Tetrahedron Letters Vol. 21, pp 2845 - 2848
© Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0715-2845$02.00/0

PERCHLOROTOLANE. A NEW SYNTHESIS AND ITS THERMAL DIMERIZATION

M. Ballester,[+] J. Castañer, J. Riera and O. Armet
Instituto de Química Orgánica Aplicada (C.S.I.C.)
Jorge Girona Salgado, Barcelona 34. Spain.

Summary: A new synthesis of perchlorotolane (perchlorodiphenylacetylene; I) is described. It dimerizes at high temperature to give perchloro-1,2,3-triphenylnaphthalene (III) and perchloro-2,3,8-triphenylbenzofulvene (IV). Under the same conditions the latter yields perchloro-5,10-diphenylidene(2,1-a)indene (V).

On account of their molecules being shielded by the chlorine substituents, and in sharp contrast with their non-chlorinated counterparts, perchloroarylethylenes are extremely inert in processes involving addition reactions. Such reactions are also hindered because the resulting adducts would possess a high internal strain.[1,2a] However, these concepts are not applicable to the perchloromonoarylacetylenes where, according to the space-filling scale atomic models, shielding of the multiple bond might be almost negligible, and the adducts strain-free.[2b]

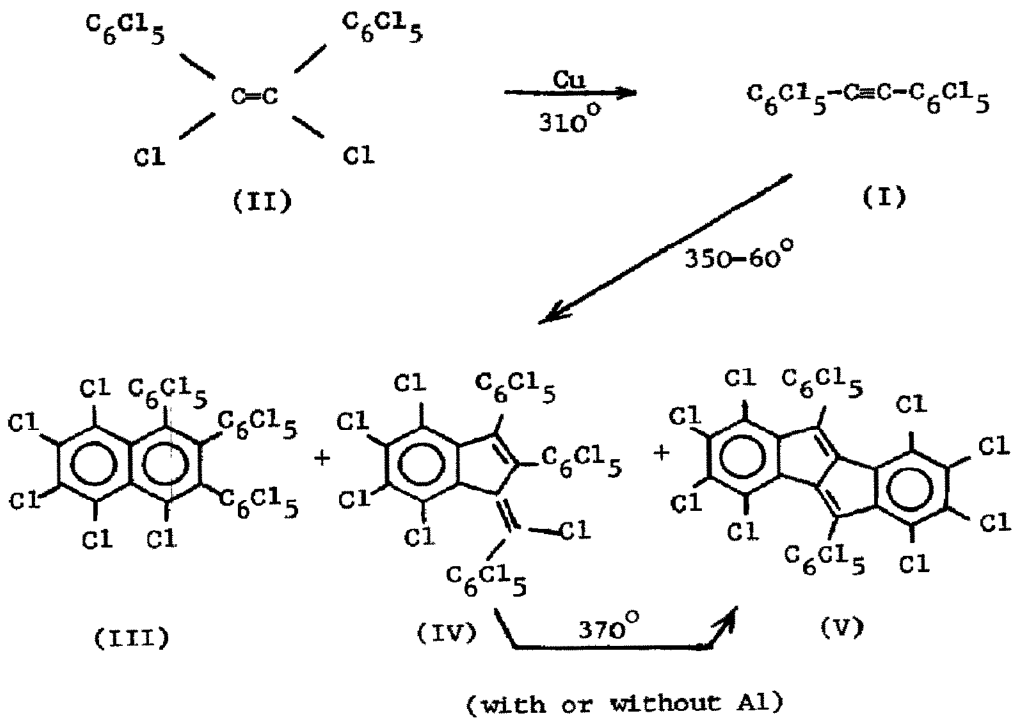
Accordingly, perchlorophenylacetylene is a reactive chlorocarbon performing normally in addition-reaction conditions;[2b-4] for example, it undergoes an easy thermal (~ 110°) oligomerization to give one dimer and two trimers.[2b,3] However this is not necessarily the case of perchlorinated diarylacetylenes were there might be some shielding of the triple bond. Consequently, for the purpose of studying its behaviour, the synthesis of perchlorotolane (I) -a chlorocarbon where the triple bond is shielded by four ortho chlorine atoms- was undertaken.

