Tetrahedron. Vol 31, pp. 1315 to 1319. Pergamon Press 1975. Printed in Great Britain

AN APPROACH TO THE SYNTHESIS OF ACETYLENE DIETHERS *VIA* TETRACHLOROBENZYNE. METHOXYCARBYNES VERSUS DIMETHOXYACETYLENE[a]

F. SERRATOSA,* P. SOLÁ, L. VILARRASA and J. FONT
Instituto de Química Orgánica de Barcelona, Patronato "Juan de la Cierva", CSIC Barcelona-17, Spain

and

J. RIVERA
Servico Nacional de Espectrometría de Masas. Patronato "Juan de la Cierva", Barcelona-17, Spain

(*Received in the UK* 18 *November* 1974; *Accepted for publication* 16 *December* 1974)

For a number of years acetylene diethers eluded all synthetic approaches, and none was known at the time we started work in the field.

In the meantime, evidence about the formation of dimethoxy- and diethoxy-acetylene as highly reactive intermediates was presented by two independent groups,[1] and later in our Laboratory, the NMR spectrum of dimethoxyacetylene at low temperature was observed for the first time, and the compound was isolated as a stable dicobalt hexacarbonyl complex.[2]

Since the extrusion method has been successfully used in the generation of highly reactive intermediates,[3] and there were good reasons to assume that acetylene diethers ought to be highly reactive compounds, we directed our efforts into this method of generating acetylenes.

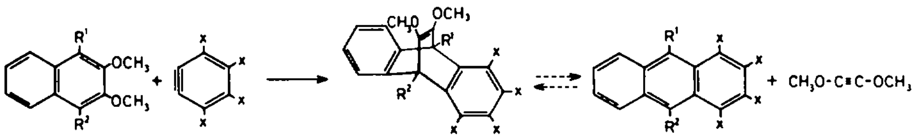
The extrusion method has been used in acetylene chemistry either as a way to protect a triple bond, and make then the pertinent manipulations on the functional groups before extrusion of the same triple bond,[4] or as a method to create a new acetylene by transfer of the triple bond from one reagent to the other.[5]

Benzynes **2** can be regarded as acetylenes[6] and 1,4-cycloaddition to 2,3-dimethoxynaphthalenes **1** should give dibenzobarrelene derivatives of type **3**, which formally are adducts from anthracenes **4** and dimethoxyacetylene **5** (Scheme 1).

Preliminary experiments showed that benzyne itself (**2**; X = H), either generated from o-fluorophenylmagnesium bromide or benzenediazonium-2-carboxylate, does not react with 2,3-dimethoxynaphthalene **1a**. However, the more electrophilic tetrachlorobenzyne (**2**, X = Cl), generated from hexachlorobenzene,[7] gave the corresponding adduct **3a** in 9–12% yield[b].

In order to have different adducts with different substituents at the bridgehead positions (**3**, R^1 and $R^2 \neq H$), to evaluate the facility of the retrodiene reaction, tetrachlorobenzyne was condensed with 1,2,3-trimethoxy- **1b**, 1,2,3,4-tetramethoxy- **1c**, 1-nitro-2,3-dimethoxy- **1d** and 1-nitro-2,3,4-trimethoxynaphthalene **1e**.[8]

1,2,3-Trimethoxynaphthalene **1b** gave the corresponding adduct **3b** in 35% yield. However, 1,2,3,4-tetramethoxynaphthalene **1c** gave two products (together with 35·8% of recovered tetramethoxynaphthalene), one of which was the expected adduct **3c** isolated in 1·3% yield, and the second product, isolated in 7·5% yield, was characterized as the dibenzosemibullvalene adduct **6** by



1 **2** **3** **4** **5**

x = Cl
a. $R^1 = R^2 = H$
b. $R^1 = OCH_3$, $R^2 = H$
c. $R^1 = R^2 = OCH_3$
d. $R^1 = NO_2$, $R^2 = H$
e. $R^1 = NO_2$, $R^2 = OCH_3$

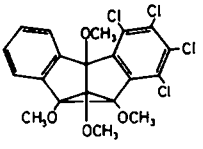
Scheme 1.

