Pergamon

Tetrahedron Vol. 51, No. 13, pp. 3929-3938, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 $9.50+0.00

0040-4020(95)00115-8

Aryne Formation from 1-(2'-Carboxyaryl)-3,3-dimethyl Triazenes

P. Christopher Buxton and Harry Heaney*

Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

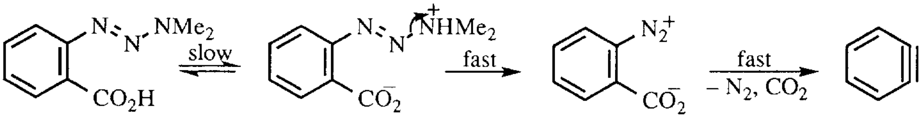
Abstract: *A study of the decomposition of 1-(2'-carboxyphenyl)-3,3-dimethyltriazene and the tetrabromo- and tetrachloro- analogues showed that the arenediazonium-2-carboxylates were intermediates in the formation of the corresponding arynes: the 1-(2'-carboxytetrahalophenyl)-3,3-dimethyltriazenes are stable precursors that enable cycloaddition reactions of the tetrahalobenzynes to be carried out in acceptable yields using substrates such as N-methylpyrrole, p-xylene and m-dimethoxybenzene.*

Introduction

Despite the fact that it is now more than forty years since the the intermediacy of benzyne intermediates was first authenticated, aryne chemistry is still being actively investigated.[1] The generation of benzyne from *o*-halophenyllithium reagents and benzenediazonium-2-carboxylate are two of the common methods used.[2] A variety of experimental methods has been reported for the generation and decomposition of benzenediazonium-2-carboxylate.[3] Our interest in the chemistry of the super-electrophilic tetrahalogeno-benzynes[4] led us to use pentachloro- and pentafluoro-phenyllithium reagents and the arenediazonium-2-carboxylates derived from tetrahaloanthranilic acid derivatives, particularly tetrachloroanthranilic acid.[5] We also used tetrabromo- and tetraiodo-anthranilic acids.[6] Some reactions that we wished to study are not amenable to the conditions involved in the decomposition of the tetrahalobenzenediazonium-2-carboxylate salts that we have used. Although pentafluoro- and pentachloro- phenyllithium reagents are readily available pentabromophenyllithium is not accessible in high yield from hexabromobenzene.[7] The preparation of 1-(2'-carboxyphenyl)-3,3-dimethyltriazene[8] and its subsequent use as a benzyne precursor[9] suggested the possibility of preparing 1-(2'-carboxytetrabromophenyl)-3,3-dimethyltriazene as an aryne precursor. We have reported the preparation of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyltriazene and its use in a reaction with cinnamaldehyde.[10] It is of interest to note that although it has been presumed that 1-(2'-carboxyphenyl)-3,3-dimethyltriazene fragments to benzyne via benzenediazonium-2-carboxylate no definitive evidence has been presented.

