Action of some bases on the tropylium cation

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The tropylium cation has been treated with the hindered bases triphenylmethyl sodium, 2,6-dimethoxyphenyl lithium, and 2,4,6-tri-*t*-butylphenyl lithium to give substituted cycloheptatrienes. Where possible its reaction with tertiary amines follows Reaction Scheme 1 to give immonium salts which can be hydrolyzed to tropylated aldehydes and ketones. Its reaction with trimethylamine gives the quaternary ammonium salt which on exposure to the atmosphere is decomposed to trimethylammonium fluoborate and a mixture of tropone and ditropyl ether.

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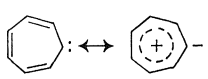
Introduction

This study arose in attempts to deprotonate the tropylium cation with the formation of the cycloheptatrienyl carbene **1**. Two reports of the generation of this species by photochemical and thermal decomposition of the sodium salt of tropone *p*-toluene sulfonylhydrazone have appeared (1).

Cycloheptatrienylidene should be relatively stable among carbenes, for the same reasons as the tropylium cation is among carbonium ions. A number of such dipolar or nucleophilic carbenes have been generated in heterocyclic systems. Wanzlick has demonstrated, *inter alia*, the formation of the dimer **4** by reaction of benzthiazolium halides **2** with triethylamine in polar solvents (2). This reaction must proceed either by dimerization of the carbene **3** formed by deprotonation, or by its attack on a benzthiazolium cation followed by deprotonation of the resulting intermediate. The biological functions of thiamine have been shown to depend on the formation of a similar intermediate (3). It should be noted in passing that species of type **3** are better referred to as heterocyclic ylids in recognition of that major canonical form in which all atoms have formal electron octets. All the canonical forms of **1** have one atom with an electron sextet and hence the term carbene would seem appropriate in this case.

Olofson and co-workers have studied the rates of deprotonation of a wide range of five-membered heterocyclic 'olium ions (4). They have found that, aside from the positive charge, deprotonation is accelerated by an increasing number of electronegative atoms in the ring, and markedly by a sulfur atom adjacent to the carbon undergoing deprotonation. This latter is explained in terms of d–σ overlap in the resulting ylid. The tropylium cation lacking these features should therefore undergo deprotonation much more slowly than say the N,N^1-dimethylimidazolium ion ($t_{1/2}$ = 4.5 min for H—D exchange at pD8–9) (4). When it is also considered that the tropylium cation reacts very rapidly with all but the weakest bases, e.g. chloride ion, to form stable substituted cycloheptatrienes it would seem improbable that it can be deprotonated by ordinary means.

In the light of this our approach has been twofold. Firstly we have examined the action of strong bases in which the basic center is sterically hindered, in the hope that preferred attack on a ring proton rather than addition to a less accessible ring carbon atom might occur. In a similar vein we reasoned that reaction with a hindered



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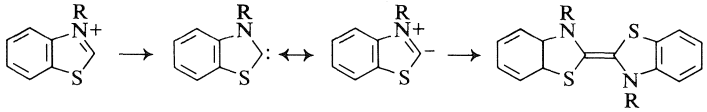
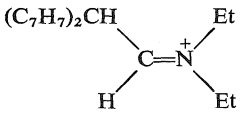


2 **3** **4**



5

$(C_7H_7)_2CH\,CHO$

6

tertiary amine might result in direct deprotonation, or in the formation of an intermediate quaternary ammonium salt which might under certain conditions be unstable relative to the carbene and the protonated amine.

