

## Synthesis of the 8-Cycloheptatrienylheptafulvenyl Cation

By Ian Fleming,\*† Department of Chemistry, McGill University, Montreal, Quebec, Canada

The chlorocarbonoid reagent prepared from methylene dichloride and sodium bistrimethylsilylamide adds, at least in part, to the central double bond of heptafulvalene, and the intermediate chlorocyclopropane ionises to give the title cation (3a). Chloro(phenyl)carbene and dichlorocarbene behave similarly to give the 8-phenyl and 8-chloro cations. The title cation is one of the most stable hydrocarbon cations yet prepared.

KITAHARA and his co-workers<sup>1</sup> have synthesised the cation (3; R = CN) ( $\lambda_{\text{max}}$  592 nm) in three stages from cyanoheptafulvene. I now report a short and moderately versatile synthesis of other cations of this highly stabilised type, including the parent cation (3a).

Heptafulvalene [bi(cycloheptatrienylydene)] (1)<sup>2</sup> in pentane reacted with the chlorocarbonoid reagent prepared<sup>3</sup> from methylene dichloride and sodium bistrimethylsilylamide at  $-10^\circ$ . The solution, initially a deep reddish brown, rapidly became paler as the methylene dichloride was added. It was then washed with water to remove the excess of base, and shaken with

aqueous trifluoroacetic acid. The aqueous layer was then a deep blue solution ( $\lambda_{\text{max}}$  600 nm) of the cation (3a). The same sequence can be carried out with chloro(phenyl)carbene<sup>4</sup> and with dichlorocarbene,<sup>5</sup> giving solutions of the blue cations (3b) and (3c) ( $\lambda_{\text{max}}$  660 and 650 nm, respectively). The n.m.r. spectra of these cations can be recorded in the corresponding deuteriated solvent: (3a)  $\tau$  1.8, 2.34, and 2.85 (each 4H, each a broad multiplet; evidently H-8 is exchanged for a deuterium atom, a not unreasonable process in the highly acidic medium); (3b)  $\tau$  2.2 (2H, d,  $J$  9 Hz, *ortho*-protons),

<sup>2</sup> W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, 1969, **91**, 6391.

<sup>3</sup> B. Martel and E. Aly, *J. Organometallic Chem.*, 1971, **29**, 61.

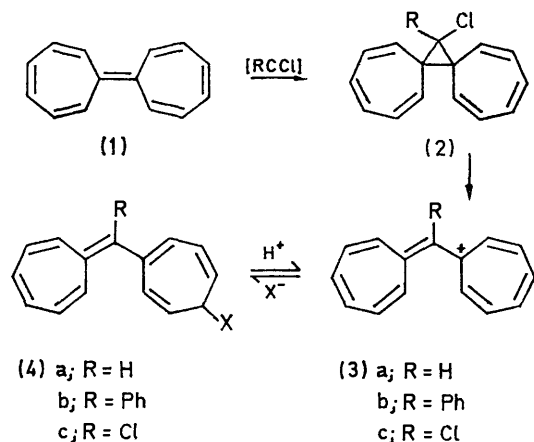
<sup>4</sup> S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.*, 1959, **81**, 2579.

<sup>5</sup> W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 1954, **76**, 6162.

† Present address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

<sup>1</sup> T. Otomo, M. Oda, and Y. Kitahara, *Chem. Comm.*, 1971, 114; C. Kabuto, M. Oda, and Y. Kitahara, *Tetrahedron Letters*, 1972, 4851.

2.55 (4H, broad m), and 2.84 with shoulders at 2.96 and 3.08 (total 11H, broad m); (3c)  $\tau$  1.8 (4H, m) and 2.4 (8H, m). The spectra are not definitive for the structures shown any more than the spectrum obtained by Kitahara is definitive, although they do show that a single



compound has been extracted into the aqueous phase. The similarity of these spectra to his, taken with the different method of synthesis, and not least the fact that his cation was also blue, make the structures shown reasonable ones.