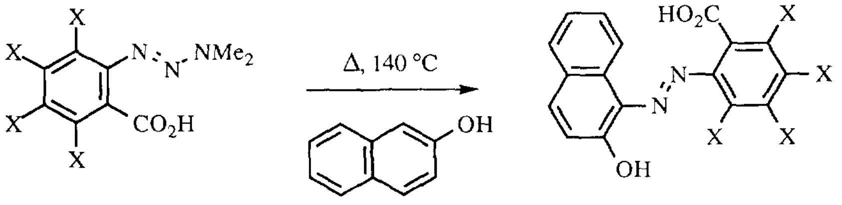
Discussion

An examination of the scope of the arylation reactions of aryltriazenes revealed that when 1-(2'-carboxyphenyl)-3,3-dimethyltriazene (**1**) was heated in benzene in the presence of hydrogen chloride, *o*-chlorobenzoic acid was formed but no biphenyl-2-carboxylic acid was detected.[8] It was shown subsequently that the triazene (**1**) functions as a benzyne precursor when heated at 150 °C.[9a,b] 1-(2'-Carboxyphenyl)-3,3-dimethyltriazene has also been used more recently in a series of Diels-Alder reactions leading to benzo-heterocycles.[9c,d,e] It should be noted that if any reagent is present that is more basic than the triazene the carboxyl proton is preferentially removed and fragmentation to benzyne does not occur. For example, benzyne formation does not proceed in the presence *N*,*N*-dimethylaniline. On the other hand the temperature at which benzyne formation occurs readily ensures that the majority of the dimethylamine produced escapes. We prepared the compound (**1**) in 70% yield by adding anhydrous dimethylamine to a suspension of benzenediazonium-2-carboxylate in dichloromethane at 0 °C. Both tetrachloro- and tetrabromo-1-(2'-carboxyphenyl)-3,3-dimethyltriazene were prepared in moderate yields by adding the appropriate tetrahalogenobenzenediazonium-2-carboxylate hydrochloride or fluoroborate to an aqueous solution of sodium carbonate containing dimethylamine, initially at 5 °C. We should note that whereas benzenediazonium-2-carboxylate is violently explosive when dry, benzenediazonium-2-carboxylate hydrochloride is reported to be significantly more stable. Nonetheless, **although we have not observed explosions we regard the tetrahalogenobenzenediazonium-2-carboxylate hydrochlorides and hydro-fluoroborates as potentially dangerous and they should be handled with extreme care using appropriate screens.** The triazenes, which are stable compounds afford the arynes at temperatures well above those at which arenediazonium-2-carboxylates fragment to arynes. Thus a reasonable mechanism for aryne formation from the triazenes involves, as the slow step, an equilibration of the neutral and dipolar forms followed by the rapid thermal ejection of first, dimethylamine to give the arenediazonium-2-carboxylates, the well established aryne precursors, and then nitrogen and carbon dioxide. A number of competing pathways are known to occur when benzenediazonium-2-carboxylate fragments; the precise route or routes that are followed depend on the polarity and nucleophilicity of the solvent. The loss of nitrogen to afford an aryl σ-cation being an important competing pathway to the concerted loss of nitrogen and carbon dioxide that results in the formation of benzyne. This is exemplified by the formation, after hydrolysis, of *N*-acetylanthranilic acid in reactions of benzenediazonium-2-carboxylate that are carried out in acetonitrile.[11] The 2-carboxyphenyl cation has also been reported to be intercepted by acetone,[12] thiobenzophenone,[13] and 4,4'-dimethoxyselenobenzophenone.[14] The formation of *o*-chlorobenzoic acid[8] and salicylic acid[3a] are additional well known examples of capture of the 2-carboxyphenyl cation. The modes by which a number of other benzyne precursors fragment have also been studied recently.[15]



(**1**)

We heated both 1-(2'-carboxyphenyl)-3,3-dimethyltriazene (**1**) and its tetrachloro-analogue (**2**) at 140 °C in 1,1,2,2-tetrachloroethane containing 2-naphthol and were pleased to be able to isolate the azo-dyes (**3**) and (**4**) in modest yields, thereby establishing the intervention of benzenediazonium-2-carboxylate and tetrachlorobenzenediazonium-2-carboxylate in the formation of of the arynes from the triazenes. The yields of the dyes were expected to be low because of the known ease of formation of the arynes from the arenediazonium-2-carboxylates at lower temperatures than those required for the loss of dimethylamine from the triazenes (**1**) and (**2**).

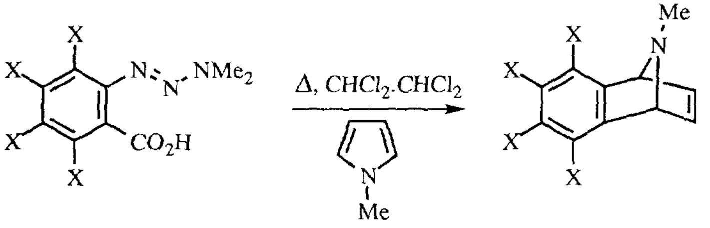


(1, X = H)
(2, X = Cl)

(3, X = H)
(4, X = Cl)

The involvement of benzenediazonium-2-carboxylate was also implicated by the formation of salicylic acid when the triazene (**1**) was heated under reflux in water. We have argued previously that the presence of electron withdrawing substituents would raise the energy barrier to loss of nitrogen from an arenediazonium-2-carboxylate while simultaneously facilitating the loss of carbon dioxide.[11] Thus the loss of nitrogen and carbon dioxide to give a tetrahalogenobenzyne occurs synchronously as indicated, for example by the failure to isolate a product derived from acetonitrile, when tetrabromobenzenediazonium-2-carboxylate was generated in a mixture of benzene and acetonitrile.[6] We were not surprised, therefore, to find that the decomposition of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyltriazene (**2**) in a number of solvents such as water and methanol led to the formation of the tetrachlorobenzyne adducts 2,3,4,5-tetrachlorophenol and 2,3,4,5-tetrachloroanisole respectively. As expected the decomposition of tetrachlorobenzenediazonium-2-carboxylate hydrofluoroborate when allowed to decompose in water or methanol gave predominantly the aryne products 2,3,4,5-tetrachlorophenol and 2,3,4,5-tetrachloroanisole respectively. The decomposition of tetrachlorobenzenediazonium-2-carboxylate hydrochloride in water gave also gave a mixture of the aryne products, 2,3,4,5-tetrachlorophenol and pentachlorobenzene; while the decomposition in methanol gave rise to a mixture 2,3,4,5-tetrachlorobenzoic acid and 2,3,4,5-tetrachloroanisole. Thus the decomposition of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyltriazene (**2**) and tetrachlorobenzenediazonium-2-carboxylate salts give rise almost exclusively to tetrachlorobenzyne whereas the decomposition of the triazene (**1**) and benzenediazonium-2-carboxylate partitions between a number of different processes.[11] Interestingly, and perhaps surprisingly, we found that 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyltriazene gave the tetrachlorobenzyne cycloadduct when photolysed in *p*-xylene. 1-(2'-Carboxyphenyl)-3,3-dimethyltriazene was recovered unchanged from an attempted photolysis experiment.