---

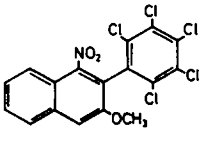
[a] Taken in part from Doctoral Thesis of L. Vilarrasa and P. Solá, University of Barcelona, 1972 and 1974. For preliminary communications see ref 13. Further details will be given on request to the authors.

[b] Attempts to prepare adducts from tetrachlorobenzyne generated via tetrachlorobenzenediazonium-2-carboxylate[7] showed that the intermediate is completely unreactive towards methoxynaphthalenes. On the other hand, tetrafluorobenzyne (**2**, X = F), generated from pentafluorophenylmagnesium chloride, gave about 5% yield of the corresponding adduct **3** (X = F), identified by IR and NMR, but the product was difficult to separate from fluorinated resins.

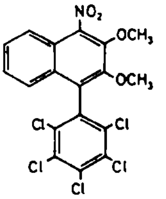
UV, IR, NMR and mass spectrometry, as well as its stability in acid medium, that precludes the presence of enol ethers[c]. On the other hand, 1-nitro-2,3-dimethoxy- **1d** and 1-nitro-2,3,4-trimethoxynaphthalene **1e**[8] failed to give Diels-Alder adducts, the products **7** and **8**, 10% and 2·1% yield, respectively, with the characteristic pattern for five chlorine atoms in the mass spectra, were isolated instead. Obviously, a nucleophilic displacement of the activated methoxy groups by pentachlorophenyl-lithium takes place. The product **8** could have the pentachlorophenyl group either at the ortho or para positions; however, on steric grounds we have formulated it as a para-derivative.



6



7



8

Although *antara, antara* Diels-Alder reactions $({}_\pi4_a + {}_\pi2_a)$ leading to semibullvalene structures are symmetrically allowed processes,[9] in practice they have only been observed in geometrically favorable intramolecular reactions.[d] The formation of the semibullvalene derivative **6** is best rationalized assuming that the addition of tetrachlorobenzyne (**2**, X = Cl) to tetramethoxynaphthalene **1c** takes place in two steps (Scheme 2), i.e. if it is a dipolar addition, as observed in most of the reactions of benzyne intermediates with electron-rich species.[11] The relatively high yield obtained in the reaction with the unsymmetrical trimethoxynaphthalene **1b** favors also a dipolar mechanism.[12]

As reported in the preliminary communications,[13] adducts **3** are sensitive to photooxidation, and no extrusion was observed in photolytic experiments. Further details are given in ref 13b.

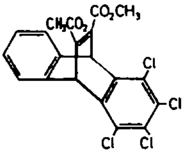
In contrast with the results reported by Sauer[14] with adducts of 9,10-dimethoxyanthracene and electron-poor olefins, adducts **3** are not in equilibrium with their components in polar solvents.

Thermolysis and fragmentation under electron impact

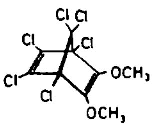
Preliminary thermolytic experiments of adducts **3** showed that they are highly stable compounds and only the dimethoxy derivative **3a** was of some interest in our studies on thermally-generated dimethoxyacetylene, a conclusion that found further support in the mass spectral studies described later.

Heating the adduct **3a** in dimethyl acetylenedicarboxylate solution, b.p. 196°, in a stream of nitrogen and collecting the volatile products in a cold trap, a new adduct **9** was isolated,[e] but no dimethoxyacetylene could be isolated or detected in the trap. Since dimethoxyacetylene should react as the electron-rich component in Diels-Alder reactions, the adduct **3a** was decomposed in hexachlorocyclopentadiene solution; tetrachloroanthracene,[f] was isolated in 75% yield after chromatography, but no adduct **10** was obtained. A Diels-Alder reaction of adduct **3a** with hexachlorocyclopentadiene prior extrusion is not excluded (see Experimental).