The three carbenes used in this work are well known<sup>6</sup> to be electrophilic, and they are therefore likely to attack the very nucleophilic, central double bond of heptafulvalene in preference to one of the peripheral double bonds. Apparently, the first-formed intermediates (2) open with great ease to give the cations (3). There is some evidence that this takes place in the cold pentane solution, and that the cation is rapidly captured by the base present at this stage, presumably at the same site as in Kitahara's compound, to give compounds of the general type (4). In acidic solution this process is reversed, and the cation is then extracted into the water. The evidence for this sequence is best in the case of the dichlorocarbene reaction, as befits the most electrophilic carbene: the u.v. spectrum ( $\lambda_{\max}$  350 nm) of the reaction mixture is similar to that of Kitahara's compound (4; R = CN, X = OMe) ( $\lambda_{\max}$  368 nm) and is not appropriate for the presumed first-formed product (2; R = Cl). The u.v. spectrum of the reaction mixture in the other two cases shows end absorption reaching to 400 nm, but there is no well defined maximum in this region. A second piece of evidence comes from an attempt to prepare the parent cation using the more

usual monochlorocarbene reagent, obtained from methylene dichloride with butyl-lithium. The colour of the heptafulvalene was again cleanly discharged, but no blue solutions were obtained with aqueous acid. This is consistent with the formation of the cation (3a) in the still basic solution; but this time the cation will be captured by a carbon nucleophile, namely the butyl group, which will not leave again under the influence of acid. This observation illustrates one limitation of this route to the cations (3): the base used to generate the carbene must be a heteroatom base. A second limitation is that the isolation of crystalline compounds is impracticable. Thus evaporation of the blue solutions gave a smear (blue with the parent cation but yellow with the other two) which could be redissolved in dilute acid; but the intensity of the blue colour was now much reduced. Presumably the increase in the concentration of the covalently bonded compounds (4) in the smear allows their polymerisation. Kitahara's compound (4; R = CN, X = OMe) is much less liable to polymerise, because the cyano-group stabilises the heptafulvalene element present in these compounds, and consequently he was able to isolate a crystalline salt of the cation.

Nevertheless, with clean solutions of the cations readily available, it was possible to test Kitahara's prediction<sup>1</sup> that the parent cation would be more stable than the cyano cation. It is, but probably for steric more than electronic reasons, no doubt because the substituent is situated on the only carbon atom which does not carry a substantial proportion of the positive charge. Thus the bulky (but electronically less destabilising\*) chloro-group gives a cation (3c) ( $pK_{R^+}$  1.85) which is a lot less stable than the cyano-cation (3; R = CN) ( $pK_{R^+}$  3.44).<sup>1</sup> The phenyl group, which is again bulkier than a cyano-group (but should be electronically much less destabilising), gives a cation (3b) ( $pK_{R^+}$  4.00) only slightly more stable than the cyano-cation.† Only the parent cation, with no electronically unfavourable groups and little resistance to coplanarity, shows the full stability of the system. With a  $pK_{R^+}$  value of 7.10 (6.85 in 50% acetonitrile in water), this cation joins the tripropylcyclopropenium ion<sup>9</sup> ( $pK_{R^+}$  7.2 in 50% acetonitrile in water) and the heptalenium ion<sup>10</sup> ( $pK_{R^+} \geq 7$ , no solvent given) as one of the most stable hydrocarbon cations.

#### EXPERIMENTAL

**8-Cycloheptatrienylheptafulvenyl Cation (3a).**—Heptafulvalene<sup>2</sup> (50 mg; freshly prepared) in dry pentane (6 ml) was cooled to  $-10^\circ$ , sodium bistrimethylsilylamide<sup>3</sup> (1.0 g) was

\*  $\sigma_m^+$  Values should be a guide to the electronic effect of the substituents: for the chloro-group it is 0.399, for the cyano-group, 0.562, and for the phenyl group, 0.109.<sup>7</sup>

† This argument is not dependent on the presumption<sup>8</sup> that substituent effects are more important in the cations (3) than in the covalently bonded compounds (4; X = OH). The covalently bonded compounds should be progressively less stable in the order CN > Cl ~ Ph > H; this order, on its own, does not explain the order of the  $pK_{R^+}$  values.

<sup>6</sup> W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971, pp. 294–302.

<sup>7</sup> H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4980.

<sup>8</sup> D. Bethell and V. Gold, 'Carbonium Ions,' Academic Press, London, 1967, p. 60.

<sup>9</sup> R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, 1962, **84**, 3168.