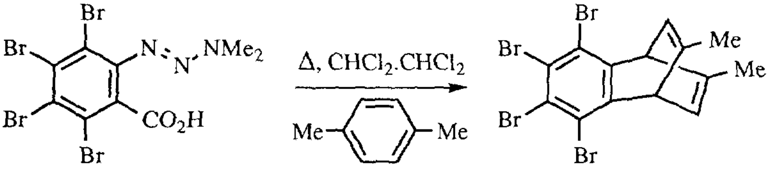
We were thus able to carry out reactions of both tetrachloro- and tetrabromo- benzyne with aromatic heterocyles such as N-methylpyrrole [equation (1)][16] and 2,5-dimethylfuran. We also found that acceptable yields of the expected adducts were obtained from carbocyclic aromatic substrates such as *p*-xylene and *m*-dimethoxybenzene [equations (2) and (3) respectively]. The product (**9**) was isolated in only a 12% yield when 2-carboxytetrachlorobenzenediazonium-2-carboxylate was decomposed at the reflux temperature of carbon tetrachloride in the presence of *m*-dimethoxybenzene.[17]



(2, X = Cl)
(5, X = Br)

(6, X = Cl, 28%)
(7, X = Br, 20%)

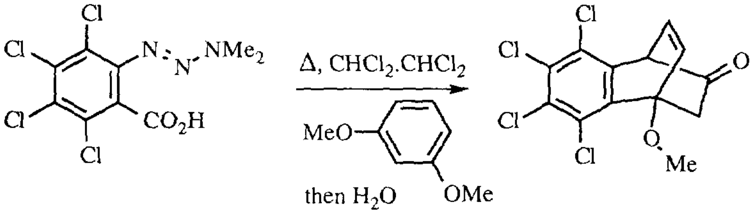
[1]



(5)

(8, 43%)

[2]



(2)

(9, 35%)

[3]

The results reported in this paper establish the mode of decomposition of 1-(2'-carboxyaryl)-3,3-dimethyltriazenes and also provide further evidence that whereas the decomposition of benzenediazonium-2-carboxylate partitions to a number of products in addition to benzyne, the decomposition of the tetrahalobenzenediazonium-2-carboxylates occur almost exclusively to afford the tetrahalogenobenzynes by the synchronous loss of nitrogen and carbon dioxide. The use of the 1-(2'-carboxytetrahalogenophenyl)-3,3-dimethyltriazenes as aryne precursors also allows improved yields of certain products to be obtained, particularly in the case of the tetrabromobenzyne adducts where a good conversion of hexabromobenzene to pentabromophenyllithium has not been reported.

Experimental

Analytical gas chromatography was carried out using hydrogen flame ionisation detection and the detector response was calibrated by using solutions of known concentration at the appropriate levels. Column chromatography was carried out on alumina (Brockman activity I) or on silica gel (Fisons, chromatography grade). Analytical tlc and preparative layer chromatography was carried out using silica gel (PF_{254} according to Stahl). ^1H Nuclear magnetic resonance spectra were determined at 60 MHz on a Perkin-Elmer R10 spectrometer.

1-(2'-Carboxyphenyl)-3,3-dimethyl triazene

Anthranilic acid (20 g, 146 mmol) and trichloroacetic acid (*ca.* 0.2 g) were dissolved in tetrahydrofuran (200 ml) and cooled to *ca.* 5 °C before pentyl nitrite (25 ml) was added dropwise.to the stirred solution. The mixture was allowed to warm to room temperature over 1.5h and the precipitate was then allowed to settle before the supernatant liquid was decanted and replaced with dichloromethane. The replacement of the solvent by dichloromethane was repeated three times.

CAUTION: The diazonium salt must on no account be allowed to become dry.

The stirred suspension was then cooled to 0 °C and anhydrous dimethylamine (25 ml) was added slowly. After 1h sulfuric acid (2 M) was added to the red solution and the organic layer was separated and dried ($MgSO_4$). Removal of the solvent gave 1-(2'-Carboxyphenyl)-3,3-dimethyl triazene (**1**) (16 g, 70%), m.p. 122-126 °C (lit.[8] m.p. 122-126 °C, lit.[9a] m.p. 119-120 °C).

1-(2'-Carboxytetrabromophenyl)-3,3-dimethyl triazene

Tetrabromoanthranilic acid[6] (4.53 g, 10 mmol) was dissolved in tetrahydrofuran (50 ml) and fluoroboric acid (10 ml, 40% aqueous). The solvent was then removed in vacuo and replaced by diethyl ether (50 ml) and cooled to 0 °C. Pentyl nitrite (2.5 ml) was then added dropwise to the cold stirred suspension and left for a further 15 min. The diazonium salt was collected by filtration, washed with ether and allowed to air dry.