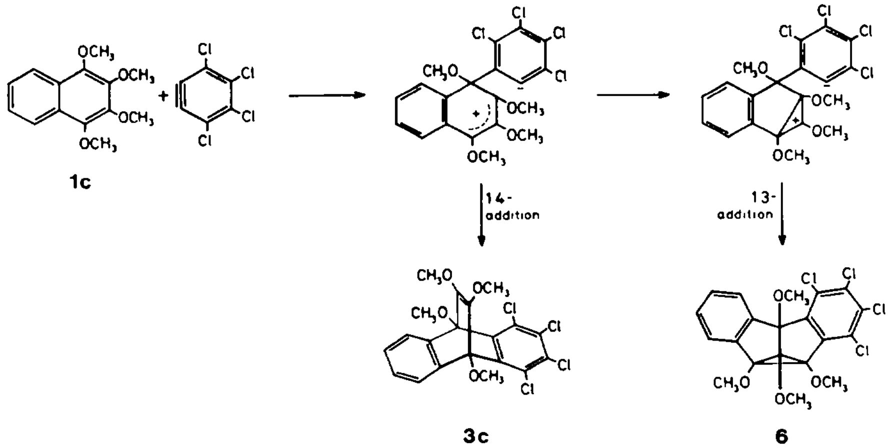
A low-pressure thermolysis was performed on adduct



9



10



Scheme 2.

---

[c] In fact, acid hydrolysis of adduct **3a** give two epimeric methoxyketones, which could be separated by TLC.

[d] The photochemical formation of semibullvalene derivatives either by $({}_\pi4_s + {}_\pi2_s)$ or $({}_\pi4_a + {}_\pi2_a)$ cycloadditions are well known processes (see ref 10).

[e] Identical with an authentic sample prepared by addition of dimethyl acetylenedicarboxylate to tetrachloroanthracene **4a**, as described in the Experimental.

[f] Identified by direct comparison with an authentic sample prepared according to the method outlined in ref 13b.

3a. The technique used was to slowly sublime the compound through a Pyrex tube filled with Fenske helices and heated at 450°, under 0·5 Torr, and trap any volatile product in a cold trap. No condensable product other than tetrachloroanthracene (48–57% yield) was isolated or detected.

Although all the experiments demonstrate that extrusion takes place, no evidence about the exact fate of the "dimethoxyacetylene" fragment was obtained. In order to get some insight into the problem a detailed mass spectral study was undertaken.

The relationship between thermolytic processes and electron-impact fragmentations has been repeatedly noted in the last ten years,[16] the retro-diene reactions observed in the mass spectrometer being the best known examples. Recently, Dougherty[17] has given the theoretical basis for such a correlation and he has shown that one should expect an analogy between electron-impact and thermally-induced retro-diene reactions if a significant metastable peak ($\sim 10^{-4} \times$ daughter ion intensity) accompanies the electron-impact reaction and if it is a high probability reaction. On the other hand, McLafferty[18] has pointed out that "the energetically most favored processes are often not those producing the most abundant fragment ions in ordinary spectra and the metastable spectra offer a superior way of studying these processes".

Introduction of the sample into the mass spectrometer by means of the direct insertion probe and subsequent heating of the sample to 220–250° gave rise to characteristic and reproducible spectra. Depending upon the voltage and the temperature of the ion source, small but significant variations were observed, as shown in Table 1.

The spectrum run at 75° and 70 eV confirmed the structure of adduct **3a**: the molecular ion appears at *m/e* 400 to 408, with the correct isotopic abundance associated with the presence of four chlorine atoms; the base peak corresponds to the loss of mass 43 (*m/e* 357–365) and the next more intense peak to tetrachloroanthracene, TCA (*m/e* 314–322). However, the peaks at 86 and 43 are both very weak. Therefore, the fragmentation takes place in such a way that methoxycarbyne is lost as a neutral fragment to give a very stable dibenzotropilium cation as the more important ion, and conventional mechanism leading to this cation can be easily visualized.