Results

Treatment of tropylium fluoborate with three increasingly hindered strong bases, triphenylmethyl sodium, 2,6-dimethoxyphenyl lithium, and 2,4,6-tri-*t*-butylphenyl lithium gave no evidence of deprotonation. The only isolated products were the corresponding substituted cycloheptatrienes in moderate yield. These were identified spectroscopically and by analysis. Addition of triethylamine to a solution of tropylium fluoborate in acetonitrile resulted in a rapid, mildly exothermic reaction. Removal of the solvent gave an oil from which there was obtained a fluoborate salt, $C_{20}H_{26}NBF_4$. The nuclear magnetic resonance (n.m.r.) spectrum of this salt, with appropriate decoupling studies, showed the presence of two tropyl groups (tropyl will be used to refer to the 1,3,5-cycloheptatrien-7-yl group), two chemically different deshielded ethyl groups, and a single low field vinylic proton coupled to a single aliphatic C—H which in turn was coupled to the C-7 protons of the tropyl groups. These findings are adequately met by the structure **5**. Confirmation of this structure came from hydrolysis either of the isolated salt or of the original reaction mixture. This resulted in a neutral substance, $C_{16}H_{16}O$, whose properties indicated it to be 2,2-ditropylacetaldehyde **6**. The formation of **5** must involve an oxidation step. The tropylium cation is well known to abstract hydride ion from suitable substrates (5). That this is operative here was demonstrated by the presence of cycloheptatriene in the reaction mixture when examined by gas–liquid chromatography.

We conclude that the tropylium cation abstracts a hydride ion from triethylamine to give the immonium salt **7**. This is then deprotonated by triethylamine to give the enamine **8** which then adds to a tropylium cation to generate a second immonium salt **9**. A further cycle of deprotonation and addition to the tropylium cation then gives the observed product. This is depicted in Reaction Scheme 1. Similar results were obtained by the use of the hindered ethyldiisopropylamine. From the reaction mixture the salt **10** was isolated. The salt **11** could not be isolated but was certainly present as hydrolysis of the reaction mixture gave two products which were separated chromatographically and found to be 2,2-ditropylacetaldehyde and 1,3-ditropyl-2-propanone, **12**.

$$C_7H_7^+ + Et_3N \rightleftharpoons C_7H_8 + CH_3CH{=}\overset{+}{N}Et_2$$

7

$$CH_3CH{=}\overset{+}{N}Et_2 + Et_3N \rightleftharpoons CH_2{=}CH{-}NEt_2 + Et_3\overset{+}{N}H$$

8

$$C_7H_7^+ + CH_2{=}CH{-}NEt_2 \rightleftharpoons C_7H_7CH_2CH{=}\overset{+}{N}Et_2$$

9

$$C_7H_7CH_2CH{=}\overset{+}{N}Et_2 + Et_3N \rightleftharpoons C_7H_7CH{=}CHNEt_2 + Et_3\overset{+}{N}H$$

$$C_7H_7CH{=}CHNEt_2 + C_7\overset{+}{H}_7 \rightleftharpoons (C_7H_7)_2CHCH{=}\overset{+}{N}Et_2$$

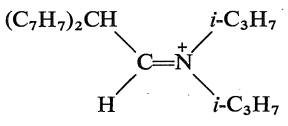
$$\text{Net } 3C_7H_7^+ + 3Et_3N \rightarrow (C_7H_7)_2CHCH{=}\overset{+}{N}Et_2 + C_7H_8 + 2Et_3\overset{+}{N}H$$

REACTION SCHEME 1

Excellent analogy for these processes exists in the reaction of tertiary amines with the triphenylmethyl carbonium ion. Damico and Broaddus (6) have shown that dodecyldimethylamine reacts with this ion to give triphenylmethane and the amine hydrochloride as the isolated products in good yield. These findings were interpreted in terms of repeated cycles of hydride abstraction from the base, and deprotonation of the immonium salt to an enamine, with the enamine then acting as substrate for the abstraction of a second hydride ion. The net result would be the formation of the above mentioned products along with a relatively small amount of polyenamines. Depending on the extent to which the first step in Reaction Scheme 1 takes place, one might expect exclusively cycloheptatriene or any of mono-, di-, or tritropyl-acetaldehyde after hydrolysis of the triethylamine reaction. With ethyldiisopropylamine the number of possible products is even greater. Careful thin-layer chromatographic examination of the products of

hydrolysis of these reaction mixtures has revealed only ditropylacetaldehyde in the case of triethylamine, and that plus the symmetrical ditropylacetone in the case of ethyldiisopropylamine. This result is independent of the way in which the reaction between base and tropylium cation is conducted. Slow addition over several hours of the tropylium cation to triethylamine, or the reverse, followed by the hydrolysis gave in comparable yields the product already obtained and no other.