CAUTION: When dry the diazonium salt is potentially explosive and suitable precautions should be taken.

The diazonium salt was added to an aqueous solution of sodium carbonate (30 ml, 10%) and dimethylamine (7 ml) maintained at 5 °C. the reaction mixture was stirred at 5 °C for 0.5h and at room temperature for 1h before filtration to remove a small amount of suspended solid. The filtrate was acidified with aqueous sulfuric acid (2 M) and the precipitate taken into ether and dried ($MgSO_4$). Removal of the solvent gave a tan solid which was recrystallised from diethyl ether - light petroleum to afford *1-(2'-carboxytetrabromophenyl)-3,3-dimethyl triazene* (**5**) (2.3 g, 41%), m.p. 137 °C (decomp.), ν_{max}: 3200-2500, 1700 cm^{-1}: δ_H ($CDCl_3$) 3.22 (s, 3H), 3.5 (s, 3H), and 6.20 (br, 1H) ppm: *Found:* C, 21.35; H, 1.4; N, 8.15%; M (mass spectrometry) 509; $C_9H_7Br_4N_3O_2$ *requires:* C, 21.25; H, 1.4; N, 8.25%; M 509.

A portion was treated with an ethereal solution of diazomethane and gave *1-(2'-methoxycarbonyltetrabromophenyl)-3,3-dimethyl triazene*, m.p. 96-98 °C (from methanol), ν_{max}: 2950, 1740 cm^{-1}: δ_H ($CDCl_3$) 3.22 (s, 3H), 3.48 (s, 3H), and 3.75 (s, 3H) ppm: *Found:* C, 22.95; H, 1.75; N; 7.75%; M (mass spectrometry) 523; $C_{10}H_9Br_4N_3O_2$ *requires*: C, 22.95; H, 1.75; N, 8.05%; M 523.

Reaction of 1-(2'-carboxyphenyl)-3,3-dimethyl triazene with 2-naphthol

The triazene (**1**) (1 g) was heated under reflux for 4h with 2-naphthol (0.75 g) in 1,1,2,2-tetrachloroethane (50 ml). The solvent was removed in vacuo and the red residue was triturated with warm benzene to give a red dye (0.175 g, 12%), m.p. 275-276 °C with identical spectra to a sample of 1-

(2'carboxyphenylazo)-2-naphthol (**3**) prepared from benzenediazonium-2-carboxylate and 2-naphthol, m.p. 274-275 °C (lit.[18] m.p. 272 °C).

Reaction of 2-carboxy-3,4,5,6-tetrachlorobenzenediazonium fluoroborate with 2-naphthol

2-Carboxy-3,4,5,6-tetrachlorobenzenediazonium fluoroborate (2.0 g), prepared from tetrachloroanthranilic acid as for the tetrabromo-analogue, was added to a solution of 2-naphthol (1 g) in chloroform (50 ml) and stirred at room temperature for 1h. The red precipitate (**4**) (3 g) was washed with chloroform and dried and a sample treated with an ethereal solution of diazomethane to give *1-(2'-methoxycarbonyl-3,4,5,6-tetrachlorophenylazo)-2-naphthol*, m.p. 215-218 C (from carbon tetrachloride), ν_{max}: 1740 cm^{-1}: λ_{max}: 224 ($\log_{10} \varepsilon$, 4.40), 285 (3.84), 303 (3.72), and 462 (4.01) nm: *Found:* C, 48.2; H, 2.35; N, 6.5%; $C_{18}H_{10}Cl_4N_2O_2$ *requires:* C, 48.6; H, 2.25: N, 6.3%.

Reaction of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyl triazene with 2-naphthol

The triazene (**2**) (1 g) was heated under reflux for 1.5h with 2-naphthol (0.5 g) in 1,1,2,2-tetrachloroethane (25 ml). The cold solution yielded a red solid (**4**) (0.472 g, 37%) which was treated with an excess of an ethereal solution of diazomethane and methanol (2 drops) to afford a further red dye, which was crystallised from benzene-methanol with spectra identical with those of a sample prepared as above.

Reaction of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyl triazene with *N*-methylpyrrole

The triazene (**2**) (1 g) was heated under reflux for 0.75h with *N*-methylpyrrole (1 g) in 1,1,2,2-tetrachloroethane (25 ml). The solution was then allowed to cool and washed with aqueous sodium carbonate (10%). The organic layer was dried (Na_2SO_4) and the solvent removed to give *5,6,7,8-tetrachloro-1,4-imino-1,4-dihydronaphthalene* (**6**) (0.245 g, 28%) m.p. 157-159 °C (from methanol) lit.[16c] m.p. 155-156 °C; ν_{max}: 3110, 2955, 2880, 2800 cm^{-1}: δ_H ($CDCl_3$) 2.20 (s, 3H), 4.80 (m, 2H), and 7.05 (m, 2H) ppm. In a repeat reaction using a longer reaction time and isolation by column chromatography without the base wash, the yield was raised to 37%.