When the 70 eV spectrum was run with the ion source at 250°C, then the peak for methoxycarbyne (Calculated for C_2H_3O: 43·018388. Found: 43·018309) is much more intense, but little variation is observed in the peak at *m/e* 86 (dimethoxyacetylene, Calc. for $C_4H_6O_2$: 86·036776. Found: 86·036595). On the other hand, the 20 eV spectrum at 250°C is almost identical with the one registered at low temperature and 70 eV. Moreover, since the spectra always show a recombination peak at *m/e* 444–452 with the isotopic distribution pattern of four chlorine atoms, we suggest that methoxycarbyne, rather than dimethoxyacetylene, is extruded from adduct **3a**. Carbynes have been generated and shown to add to double bonds with subsequent abstraction of hydrogen,[19] and a similar reaction on the highly nucleophilic double bond of adduct **3a** would explain the presence of peaks at *m/e* 444–452.

Confirmation that extrusion of dimethoxyacetylene is not an energetically favored process, and that tetrachloroanthracene (TCA) is formed by a stepwise loss of methoxycarbyne, is found in the metastable spectrum of adduct **3a**. Two metastable peaks at 320·6 and 278·15 are observed, which correspond to the transitions $402 \rightarrow 359$ (neutral fragment MeO·C:) and $359 \rightarrow 316$ (neutral fragment MeO·C:).

However, the metastable peak at 248·3, corresponding to the direct loss of dimethoxyacethylene, was not present (i.e. $402 \nrightarrow 316$). Therefore, these studies on the mass spectra of adduct **3a** show that loss of methoxycarbyne is a high probability transition and an energetically more favored process than elimination of dimethoxyacetylene. This is good evidence that the same mode of decomposition occurs thermally and it would explain the failure to trap or detect any product other than tetrachloroanthracene in thermolytic experiments.

Since elimination of dimethoxyacetylene from adduct **3a** is a reverse [$_\pi 4_s + _\pi 2_s$] cycloaddition, which is an allowed process by the Woodword-Hoffmann rules and leads to a highly stable aromatic derivative (TCA), the reported results are rather unexpected and resemble those found in the recent attempts to generate ethylenedione from bicyclo[2.2.2]octadiene-2,3-dione derivatives.[20]

An intuitive explanation of the thermal unstability of acetylene diethers ("dimers") with respect to the alkoxycarbynes ("monomers"), in terms of Linnett's theory, was advanced by one of us.[21] However, molecular orbital calculations (EHT) on dimethoxyacetylene done in our Institute[22] suggest that the molecule should be stable and singlet in the ground state.

In any case, the results of this study suggest that adducts **3** are unlikely to serve as precursors for acetylene diethers.

In contrast with adduct **3a**, the mass spectra of adducts **3b** and **3c** show that practically 50% of the total ion current is due to two exclusive fragmentations (Table 2): the predominant one representing the loss of a methyl group $(M-15)^+$, and another involving the loss of a methoxy group $(M-31)^+$. In the semibullvalene derivative **6** the corresponding metastable peaks at 432·38 and 400·21 are apparent, associated with the great stability of the molecular ion and the exceptionally high abundance of the recombination peak at $(M+44)^+$.

As reported in a preliminary communication,[13c] the

Table 1. Mass spectra of adduct **3a**

			m/e					
			43^+	86^+	$(M-86)^+$			
T_i[a]	T_s[b]	eV	MeOC:	MeOCCOMe	TCA	$(M-43)^+$	M^+	$(M+44)^+$
240°	75°	70	6·7	0·2	34·9	100	68·4	3·9
250°	250°	70	46·7	0·7	31·2	100	58·4	4·6
220°	250°	20	8	—	20	100	74	11

[a] Temperature of insertion probe.

[b] Temperature of ion source.

Table 2. Mass spectra of adducts **3b**, **3c** and **6**

			Per cent of the total ion current				
Adduct	T. (°C)	eV	$(M-15)^+$	$(M-31)^+$	M^+	$(M+44)^+$	Other
3b	210	70	35·7	17·5	3·92	—	42·88
3c	120	70	33·0	3·3	4·30	—	49·40
6	120	70	10·06	10·0	18·67	8·09	53·18

great stability of the ions $(M-15)^+$ is explainable in terms of aromatic cyclooctatetraene dications formed from the extremely electron-rich species **3b**, **3c** and **6**.