Cis-perchlorostilbene (II)[5] eliminates chlorine with copper dust at 310° giving (I) (90% yield). (I) had been synthesized previously by a condensation reaction;[6] however, its reported uv molar absorptivities[6] are erroneous by a factor of about forty (λ_{max} ($CHCl_3$) 245, 254, 295 (sh), 303 (sh), 314, 320 (sh) and 335 nm; ε 39,800, 35,800, 21,500, 25,800, 40,200, 31,100 and 39,600). Therefore (I) has been characterized fully by mp, C and Cl analyses, and ir and mass spectra. Its structure has been checked further by photochlorination with Cl_2 to trans-perchlorostilbene[5] (96%).

Chlorocarbon (I) is stable to temperatures up to 320° (1 h). About 350-60°

(2 h) it gives a mixture containing perchloro-1,2,3-triphenylnaphthalene (III (30.0%), white crystals mp 346°, (E)-perchloro-2,3,8-triphenylbenzofulvene (I (10.3%), yellow powder dec. 370° (DSC) and perchloro-5,10-diphenylidene(2,1-a indene (perchloro-5,10-diphenyldibenzo(a,e)pentalene) (V) (23.1%), dark-red crystals infusible up to 330°. Some (I) (9,3%) might be recovered. Compound (III): UV-Vis. λ_{max} ($CHCl_3$) 271, 322 (sh) and 335 nm; ε 54,200, 9960 and 10,6 MS m/s 1036 (M^+, 20 Cl). Compound (IV): UV-Vis. λ_{max} ($CHCl_3$) 275 and 360 nm, 39,300 and 7500. MS m/s 1036 (M^+, 20 Cl). IR (KBr) 1590 cm^{-1}. Compound (V) UV-Vis. λ_{max} (C_6H_{12}) 217, 244, 300, 312, 397, 423, 448 and 480 nm, ε 143,000, 54,100, 59,400, 77,500, 3060, 7900, 16,200 and 19,800. MS m/e 966 (M^+, 18 Cl IR (KBr) 1615 cm^{-1}.

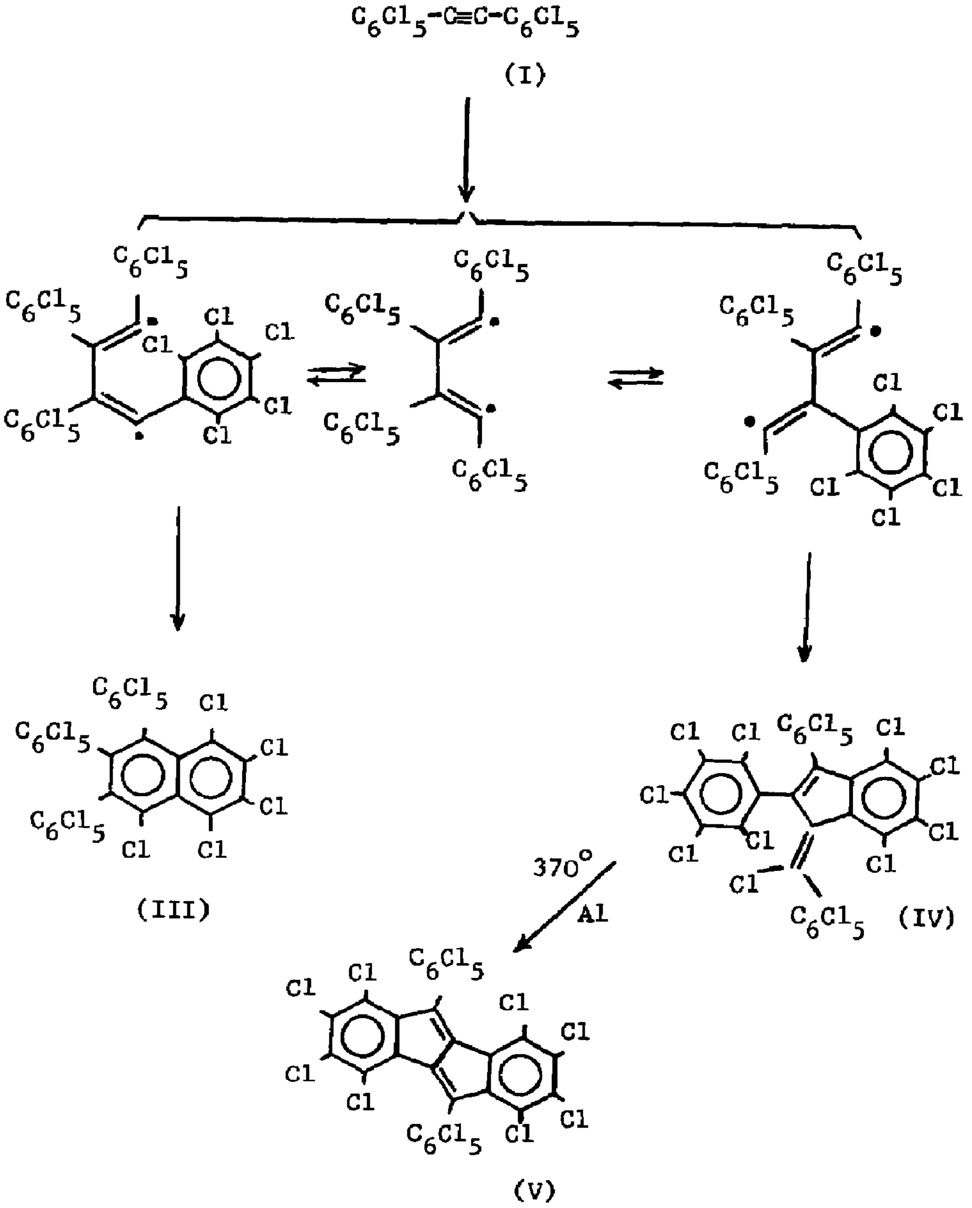
(IV) dechlorinates partly to (V) (16% yield; 60% recovery) when submitted somewhat higher temperatures (370°; 10 min.) This dechlorination can be effe ted in a higher yield (81%) when (IV) is mixed with Al powder (370°; 10 min.)



