditions which involved less than 50% diene consumption nor were adducts derived from them detected. This kind of decomposition has not been noted by other workers  $\begin{bmatrix} 2,3 \end{bmatrix}$ Although this evidence is not conclusive it seems reasonable to use as a working hypothesis the idea that the product distributions are under kinetic control.

Addition to the double bond occurred more rapidly than addition to the triple bond for both the conjugated vinylacetylene and the methylene interrupted pent-1-en-4-vn. We have previously shown that for  $CF_{2}$  radicals the rate constant for addition to ethylene relative to that for addition to acetylene is 2.4 at 437 K  $\boxed{9}$ , and the present results provide confirmation from intramolecular competition of the greater reactivity of the double bond. Poutsma and Ibarbia also found that Me<sub>2</sub>Sn. radicals add more rapidly to the double bonds of conjugated enynes [7]. The table shows that  $CCl_3$ . radical addition to pent-1-en-4-yn occurred exclusively at the double bond. This is probably a reflection of the greater selectivity of  $CCl_3$  as compared with  $CF_3$  radicals. Curiously the bromine atoms generated from CCl<sub>3</sub>Br appeared to add most readily to the triple bond. It is possible however that a minor unidentified product (see experimental) could be the dibromide BrCH<sub>2</sub>CHBrCH<sub>2</sub>CECH.

TABLE

Adducts	formed	from	$CF_{2}I$	and	CC1,Br	addition	to	dienes	and	enzymes
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Diene/Enyne Addend		1,2-Adduct	1,4-Adduct	Other
CH2=CHCH=CH2	CF31		$CF_3CH_2CH=CHCH_2I$ (t/c = 4.1)	
CH2=CHC=CH	CF <sub>3</sub> I	$CF_3CH=CICH=CH_2$ (t/c ~2.5)	CF <sub>3</sub> CH <sub>2</sub> C=C=CHI	telomers
CH2=CHCH=CHCH3	CF <sub>3</sub> 1	CF <sub>3</sub> CH <sub>2</sub> CHICH=CHCH <sub>3</sub> (25%)	CF <sub>3</sub> CH <sub>2</sub> CH=CHCHICH <sub>3</sub> (75%) (t/c = 10)	H-abstrn. products
CH2=CHCH=CHCH3	℃1 <sub>3</sub> Br	CCl <sub>3</sub> CH <sub>2</sub> CHBrCH=CHCH <sub>3</sub> (20%)	$CC1_3CH_2CH=CHCHBrCH_3$ (80%) (t/c = 18)	CHC13
$CH_2 = CHCH_2CH = CH_2^a$	CF <sub>3</sub> I	CF3CH2CHICH2CH=CH2		Diadduct
CH2=CHCH2C=CH	CC1 <sub>3</sub> Br	CC1 <sub>3</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> CECH BrCH=CBrCH <sub>2</sub> CH=CH <sub>2</sub>		снс1 <sub>3</sub> <sup>С</sup> 2 <sup>С1</sup> 6

<sup>a</sup>Results of N.O. Brace, ref. 3 .

#### EXPERIMENTAL

The apparatus and experimental techniques have been described in previous papers [9]. N.m.r. spectra were obtained on CCl<sub>4</sub> solutions at ambient temperature with Me<sub>4</sub>Si or CCl<sub>3</sub>F as internal standard; a Varian HA 100 instrument being employed. G.l.c. analysis was carried out using a modified Griffin and George D6 gas density balance chromatograph with columns of 10% Embaphase silicone oil, 15% tritolylphosphate, or 12%  $\beta\beta'$ -oxydipropionitrile on 60-100 mesh Embacel. The same columns, in a Pye 105 flame-ionization chromatograph, were used in preparative g.l.c. work. Coupled g.l.c.-mass spectrometry was carried out using the same columns in a Pye 104 gas chromatograph coupled via a Biemann separator to an A.E.I. m.s. 902 mass spectrometer.

Reactants were commerical materials except for vinylacetylene which was prepared by the method of Eglinton and Whiting  $\begin{bmatrix} 10 \end{bmatrix}$  and pent-1-en-4-yn, which was synthesised from ethynylmagnesium bromide and allyl bromide; the product being purified by preparative g.l.c.