EXPERIMENTAL

M.ps are uncorrected, and were determined on a Kofler microscope. UV, IR and NMR spectra were recorded on Perkin Elmer spectrometers, models 157-UV, 457 and R-12, respectively, and mass spectra with a AEI apparatus, model MS 902 S.[*] All the compounds prepared throughout the work showed correct spectra, even if they are not explicitly mentioned in the text. The values given below 220 nm are less reliable.

Adducts

(a) 2,3 - (*Tetrachlorobenzo*) - 5,6 - *benzo* - 7,8 - *dimethoxy* - *bicyclo*[2.2.2]*octa* - 2,5,7 - *triene*, **3a**. In a 2-1 three-necked flask, fitted with a mechanical stirrer, a low temperature thermometer, a pressure-equalized dropping funnel and a $CaCl_2$-tube, were introduced 14·5 g (0·05 mol) of hexachlorobenzene and 800 ml of dry ether. Under an atmosphere of dry N_2, the mixture was stirred while the temperature was reduced to −25 to −35° by means of an acetone-dry ice cooling bath, and n-butyl-lithium (1 equivalent) in ether solution was added dropwise to the hexachlorobenzene suspension over a period of about 60 min; care was taken that the temperature did not rise above −25°. The mixture was then stirred at this temperature for 1 hr and 9·4 g (0·05 mol) of solid 2,3-dimethoxynaphthalene **1a** were added, followed by 800 ml of dry hexane. The apparatus was then removed from the cooling bath and converted to distillation and, while hexane was added dropwise, the ether was distilled until the vapor temperature reached ~60°. At this stage, the reaction mixture was refluxed for 12 hr, and the solid was filtered off and washed several times with hot hexane. The combined solutions were evaporated under vacuum, the residue was dissolved in a small amount of hexane and passed through alumina (1:10). Elution with hexane gave unreacted hexachlorobenzene, then the adduct **3a** (14%) and finally 2,3-dimethoxynaphthalene. Further chromatography on alumina (1:25) of the crude product and elution with hexane gave 1·8–2·4 g (9–12% yield) of adduct **3a**, m.p. 178–9°. The product is sensitive to photooxidation[13] and is best handled in diffuse light.

UV (cyclohexane), λ_{max} 222 (ϵ = 28200), 276 (2730) and 309 nm (2090); IR (KBr), $\nu_{C=C}$ 1675 cm^{-1}; NMR (CCl_4), τ 2·50–3·10 (m, AB system) (4H), 4·83 (s)(2H) and 6·28 (s)(6H) (Found: C, 53·51; H, 3·06; Cl, 35·44. $C_{18}H_{12}Cl_4O_2$ requires: C, 53·77; H, 3·01; Cl, 35·27%).

(b) 2,3 - (*Tetrachlorobenzo*) - 5,6 - *benzo* - 1,7,8 - *trimethoxy* - *bicyclo*[2.2.2]*octa* - 2,5,7 - *triene*, **3b**. This adduct may be obtained by essentially the same method using 1,2,3-trimethoxynaphthalene[8] (10·9 g, 0·05 mol) in place of 2,3-dimethoxynaphthalene. After chromatography on alumina (1:25) the product was recrystallized from hexane to give 7·56 g of colorless crystals (35% yield), m.p. 146–7°.

UV (cyclohexane), λ_{max} 224 (ϵ = 37000), 276 (4400), 298 (1800) and 307 nm (1900); IR (KBr), $\nu_{C=C}$ 1675 cm^{-1}; NMR ($DCCl_3$), τ 2·30–3·10 (m)(4H), 4·83 (s)(1H), 6·02 (s)(3H), 6·23 (s)(3H) and 6·34 (s)(3H) (Found: C, 52·80; H, 3·15; Cl, 33·10. $C_{19}H_{14}Cl_4O_3$ requires: C, 52·82; H, 3·26; Cl, 32·83%).