Reaction of 1-(2'-carboxytetrabromophenyl)-3,3-dimethyl triazene with *N*-methylpyrrole

The triazene (**5**) (1 g) was heated under reflux for 2h with *N*-methylpyrrole (3 g) in 1,1,2,2-tetrachloroethane (50 ml). The solvent was removed in vacuo and the residue dissoved in chloroform and washed with aqueous sodium carbonate (50 ml, 10%). The organic layer was dried (Na_2SO_4), evaporated, and the residue dissolved in benzene and treated with charcoal to yield a brown solid (20%). Recrystallisation from benzene-light petroleum gave *5,6,7,8-tetrabromo-1,4-imino-1,4-dihydronaphthalene* (**7**) (185 mg, 20%) m.p. 202-204 °C: ν_{max}: 3000, 2945, 2870, 2795 cm^{-1}: δ_H ($CDCl_3$) 2.20 (s, 3H), 4.75 (m, 2H), and 6.95 (br, 2H) ppm: *Found:* C, 28.50; H, 1.55; N, 3.20%; M (mass spectrometry) 473; accurate mass 468.7314; $C_{11}H_7Br_4N$ requires C, 27.90; H, 1.5; N, 2.95%; M 473; $C_{11}H_7{}^{89}Br_4N$ requires 468.7315.

Reaction of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyl triazene with 2,5-dimethylfuran

The triazene (**5**) (1 g) was heated under reflux with 2,5-dimethylfuran (1 g) in 1,1,2,2-tetrachloroethane (50 ml). After 1h the mixture became black and the reaction was terminated, washed with aqueous sodium carbonate (10%). The aqueous phase gave, after acidification, recovered triazene (321 mg). The organic layer was dried ($MgSO_4$) and evaporated to yield a black oil which, after chromatography on alumina, gave *5,6,7,8-tetrachloro-1,4-dimethyl-1,4-epoxy-1,4-dihydronaphthalene* (167 mg, 26% conversion), m.p. 69-71 °C: ν_{max}: 3000, 1270, cm^{-1}: δ_H ($CDCl_3$) 1.95 (s, 6H) and 6.76 (s,2H) ppm: *Found:* C, 46.60; H, 2.50; M (mass spectrometry) 310; $C_{12}H_8Cl_4O$ requires C, 46.50; H, 2.60; M 310.

Reaction of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyl triazene with 1,3-dimethoxybenzene

The triazene (**2**) (1 g) was heated under reflux for 3h with 1,3-dimethoxybenzene (1 g) in 1,1,2,2-tetrachloro-ethane (50 ml). The cold solution was then washed with aqueous sodium carbonate (10%). The aqueous phase gave, after acidification, recovered triazene (284 mg). The organic layer was dried ($MgSO_4$) and evaporated to yield an oil which, after chromatography on silica gel, gave 5,6,7,8-tetrachloro-1-methoxy-1,4-ethenotetral-3-one (**9**) (346 mg, 35% conversion), m.p. 146-148 °C (from methanol benzene) (lit.[16] m.p.146-148 °C) : ν_{max}: 3005, 2930, 1750, cm^{-1}: δ_H ($CDCl_3$) 2.10-2.75 (dxd, 2H, J_{A-B} = 17.7 Hz), 3.65 (s, 3H), 4.87-5.12 (m, 1H), 6.50-7.05 (m, 2H) ppm: *Found:* C, 46.40; H, 2.10; Mass spectrometry 296 M – $CH_2C{=}O$) Calc. for $C_{13}H_8Cl_4O$ C, 46.20; H, 2.40% M 338.

Reaction of 1-(2'-carboxytetrabromophenyl)-3,3-dimethyl triazene with 1,4-dimethylbenzene

The triazene (**5**) (688 mg) and 1,4-dimethylbenzene (50 ml) were heated under reflux for 3h after which the solvent was removed in vacuo to leave a tan solid which was placed on a column of alumina. Elution with light petroleum gave 5,6,7,8-tetrabromo-1,4-dihydro-2,10-dimethyl-1,4-ethenonaphthalene, (**8**) (287 mg, 43%), m.p. 166-168 C (lit.[6] m.p. 167 C); δ_H ($CDCl_3$) 1.90 (d, 6H), 4.85-5.05 (m, 2H), 6.20-6.40 (m, 2H) ppm: *Found:* C,33.70; H, 2.00%; M 498 (mass spectrometry) Calc. for $C_{14}H_{10}Br_4$ C, 33.75; H, 2.00%.