# Photochemical reaction of CF3I with buta-1,3-diene.

Trifluoromethyl iodide (38.1 X 10<sup>-4</sup> mol dm<sup>-3</sup>), butadiene (5.9 x  $10^{-4}$  mol dm<sup>-3</sup>) and ethylene (21.6 mol dm<sup>-3</sup>) were irradiated in the gas phase in a quartz vessel with light from a medium pressure mercury arc for 120 min. at 140 °C. Gas chromatography showed the presence of three products and the mass-spectra indicated the first eluted compound to be  $CF_3CH_2CH_2I$  and the other two to be isomeric adducts from butadiene  $(CF_3C_4H_6I)$ . The major isomer was separated by preparative g.l.c. The <sup>1</sup>H n.m.r.;  $\delta$  2.83 (m, 2H,  $J_{HC}, CF_3^{-1} = 10.8$  Hz),  $\delta$  3.85 (d, 2H,  $J_{HdHb} = 7.5$  Hz),  $\delta$  5.76 (m, 2H). Spin decoupling by irradiation at  $\delta$  3.85 simplified the spectrum to a doublet

 $(J_{H^{a}H^{b}} = 15.5 \text{ Hz})$  and a doublet of triplets  $(J_{H^{a}H^{b}} = 15.5 \text{ Hz})$ ;  $J_{\mu 2 \mu c} = 7.0$  Hz). Irradiation at  $\delta 2.83$  simplified the spectrum



to a doublet  $(J_{H}a_{H}b = 15.5 \text{ Hz})$ , and a doublet of triplets  $(J_{H}a_{H}b = 15.5 \text{ Hz}; J_{H}b_{H}c = 7.5 \text{ Hz}).$  The <sup>19</sup>F n.m.r. spectrum consisted of a triplet at  $\phi$  66.9 ppm (J<sub>L H</sub>c = 10.8 Hz). This data is consistent with structure (3) and  $J_{H} {\bm a}_{H} {\bm b}$  (15.5 Hz) lies in the range expected for a trans isomer. The mass spectrum of the minor product was virtually identical to that of (3), but there was insufficient material for n.m.r. analysis. On the basis of its mass spectrum it was assigned structure (4), rather than (5).

 $\frac{\rm Photochemical\ Reaction\ of\ CF_3I\ with\ vinylacetylene}{\rm CF_3I\ (27\cdot 2\ mol\ dm^{-3})\ and\ vinylacetylene\ (8\cdot 6\ x\ 10^{-4}\ mol\ mol\ s^{-4})}$ dm<sup>-3</sup>) were photolysed in the gas phase for 2h at 160  $^{\circ}C$ . Coupled g.l.c. - mass spectrometry indicated that there were three main components which were all isomeric adducts,  $(CF_3C_4H_4I)$ . The three peaks were isolated by preparative g.l.c. and <sup>1</sup>H n.m.r. spectra obtained. The first eluted component showed resonances at  $\delta \ 2 \cdot 4$  (m,  $2H^{C}$ ),  $\delta \ 4 \cdot 6$ (dt, 1H<sup>b</sup>,  $J_{H^{b}H^{c}} = 8$  Hz;  $J_{H^{b}H^{a}} = 6$  Hz) and  $\delta$  5.5 (dt, 1H<sup>a</sup>,  $J_{Haub} = 6 \text{ Hz}; J_{HaHC} = \text{ca. } 1.5 \text{ Hz}), \text{ which is consistent with}$ structure (6)



However, the n.m.r. showed the presence of a second component which could not be identified. The n.m.r. spectra of the other two components showed them to be the trans- and cisadducts (7) and (8). Peak 2;  $\delta 5.4$  (d, 1H, J = 10 Hz),  $\delta 5.6$  (d, 1H, J = 16 Hz),  $\delta 6.2$  (dd, 1H, J = 10, 15 Hz),



 $\delta 6.3$ , (q, 1H, J = 7.5 Hz). Peak 3;  $\delta 5.2$  (d, 1H, J = 10 Hz)  $\delta$  5.6 (d, 1H, J = 15 Hz),  $\delta$  5.8 (dd, 1H, J = 10, 15 Hz),  $\delta$  6.2 (q, 1H, J = 7.5 Hz). The n.m.r. spectra showed the presence of additional unidentified components eluted with both peaks.