Since all of the steps in Reaction Scheme 1 are presumably reversible it is probable that the observed products are derived from the most stable immonium salts. That steric effects are of importance is inferred from the formation of 1,3-ditropyl-2-propanone as against the 1,1-derivative and from the following. When the tropylium cation was allowed to react with tri-*n*-propylamine under identical conditions, there were obtained from the hydrolysis two products in the ratio of 1:15. The minor product proved to be 2,2-ditropylpropionaldehyde **13** and the major, the corresponding monotropyl derivative **14**. We ascribe this to the destabilizing effect of a quaternary carbon *cis* to the propyl group in the intermediate **15**.



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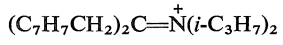

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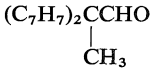

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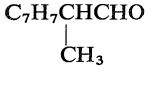

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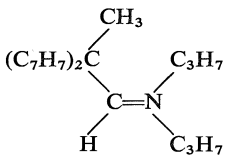

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We have also investigated the action of trimethylamine since this cannot be converted to an enamine. This resulted only in formation of the quaternary ammonium salt. On the basis of the n.m.r. spectrum of the crude product, no compounds derived by hydride transfer were formed. The n.m.r. spectrum of the salt in deuteriodichloromethane was of interest in that it showed a sharp singlet at τ 7.12 for *N*-methyl protons and a slightly broadened singlet (half-width ca. 3 c.p.s.) for the seven protons of the ring at τ 3.75. In this solvent there must be an equilibrium between the quaternary salt and tropylium fluoborate – trimethylamine which makes the ring protons equivalent. The position of this absorption at considerably higher field than occurs for tropylium fluoborate in acetonitrile (τ 0.45) is in accord with this. This salt is stable in solution under nitrogen or dry air. Heating a sample under high vacuum to 150° resulted in decomposition without the formation of any volatile product. On exposure to the atmosphere the salt decomposed to trimethylammonium fluoborate and a mixture of tropone and ditropyl ether. We interpret this to be reaction with atmospheric moisture. It is reasonable that in the presence of water vapor some hydrolysis of the salt to ditropyl ether should occur. It is already known (7) that ditropyl ether disproportionates to tropone and cycloheptatriene in the presence of the tropylium cation.

Experimental

General

Melting points were taken on a Köfler melting point apparatus and are uncorrected. Analyses were performed by the Microanalytical Laboratory of this department.

7-Triphenylmethyl-1,3,5-cycloheptatriene

Triphenylmethyl sodium (8) (25 ml of a standard ethereal solution) was added to a stirred suspension of tropylium fluoborate (9) (0.353 g; 1 equivalent) in diethylene glycol dimethyl ether (25 ml) under nitrogen. The red color of the anion disappeared within a few minutes. The reaction mixture was poured into water after 10 min and the product isolated by extraction into pentane. It was chromatographed on Grade I alumina. Elution with 1:1 benzene–heptane gave triphenylmethane (50 mg) and 7-triphenylmethyl-1,3,5-cycloheptatriene (470 mg; 71%). The analytical sample recrystallized from dichloromethane–methanol and had m.p. 137–140°.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.35; H, 6.44.

Nuclear magnetic resonance spectrum ($CDCl_3$): τ 2.82 (15H, singlet), τ 3.15, 3.85, 4.73 (3 × 2H, multiplets), τ 7.07 (1H, triplet) assigned to the phenyl groups, the three pairs of vinylic protons and the C-7 proton of the cycloheptatriene ring respectively.

7-(2,6-Dimethoxyphenyl)-1,3,5-cycloheptatriene

Solid tropylium fluoborate (1.88 g) was added slowly in batches to a stirred suspension of 2,6-dimethoxyphenyl

lithium (1.55 g) in 50 ml of diethyl ether under nitrogen. After complete addition the mixture was stirred for a further 10 min, filtered, washed with water, dried, and the solvent removed. The resulting oil on crystallization from methanol gave 7-(2,6-dimethoxyphenyl)-1,3,5-cycloheptatriene (1.57 g; 65%). The analytical sample, recrystallized as plates from methanol, had m.p. 91–92°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.89; H, 6.94.