The photolysis of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyl triazene in 1,4-dimethylbenzene

The triazene (**2**) (500 mg) was suspended in 1,4-dimethylbenzene (50 ml) and photolysed for 48h with a medium pressure external mercury source. The reaction mixture was extracted with an aqueous solution of sodium carbonate (10%), separated and the aqueous phase acidified to give unreacted triazene (342 mg, 68%). The organic phasewas dried ($MgSO_4$) and evaporated in vacuo to afford 5,6,7,8-tetrachloro-2,10-dimethyl-1,4-dihydro-1,4-ethenonaphthalene (146 mg, 30%), m.p. and mixed m.p. 128-130 °C (lit.[5b] m.p. 128-130 °C).

Reaction of 1-(2'-carboxyphenyl)-3,3-dimethyltriazene with water

The triazene (**1**) (1.0 g) was heated under reflux in water (50 ml) for 2h and the water removed in vacuo to leave an oily solid which was crystallised and shown to be identical to an authentic sample of salicylic acid, m.p. and mixed m.p. mp 156-158 °C (lit.[19] m.p. 159 °C), infrared spectrum identical to that of an authentic sample.

Reaction of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyltriazene with water

The triazene (**2**) (1.0 g) was heated under reflux in water (50 ml) for 2h and the red solution was extracted into ether and washed with aqueous sodium hydrogencarbonate solution (10%) Acidification of the aqueous layer and extraction into ether gave, after evaporation of the solvent, recovered triazene (211 mg). The organic layer was extracted with aqueous sodium hydroxide (2 M) and acidified to give 2,3,4,5-tetrachlorophenol (86 mg, 12%), m.p. and mixed m.p. 115 °C (lit.[20] m.p. 115 °C).

Reaction of 1-(2'-carboxytetrachlorophenyl)-3,3-dimethyltriazene with methanol

The triazene (**2**) (1.0 g) and methanol (1 ml) were heated under reflux in 1,1,2,2-tetrachloroethane for 4h. The cold solution was extracted with aqueous sodium hydroxide (2 M) and the organic phase was evaporated in vacuo to afford a crystalline solid shown to be 2,3,4,5-tetrachloroanisole, (512 mg, 67%), m.p. 82-84 °C (lit.[21] m.p. 82-83 °C).

The decomposition of 2-carboxy-3,4,5,6-tetrachlorobenzenediazonium fluoroborate in water

The diazonium salt (1.0 g) was added to a solution of water (3 ml) in acetonitrile (30 ml) at room temperature. A spontaneous evolution of gas lasted for *ca.* 0.5h after which the solvents were removed and replaced with ether. Extraction into aqueous sodium hydroxide (2M) an acidification of the aqueous layer gave a tan solid shown by tlc and ir comparison to be 2,3,4,5-tetrachlorophenol (362 mg, 58%) m.p. and mixed m.p. 115 °C (lit.[20] m.p. 115 °C).

The decomposition of 2-carboxy-3,4,5,6-tetrachlorobenzenediazonium fluoroborate in methanol

The diazonium salt (1.0 g) was added to methanol (30 ml). After the spontaneous evolution of gas was complete the solvent was removed, replaced with carbon tetrachloride and extracted with aqueous sodium carbonate (10%). Acidification of the aquoeus layer gave 2,3,4,5-tetrachlorobenzoic acid m.p. 164-165 °C (lit.[22] m.p. 168 °C), (79 mg, 10%). The organic phase was dried ($MgSO_4$) and evaporated to leave 2,3,4,5-tetrachloroanisole (480 mg, 63%), m.p. 82-84 °C (lit.[21] m.p. 82-83 °C).

The decomposition of 2-carboxy-3,4,5,6-tetrachlorobenzenediazonium chloride in water

The diazonium salt (1.0 g) was added to a solution of water (3 ml) in acetonitrile (30 ml) at room temperature. A spontaneous evolution of gas lasted for *ca.* 0.5h after which the solvents were removed and replaced with ether. Extraction into aqueous sodium hydroxide (2M) an acidification of the aqueous layer gave a tan solid shown by tlc and ir comparison to be 2,3,4,5-tetrachlorophenol (274 mg, 38%) m.p. and mixed m.p. 115 °C (lit.[20] m.p. 115 °C).

The decomposition of 2-carboxy-3,4,5,6-tetrachlorobenzenediazonium chloride in methanol

The diazonium salt (1.0 g) was added to methanol (30 ml).. After the spontaneous evolution of gas was complete (*ca.* 0.5h) the solvent was removed, replaced with carbon tetrachloride and extracted with aqueous sodium carbonate (10%). Acidification of the aqueous layer gave 2,3,4,5-tetrachlorobenzoic acid m.p. 164-165 °C (lit.[22] m.p. 168 °C), (89 mg, 11%). The organic phase was dried ($MgSO_4$) and evaporated to leave 2,3,4,5-tetrachloroanisole (567 mg, 76%), m.p. 82-84 °C (lit.[21] m.p. 82-83 °C).

We thank the SERC for a research training award to (PCB).