 $\frac{\text{Reaction of CF}_{3}\text{I with trans- and cis-penta-1,3-diene.}}{\text{CF}_{3}\text{I }(43\cdot5\text{ x }10^{-4}\text{ mol dm}^{-3}) \frac{\text{trans-penta-1,3-diene }(8\cdot \textbf{6} \text{ x }1)}{\text{trans-penta-1,3-diene }(8\cdot \textbf{6} \text{ x }1)}$  $10^{-4}$  mol dm<sup>-3</sup>) and ethylene (11.7 x  $10^{-4}$  mol dm<sup>-3</sup>) were photolysed together for  $2 \cdot 3$  h at 130 <sup>O</sup>C. The g.l.c. showed 4 low boiling components; (i) cis-penta-1,3-diene, (ii) deca-1,3,7, 9-tetraene  $(M^+ 134)$ ; formed by combination of two pentadienyl radicals and probably accompanied by other geometrical isomers; (iii) 1,1,1-trifluorohex-3-ene ( $M^+$  138) and (iv) CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I. No adducts were detected in these gas phase reactions. When cis-penta-1,3-diene (3.0 mmol) and  $CF_{2}I(2.5 \text{ mmol})$  were degassed. sealed into a pyrex tube and photolysed at 20 °C for 4.5h, the volatile products were observed together with three other components which were shown to be adducts,  $\mathrm{CF_2C_5H_8I}$  , by their mass spectra. The first two components were not well resolved and were collected as a single fraction by preparative g.l.c. The major component showed the following <sup>1</sup>H n.m.r.;  $\delta$  1.52  $(d, 3H, J = 7 Hz), \delta 2 \cdot 28 (dq, 2H, J = 7 Hz, 11 Hz), \delta 4 \cdot 35$ (quintet, 1H, J = 8 Hz),  $\delta 5.15$  (dt, 1H, J = 7 Hz, 15 Hz),  $\delta$  5.70 (d.d, J = 8 Hz, 15 Hz). The <sup>19</sup>F n.m.r. showed a triplet  $\phi$  = 66.89 (J = 11 Hz). These spectra are consistent with

structure (9); the 15 Hz coupling constant between the vinylic hydrogens suggesting the trans arrangement. The



spectra of minor component were partly obscured by peaks from the major component. The <sup>19</sup>F n.m.r. spectrum showed a triplet  $\phi =$ 66.58(J = 11 Hz) and the <sup>1</sup>H n.m.r. showed S 1.40 (d, J = 7Hz).  $\delta$  3.4 (m) and some signal in the vinyl region. It seems probable that it was the cis-adduct (10). The proportions of the two were 10 trans to 1 cis. The third component was obtained in only a very small amount by preparative g.l.c. The very weak <sup>1</sup>H n.m.r. spectrum showed  $\hat{o} 1 \cdot 0$  (d, J = 7 Hz),  $\delta 2 \cdot 7$ (m),  $\delta 3.8$  (m),  $\delta 5.4 - 64$  (m), which is consistent with structure (11). The stereochemistry about the double bond could not be determined.

 $\frac{\text{Reaction of CCl}_{3}\text{Br with cis-penta-1,3-diene}}{\text{CCl}_{3}\text{Br (20 mmol) and } \underline{\text{cis-penta-1,3-diene}} (15 \text{ mmol) were}$ photolysed in a thin-wall pyrex tube at 20 <sup>O</sup>C for 5.5h. The mixture showed two main products which were isolated by preparative g.l.c. The mass spectra showed molecular ion clusters and fragmentation patterns which established both components as adducts  $CCl_2C_5H_2Br$ . The <sup>1</sup>H n.m.r. of the first component was as follows:  $\delta$  1.8 (d, 3H, J = 7 Hz),  $\delta$  3.4 (d, 2H, J = 7 Hz),  $\delta$  4.6 (quintet, 1H, J = 7 Hz),  $\delta$  5.9 (m, 1H,  $J_{HaHb} = 15 \text{ Hz}$ ,  $J_{HCHa} = 7 \text{ Hz}$ ,  $J_{HbHd} = 7 \text{ Hz}$ ). Its structure is



therefore (12). This n.m.r. showed minor amounts of the <u>cis</u> adduct (13) to be present; <u>trans</u> to <u>cis</u> ratio 18:1. The second peak showed the following <sup>1</sup>H n.m.r.:  $\delta$  1.4 (d, 3H, J = 7 Hz),  $\delta$  3.2 (m, 1H),  $\delta$  3.9 (d, 2H, J = 7 Hz),  $\delta$  5.8 (m, 2H). The structure is therefore most probably the <u>trans</u> -1,2-adduct (14). Products (12) and (14) were formed in a 4 to 1 ratio. Some volatile products were formed but none could be identified with certainty. It was established by retention time comparisons with authentic material that no <u>trans</u>-1-bromopenta-2,4-diene was formed.

### Reaction of CCl3Br with Pent-1-en-4-yn.

BrCH=CBrCH<sub>2</sub>CH=CH<sub>2</sub> 
$$CC1_3CH_2CHBrCH_2C\equiv CH$$
  
(15) (16)

chemistry about the trisubstituted double bond could not be determined. Peak (iii)  $\delta 2 \cdot 1$  (t, 1H, J = 2 Hz),  $\delta 2 \cdot 9$  (m, 2H),  $\delta 3 \cdot 4$  (m, 2H),  $\delta 4 \cdot 4$  (quintet, 1H, J = 6 Hz). This indicates (16) as the structure. No other adducts were detectable.

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