(c) 2,3-(*Tetrachlorobenzo*) - 5,6 - *benzo* - 1,4,7,8 - *tetramethoxy*-*bicyclo*[2.2.2]*octa* - 2,5,7 - *triene* **3c** *and* 3,4 - (*tetrachlorobenzo*)-6,7 - *benzo* - 1,2,5,8 - *tetramethoxy* - *tricyclo*[3.3.0.$0^{2,8}$]*octa* - 3,6-*diene* **6**. Starting from 12·4 g (0·05 mol) of 1,2,3,4-tetramethoxynaphthalene,[8] by the same procedure described above, a mixture of **3c** and **6**, together with starting materials, was obtained. Chromatography on alumina (1:10) and elution with a mixture of hexane–ether (9:1), gave hexachlorobenzene, followed by adduct **3c**, then 1,2,3,4-tetramethoxynaphthlane (4·4 g, 35·8% recovery), and finally the adduct **6**. Purification of fractions 2 and 4 on alumina (1:25), and recrystallization from hexane gave: (i) 0·3 g (1·3% yield) of adduct **3c**, m.p. 245–6°; UV (cyclohexane), λ_{max} 227 (ϵ = 25000) and 276 nm (2450); IR (KBr), $\nu_{C=C}$ 1675 cm^{-1}; NMR ($DCCl_3$), τ 2·40–2·95 (m)(4H), 6·04 (s)(6H) and 6·20 (s)(6H) (Found: C, 51·92; H, 3·62; Cl, 30·78. $C_{20}H_{16}Cl_4O_4$ requires: C, 51·97; H, 3·51; Cl, 30·68%). (ii) 1·73 g (7·5% yield) of adduct **6**, m.p. 209–10°; UV (cyclohexane), λ_{max} 216 (ϵ = 71900), 223 (53100) and 300 nm (1602); IR (KBr), no absorption between 2820 and 1465 cm^{-1}; NMR ($DCCl_3$), τ 2·72–3·95 (m)(4H) and 6·0 (pseudosinglet)(12H) (Found: C, 51·93; H, 3·56; Cl, 30·59. $C_{20}H_{16}Cl_4O_4$ requires: C, 51·97; H, 3·51; Cl, 30·68%).

(d) 1 - *Nitro* - 2 - *pentachlorophenyl* - 3 - *methoxynaphtalene*, **7**. Starting from 11·6 g (0·05 mol) of 1-nitro-2,3-dimethoxynaphthalene **1d**,[8] by the same method used for the di-, tri- and tetra-methoxynaphthalenes, after a chromatography of the crude reaction mixture on alumina (1:25) and elution with CCl_4, hexachlorobenzene, the crude adduct **7** and 7·2 g of 1-nitro-2,3-dimethoxynaphthalene were obtained. Recrystallization from CCl_4 gave 2·3 g (10% yield) of the product **7**, as yellow crystals, m.p. 234–7°; UV (cyclohexane), λ_{max} 215 (ϵ = 96300) and 232 nm (108000); NMR ($DCCl_3$), τ 2·00–2·72 (m)(5H) and 6·10 (s)(3H) (MS found: 448·884451. $C_{17}H_8Cl_5NO_3$ requires: 448·894683).

(e) 1 - *Nitro* - 2,3 - *dimethoxy* - 4 - *pentachlorophenyl*-*naphthalene*, **8**. Operating as described, from 5 g (0·02 mol) of 1-nitro-2,3,4-trimethoxynaphthalene **1e**,[8] after chromatography on alumina (1:25) and elution with hexane, 0·2 g (2·1% yield) of **8**, m.p. 209–210·5°, were obtained (together with 83% of the starting naphthalene **1e**); UV (cyclohexane), λ_{max} 215 (ϵ = 90300), 227 (109900) and 337 nm (20135); NMR ($DCCl_3$), τ 1·60–3·00 (m)(4H), 5·98 (s)(3H) and 6·19 (s)(3H) (MS, found: 478·897116. $C_{18}H_{10}Cl_5NO_4$ requires: 478·905247).