Nuclear magnetic resonance spectrum ($CDCl_3$): τ 2.77 (1H, multiplet), τ 3.36 (4H, multiplet), τ 3.82 (2H, multiplet), τ 4.59 (2H, multiplet), τ 6.23 (6H, singlet), τ 6.48 (1H, triplet).

7-(2,4,6-Tri-t-butylphenyl)-1,3,5-cycloheptatriene

Butyl lithium (2.3*M*, 0.72 ml) was added to a stirred solution of 2,4,6-tri-*t*-butylbromobenzene (10) (0.540 g) in ether (25 ml). The mixture was refluxed gently for 1 h, cooled, and solid tropylium fluoborate (0.355 g; 1.2 molar equivalents) added. After being stirred for a further 1 h the reaction mixture was filtered, and the filtrate washed with water, and dried. The crude material was filtered through a column of silica gel (50 g) in benzene, and the resulting product crystallized from chloroform–ethanol to give 7-(2,4,6-tri-*t*-butylphenyl)-1,3,5-cycloheptatriene (352 mg; 63%). The analytical sample had m.p. 150°.

Anal. Calcd. for $C_{25}H_{36}$: C, 89.22; H, 10.78. Found: C, 89.08; H, 10.82.

Nuclear magnetic resonance spectrum ($CDCl_3$): τ 2.58 (2H, singlet), τ 3.80 (4H, multiplet), τ 5.88 (2H, multiplet), τ 6.78 (1H, multiplet), τ 8.55 (18H, singlet), τ 8.68 (9H, singlet).

N,N-Diethyl-2,2-ditropylacetaldimine Fluoborate (5)

A stirred solution of tropylium fluoborate (5.16 g) in dry acetonitrile (50 ml) was treated with triethylamine (4.05 ml). A rapid mildly exothermic reaction ensued. The mixture was allowed to stand 2 h, and then evaporated *in vacuo* to a gum. This was taken up in dichloromethane, washed with water, to remove triethylammonium fluoborate, and dried. Removal of the solvent left an oil which was crystallized from dichloromethane – ethyl acetate to give the imine fluoborate salt (2.56 g; 72%). The analytical sample, m.p. 96–97°, formed prisms from dichloromethane – ethyl acetate.

Anal. Calcd. for $C_{20}H_{26}NBF_4$: C, 65.42; H, 7.14; N, 3.90. Found: C, 65.13; H, 7.00; N, 3.94.

Nuclear magnetic resonance spectrum ($CDCl_3$): (*1*) τ 1.82 (1H, doublet, J = 11 c.p.s.), (*2*) τ 3.40, 3.70, 4.65 (3 × 4H, multiplets), (*3*) τ 6.07, 6.35 (2 × 2H, quartets, J = 7 c.p.s.), (*4*) τ 6.69 (2H, multiplet), (*5*) τ 7.03 (1H, multiplet), (*6*) τ 8.56, 8.67 (2× 3H, triplets, J = 7 c.p.s.). Decoupling indicated that proton (*1*), assigned to the aldimine CH, is coupled to proton (*5*), the aliphatic CH, which in turn is coupled to protons (*4*), the C-7 protons of the cycloheptatriene rings, with J = 8 c.p.s. Protons (*2*) were assigned to the cycloheptatriene rings and (*3*) and (*6*) to the methylenes and methyls of the *N*-ethyl groups respectively.

N,N-Diisopropyl-2,2-ditropylacetaldimine Fluoborate (10)

This was prepared by the above process in 26% yield. No other product could be isolated from the mother liquors of the crystallization. The analytical sample from dichloromethane – ethyl acetate had m.p. 156–157°.

Anal. Calcd. for $C_{22}H_{30}NBF_4$: C, 66.83; H, 7.65; N, 3.54. Found: C, 67.07; H, 7.79; N, 3.55.

Nuclear magnetic resonance spectrum ($CDCl_3$): τ 1.53 (1H, doublet, J = 10 c.p.s.), τ 3.45, 3.75, 4.62 (3 × 4H, multiplets), τ 5.75 (2H, multiplet), τ 6.65 (3H, multiplet), τ 8.47, 8.55 (2 × 6H, doublets, J = 7 c.p.s.).