REFERENCES

1. Hart,H.; Ok, D. *J. Org. Chem.*, **1986**, *51*, 979-986; Best, W.M.; Wege, D. *Austral. J. Chem.*, **1986**, *39*, 635-645; Cresp, T.M.; Wege, D. *Tetrahedron*, **1986**, *42*, 6713-6718; Radom, I.; Nobes, R.H.; Underwood, D.J.; Li, W.K. *Pure Appl. Chem.*, **1986**, *58*, 75-88; Pansegrau, P.D.; Rieker, W.F.; Meyers, A.I. *J. Am. Chem. Soc.*, **1988**, *110*, 7178-7184; Bennett, M.A.; Schwemlein, H.P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296-1330; Giles, R.G.F.; Sargent, M.V.; Sianipar, H. *J. Chem. Soc. Perkin Trans. 1*, **1991**, 1571-1579; Gingrich, H.L.; Huang, Q.; Morales, A.L.; Jones, M. *J. Org. Chem.*, **1992**, *57*, 3803-3806; Matsumoto, T.; Hosoya, T.; Suzuki, K. *J. Am. Chem. Soc.*, **1992**, *114*, 3568-3570; Hoke, S.H.; Molstad, J.; Dilettato, D.; Jay, M.J.; Carlson, D.; Kahr, B.; Cooks, R.G. *J. Org. Chem.*, **1992**, *57*, 5069-5071; Conway, S.C.; Gribble, G.W. *Heterocycles*, **1992**, *34*, 2095-2108; Paz, M.; Saa, C.; Guitian, E.; Castedo, I.; Saa, J.M. *Heterocycles*, **1993**, *36*, 1217-1223; Birkett, M.A.; Knight, D.W.; Mitchell, M.B. *Tetrahedron Lett.*, **1993**, *34*, 6935-6938; Matsumoto, Sohma, T.; Hatazaki, S.; Suzuki, K. *Synlett*, **1993**, 843-846; Wickham, P.P.; Reuter, K.H.; Senanayake, D.; Guo, H.; Zalesky, M.; Scott, W.J. *Tetrahedron Lett.*, **1993**, *34*, 7521-7525; Karadakov, P.B.; Gerratt, J.; Raos, G.; Cooper, D.L.; Raimondi, M. *Israel J. Chem.*, **1993**, *33*, 253-264; Hosoya, T.; Takashiro, E.; Matsumoto, T.; Suzuki, K. *J. Am. Chem. Soc.*, **1994**, *116*, 1004-1015; Pu, I.; Grubbs, R.H. J. Org. Chem., 1994,59, 1351-1353; Shimano, N.; Meyers, A.I. *J. Am. Chem. Soc.*, **1994**, *116*, 6437-6438; Birkett, M.A.; Knight, D.W.; Mitchell, M.B. *Synlett*, **1994**, 253-254.
2. (a) Hoffmann, R.W. "*Dehydrobenzene and Cycloalkynes*", Academic Press, New York, **1967**; (b) Gilchrist, T.L. in "*Supplement C, The Chemistry of Triple-Bonded Functional Groups, Part 1* ", Eds. Patai, S; Rappoport, Z. Wiley, Chichester, **1983**, pp 383-419; (c) Reinecke, M.G. in "*Reactive Intermediates, Part 2* ", Ed. Abramovitch, R.A. Plenum, New York, **1982**, pp 367-526.
3. (a) Hantzsch, A.; Davidson, W.B. *Chem. Ber.*, **1896**, *29*, 1522-1536; (b) Stiles, M.; Miller, R.G. *J. Am. Chem. Soc.*, **1960**, *82*, 3802; (c) Stiles, M.; Miller, R.G.; Burckhardt, U. *J. Am. Chem. Soc.*, **1963**, *85*, 1792-1797; (d) Logullo, F.M.; Seitz, A.H.; Friedman, L. *Org. Synth.*, **1968**, *48*, 12-17; *Org. Synth., Coll. Vol. V*, **1973**, 54-59; (e) Friedman, L.; Logullo, F.M. *J. Am. Chem. Soc.*, **1963**, *85*, 1549; (f) Friedman, L.; Logullo, F.M. *J. Org. Chem.*, **1969**, *34*, 3089-3092; (g) Cava, M.P.; Mitchell, M.J. "*Selected Experiments in Organic Chemistry*", W.A. Benjamin, New York, **1966**, pp 92-94; (h) Roberts, R.M.; Gilbert,J.C.; Rodewald, L.B.; Wingrove, "*An Introduction to Modern Experimental Organic Chemistry*", Holt, Rinehart and Winston, New York, **1969**, pp 196-201; (i) Barton, T.J.; Nelsen, A.J.; Clardy, J. *J. Org. Chem.*, **1972**, *37*, 895-901; (j) Ghisalberti, E.L.;

Jefferies, P.R.; Mori, T.A.; Skelton, B.W.; White, A.H.; Whiteside, N.J. *J. Chem. Research (S)*, **1993**, 474-475.