The structures of chlorocarbons (III) and (V) have been unequivocally established by X ray analysis[7] in collaboration with the authors. In this connection it is mentioned that the uv-vis spectra of (III) and (V) are very similar to those of the perchlorophenylnaphthalenes[8] and the perchloroindene(2,1-a)indene,[9] respectively.

The ir and uv-vis spectra of (IV) are consistent with the structure given. However, the main evidence for the latter originates from its capacity to cyclize to (V). It is also pointed out that the pyrolysis of the tolane hydrocarbon in the presence of $NiBr_2$ yields the hydrocarbon counterpart of (IV).[10]

The formation of dimers (III) and (IV) is interpreted as follows:



A similar mechanism has been suggested for the formation of perchloro-1-phenylnaphthalene from perchlorophenylacetylene.[2b,3] However, in the present reaction both steric shielding and internal cyclization prevent trimer formation (perchlorohexaphenylbenzene). Notice that fulvenes of type (IV), and consequently compounds of type (V), have not been isolated in the thermal oligomerization of perchlorophenylacetylene.[2b,3] This will be accounted for in a forthcoming publication.

REFERENCES

1) M. Ballester, J. Castañer and J. Riera, J. Amer. Chem. Soc., 88, 957 (1966
M. Ballester, J. Riera and C. Badía, Tetrahedron Lett., 1974, 1199;
M. Ballester and J. Castañer, Anales Real Soc. Españ. Fís. Quím., 62B, 397 (1966).

2) M. Ballester and S. Olivella, "Polychloroaromatic compounds", ed. H. Suschitzky, Plenum (1974), a) page 89, b) pages 111-3.

3) I. Tabernero, Doctoral Thesis, University of Barcelona (1976).

4) M. Ballester, J. Castañer, J. Riera, I. Tabernero and C. Cornet, Tetrahedron Lett., 1977, 2353.

5) M. Ballester, C. Molinet and J. Rosa, Anales Real Soc. Españ. Fís. Quím., 55B, 437 (1959).

6) A. E. Jukes, S. S. Dua amd H. Gilman, J. Organometal. Chem., 12, 44 (1968)

7) S. Galí, X. Solans, C. Miravitlles, M. Font-Altaba and O. Armet, Acta Cryst., B34, 1011 (1978); C. Miravitlles, X. Solans, G. Germain and J. P. Declerq, Acta Cryst., B35, 2809 (1979).

8) M. Ballester, J. Castañer, J. Riera and J. Parés, Ann. Quím., in press.

9) A. Roedig, G. Bonse and R. Helm, Chem. Ber., 106, 2825 (1973).

10) J. F. W. McOmie and B. K. Bullimore, Chem. Commun., 4, 63 (1965).

(Received in UK 9 May 1980)