Ditropylacetaldehyde (6)

A solution of tropylium fluoborate (12 g) in acetonitrile (120 ml) was treated with triethylamine (11.4 ml). After 2 h, water (60 ml) was added and the solution left for ca. 18 h. It was then poured into water (600 ml), the product isolated by extraction into ether, and distilled to give ditropylacetaldehyde (3.5 g, 66%), b.p. 112–113° at 0.01 mm pressure.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.54; H, 7.33.

Infrared spectrum: ν_{max} (film) 1725 cm^{-1}. Nuclear magnetic resonance spectrum ($CDCl_3$): τ 0.1 (1H, doublet, J = 3.5 c.p.s.), τ 3.37, 3.80, 4.75 (3 × 4H, multiplets), τ 7.03 (1H, triplet of doublets, J = 3.5 and 7.5 c.p.s.), τ 7.72 (2H, multiplet). The last two absorptions are assigned to the proton α to the carbonyl and the C-7 protons of the rings respectively.

1,3-Ditropyl-2-propanone (12)

By the same procedure as for the above aldehyde tropylium fluoborate (8 g) in acetonitrile (80 ml) was treated with ethyldiisopropylamine (7.85 ml). After 2 h, water (40 ml) was added to effect hydrolysis. The isolated crude product was chromatographed on silica gel (500 g). Elution with benzene gave firstly ditropylacetaldehyde (2.04 g) and then 1,3-ditropyl-2-propanone (1.80 g). The analytical sample of the ketone, m.p. 88–89°, was obtained by sublimation at 130–140°/0.05 mm.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.39; H, 7.56.

Infrared spectrum: ν_{max} (Nujol) 1712 cm^{-1}. Nuclear magnetic resonance spectrum ($CDCl_3$): τ 3.39, 3.84, 4.86 (3 × 4H, multiplets), τ 7.27 (4H, doublet, J = 8 c.p.s.) τ 7.69 (2H, multiplet).

2-Tropylpropionaldehyde (14) and 2,2-Ditropylpropionaldehyde (13)

Tropylium fluoborate (2.1 g) in acetonitrile (20 ml) was treated with tri-*n*-propylamine (2.25 ml). The mixture was left 2 h, treated with water (10 ml), and left for a further 18 h. The crude product, isolated by dilution of the reaction mixture with water and extraction into ether, was chromatographed on silica gel (50 g). Elution with benzene gave firstly 2,2-ditropylpropionaldehyde (50 mg) followed by the more polar monotropyl-propionaldehyde (750 mg). An analytical sample of the former compound was prepared by sublimation at 130°/0.05 mm. It had m.p. 113–114.5°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.80; H, 7.79.

Infrared spectrum: ν_{max} (film) 1725 cm^{-1}. Nuclear magnetic resonance spectrum ($CDCl_3$): τ 0.15 (1H, singlet), τ 3.25, 3.75, 4.75 (3 × 4H, multiplets), τ 7.88 (2H, broad triplet), τ 8.59 (3H, singlet). An analytical sample of the latter compound was obtained by evaporative distillation at 80–85°/0.05 mm.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.94; H, 8.31.

Infrared spectrum: ν_{max} (film) 1725 cm^{-1}. Nuclear magnetic resonance spectrum ($CDCl_3$): τ 0.30 (1H, doublet, $J = 2$ c.p.s.), τ 3.33, 3.75, 4.75 (3 × 2H, multiplets), τ 7.3 (1H, multiplet), τ 8.05 (1H, multiplet), τ 8.82 (3H, doublet, $J = 7$ c.p.s.).

Tropyltrimethylammonium Fluoborate

A solution of tropylium fluoborate (4.12 g) in acetonitrile (40 ml) under nitrogen was cooled in an acetone–CO_2 bath to −20°. Trimethylamine (2.52 *M*) in acetonitrile (9.5 ml) was added and the solution was allowed to rise to room temperature. Removal of the solvent *in vacuo* gave an oil which crystallized. It was recrystallized from dichloromethane – ethyl acetate under nitrogen to give tropyltrimethylammonium fluoborate, m.p. 73–78°. A satisfactory analysis was not obtained.

Nuclear magnetic resonance spectrum (CD_2Cl_2): τ 3.75 (7H, broad singlet), τ 7.12 (9H, singlet).

Acknowledgments

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