4. Heaney, H. *Top. Curr. Chem.*, **1970**, *16*, 35-74.
5. (a) Heaney, H,; Jablonski, J.M. *Tetrahedron Lett.* **1966**, 4529-4531; (b) *J. Chem. Soc. (C)*, **1968**, 1895-1898.
6. Heaney, H.; Mason, K.G.; Sketchley, J.M. *J. Chem. Soc. (C)*, **1971**, 567-572.
7. Berry, D.J.; Wakefield, B.J. *J. Chem. Soc. (C)*, **1969**, 2342-2346.
8. Elks, J.; Hey, D.H. *J. Chem. Soc.*, **1943**, 441-445.
9. (a) Gompper, R.; Kutter, E.; Seybold, G. *Chem. Ber.*, **1968**, *101*, 2340-2350; (b) Nakayama, J.; Simamura, O.; Yoshida, M. *J. Chem. Soc., Chem. Commun.*, **1970**, 1222; (c) Moody, C.J. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2505-2508; (d) Jackson, P.M.; Moody, C.J. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2156-2158; (e) Jackson, P.M.; Moody, C.J. *Tetrahedron*, **1992**, *48*, 7447-7466; (e) Andrews, J.F.P.; Jackson, P.M.; Moody, C.J. *Tetrahedron*, **1993**, *49*, 7353-7372.
10. Heaney, H.; Jablonski, J.M.; McCarty, C.T. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2903-2910.
11. Buxton, P.C.; Fensome, M.; Heaney, H.; Mason, K.G. *Tetrahedron*, **1995**, *51*, in press.
12. Chiusoli, G.P.; Venturello, C. *J. Chem. Soc., Chem. Commun.*, **1969**, 771.
13. Dittmer, D.C.; Whitman, E.S. *J. Org. Chem.*, **1969**, *34*, 2004-2006.
14. Okuma, K.; Kojimo, K.; Kaneko, I.; Tsujimoto, Y.; Ohta, H.; Yokomori, Y. *J. Chem. Soc., Perkin Trans. 1*, **1994**, 2152-2159.
15. Beringer, F.M.; Huang, S.J. *J. Org. Chem.*, **1964**, *29*, 445-448; Himishima, Y.; Sonoda, T.; Kobayashi, H. *Chemistry Lett.*, **1983**, 1211-1214; Shankaran, K.; Snieckus, V. *Tetrahedron Lett.*, **1984**, *27*, 2827-2830; Del Mazza, D.; Reinecke, M.G. *J. Org. Chem.*, **1988**, *53*, 5799-5806; Luis, S.V.; Gavina, F.; Ferrer, P.; Safont, V.S.; Torres, M.C.; Burguete, M.I. *Tetrahedron*, **1989**,*45*, 6281-6296; Ballard, H.H. *Tetrahedron Lett.*, **1989**, *30*, 2345-2348; Luis, S.V.; Ferrer, P.; Burguete, M.I. *J. Org. Chem.*, **1990**, *55*, 3808-3812; Matsumoto, T.; Hosoya, T.; Katsuki, M.; Suzuki, K. *Tetrahedron Lett.*, **1991**, *32*, 6735-6736; Wickham, P.P.; Hazen, K.H.; Guo, H.; Jones, G.; Reuter, K.H.; Scott, W.J. *J. Org. Chem.*, **1991**, *56*, 2045-2050.
16. (a) Gribble, G.W.; Easton, N.R. jun.; Eaton, J.T. *Tetrahedron Lett.*, **1970**, 1075-1078; (b) Heaney, H.; Ley, S.V. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 2698-2701; (c) Gribble, G.W.; Allen, R.W.; LeHoullier, C.S.; Eaton, J.T.; Easton, N.R. jun.; Slayton, R.I.; Sibi, M.P. *J. Org. Chem.*, **1981**, *46*, 1025-1026.
17. Buxton, P.C.; Hales, N.J.; Hankinson, B.; Heaney, H.; Ley, S.V.; Sharma, R.P. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 2681-2687.
18. Heller, G. *Chem. Ber.*, **1910**, *43*, 1907-1915.
19. Atkinson, E.R.; Holm-Hansen, D.; Nevers, A.D.; Marino, S.A. *J. Am. Chem. Soc.*, **1943**, *65*, 476-477.
20. Howe, R.J. *J. Chem. Soc. (C)*, **1966**, 478-480.
21. Bures, E.; Havlínová, B. *C. csl. Lékarn.*, **1929**, *9*, 129-134; Chem. Abs., **1930**, *24*, 2998; Beilstein's "*Handbuch der Organischen Chemie*" [E II, 182].
22. Tust, P. *Chem. Ber.*, **1887**, *20*, 2439-2442; Nordlander, B.W.; Cass, W.E. *J. Am. Chem. Soc.*, **1947**, *69*, 2679-2682.

(*Received in UK* 13 *January* 1995; *revised* 31 *January* 1995; *accepted* 3 *February* 1995)