<sup>10</sup> H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 4657.

added, and the mixture was stirred under dry nitrogen as methylene dichloride (0.1 ml) was added dropwise from a syringe during 15 min. Water (20 ml) was added, the mixture was shaken and rapidly separated, and the organic layer was shaken at 0° with a mixture of trifluoroacetic acid (0.5 ml) and water (0.5 ml). The aqueous layer became very deep blue,  $\lambda_{\text{max}}$  (after considerable dilution in water) 235, 325, and 600 nm. The intensity of the colour was very dependent upon the care with which the various operations were carried out, especially on the length of time taken over the addition of the methylene dichloride. An estimate of  $\epsilon$  values (and/or yield) was not therefore convincing. The n.m.r. spectrum quoted in the text was taken by use of a solution of trifluoroacetic anhydride in deuterium oxide, with a drying ( $\text{MgSO}_4$ ) stage inserted after the washing with water. The strength of this spectrum indicated that at least several mg of the cation were present. The n.m.r. spectrum also showed the complete but weak spectrum of n-butylamine (identical with that of an authentic sample), which must have come in low yield from the reaction of butyl chloride with sodium bistrimethylsilylamide in the course of the preparation of the latter.<sup>3</sup> The only other signal in the n.m.r. spectrum was that from the protons which have unavoidably contaminated the solvent. This signal could be moved downfield without affecting the rest of the spectrum by adding trifluoroacetic anhydride; this showed that the signal from H-8 had not simply been obscured by the solvent peak.

**8-Chloro- and the 8-Phenyl-8-cycloheptatrienylheptafulvenyl Cations (3c) and (3b).**—The procedure was closely similar to that used for the parent cation, except that potassium t-butoxide was used at 0° and chloroform and benzylidene dichloride respectively were added from the syringe. The reaction sometimes took up to 1 h, as judged by the change of colour from reddish brown to yellow. The 8-chloro-cation had  $\lambda_{\text{max}}$  228, 275, and 650 nm, with a shoulder at 300 nm. It was unstable in 3N-hydrochloric acid: after a few minutes the solution was green, after a few hours yellow ( $\lambda_{\text{max}}$  450 nm), and after a few days colourless, having deposited an intractable, colourless, and probably polymeric precipitate. The 8-phenyl cation had  $\lambda_{\text{max}}$  232 and 660 nm, with shoulders at 270 and 340 nm. The n.m.r. spectra are quoted in the text; the only other signals present were weak ones from t-butyl alcohol and solvent protons.

**Stability of the Cations.**—The parent and phenyl cations were not noticeably unstable in acid, as the chloro-cation was (see before). The parent and the phenyl cations decomposed over about a week at room temperature in 0.1N-hydrochloric acid, but little decomposition took place over several weeks at 0°. These two cations, moreover, decomposed at similar rates, implying that decomposition

was not taking place by an electrocyclic transformation involving bond formation between C-1 and C-1'.

Attempts to reduce the cations by hydrogenation or with zinc and hydrochloric acid were successful in that the colour was rapidly discharged. Further hydrogenation followed by work-up gave a visible but involatile product, presumably because initial reduction gave compounds of the type (4; X = H), which polymerised faster than they underwent reduction. This explanation is consistent with the low and slow uptake of hydrogen after the colour had been discharged.

The evaporation experiments described in the text were also carried out with several potentially non-nucleophilic anions present, and in several different ways. Loss of intensity in the regenerated blue solutions was always observed, and there were no crystals evident in the smears obtained.

**$pK_{R^+}$  Measurements.**—These measurements, reported in the text, were made spectroscopically at 25° on solutions in 23% v/v ethanol in water (the solvent used by Kitahara<sup>1</sup>) and, for the parent cation, in 50% acetonitrile in water (the solvent used by Breslow<sup>9</sup>) as well; the wavelength of the maximum in the visible region was used. In each case the titration was begun at low pH and taken to high pH by injecting sodium hydroxide solution into the cell. Back titration with dilute hydrochloric acid restored the blue colour of the parent (3a) and phenyl (3b) cations at lower intensity (about 65% of the original when the whole titration took about 1 h) but the pH values at the midpoint (and hence the  $pK_{R^+}$  values) were the same in each direction for these two cations. The error for these cations is  $\pm 0.05$ . That for the chloro-cation (3c) is a less exact measurement, giving reproducibly a  $pK_{R^+}$  of 1.4 in the first titration and of 1.85 in the back titration, and a greater loss in intensity of the restored colour. Furthermore, the restored colour was green (see before). The latter value is quoted in the text on the grounds that the acid-catalysed decomposition to the yellow compound is taking place at an appreciable rate only at the very end of that titration when the additions of acid take relatively little time. The former value is almost certainly no better than a minimum value: the intensity of the blue colour was dropping at an appreciable rate in the time taken over the first half of the titration curve, when the additions of alkali have to be made cautiously.

I thank Dr. L. Yaffe and his colleagues for the hospitality and help they gave me during my sabbatical leave at McGill. I also thank the Royal Society for a Nuffield Foundation Bursary, and Dr. E. J. Thomas for carrying out an early and encouraging experiment.

[2/2626 Received, 20th November, 1972]