(f) 2,3 - (*Tetrachlorobenzo*) - 5,6 - *benzo* - 7,8 - *dicarbomethoxy*-*bicyclo*[2.2.2]*octa* - 2,5,7 - *triene* **9**. A mixture of 790 mg (2·5 mmol) of 1,2,3,4-tetrachloroanthracene[13b] and 1 ml of dimethyl acetylenedicarboxylate was carefully heated over a flame until a smooth reaction began, and then refluxed for just 1 min. The reaction mixture was cooled down, the crystals were then removed from the oily material by filtration in vacuo, and recrystallized from benzene–hexane, to give ~100% yield of white crystals, m.p. 200–1°; UV (cyclohexane), λ_{max} 211 (ϵ = 29200) and 228 nm (31500); IR (KBr), ν_{max} 1745, 1715 and 1645 cm^{-1}; NMR (CCl_4), τ 2·20–2·85 (m, AB system)(4H), 3·90 (s)(2H) and 6·10 (s)(6H) (Found: C, 52·18; H, 2·70; Cl, 30·95. $C_{20}H_{12}Cl_4O_4$ requires: C, 52·44; H, 2·66; Cl, 30·95%).

Thermolysis of adduct **3a**

(a) *In dimethyl acetylenedicarboxylate solution.* In a small two-necked flask, fitted with an inlet capillary tube and a condenser connected to a trap cooled with acetone-dry ice, were introduced 300 mg (0·74 mmol) of adduct **3a** dissolved in 5 ml of dimethyl acetylenedicarboxylate. Nitrogen was bubbled through the capillary and the mixture refluxed for 3 hr. The analysis of the

---

[*] In the first part of our work some mass spectra were recorded with an Atlas-Varian, model CH-5, by Dr T. Axenrod (Department of Health, Education and Welfare, Bethesda, Maryland, U.S.A.) to whom the authors wish to express their indebtedness.

condensed volatile products showed no products other than those found in a blank experiment.

Elimination of excess of dimethyl ester and chromatography of the reaction mixture on silica gave, after elution with benzene, 130 mg (39% yield) of the new adduct **9**, identical with an authentic sample prepared as described above, and 806 mg of a crystalline compound, m.p. 118–9° (from benzene) that was identified by elemental analysis, UV, IR and NMR spectra as a "dimer" of dimethyl acetylenedicarboxylate, already described in the literature.[24]

(b) *In hexachlorocyclopentadiene solution.* Under an atmosphere of purified nitrogen, a stirred solution of 300 mg (0·74 mmol) of adduct **3a** in 5 ml of hexachlorocyclopentadiene was heated at 200° for 3 hr. The excess solvent was distilled under vacuum and the residue chromatographed on silica (150 ml): 175 mg (75% yield) of tetrachloroanthracene[13b] were eluted in the fractions from hexane : benzene (7 : 3) up to benzene : ether (7 : 3). Therefore, a Diels-Alder reaction of adduct **3a** with hexachlorocyclopentadiene and subsequent extrusion in the chromatographic column is not excluded. However, adduct **10** could not be isolated or detected.

(c) *Low-pressure thermolyses.* Low-pressure thermolysis of **3a** was carried out, with similar results, either by the technique described by de Mayo *et al.*[15] or using the more sophisticated system described below. A Pyrex tube (28 × 2 cm) with ground glass joints at the ends, fitted with an inlet capillary tube at one end and connected to two traps in the other, was filled with Fenske helices and furnished with two independent electrical heaters. In a typical run, 500 mg (1·24 mmol) of **3a** were introduced into the system. A small balloon filled with purified nitrogen was connected to the capillary tube, vacuum was regulated at 0·5 Torr and the traps immersed in acetone–dry ice cooling baths. One of the electrical resistance was heated at 300° to slowly sublime the product, over a period of 2 hr, into the Fenske helices section heated at 450° by means of the second electrical resistance. All the products condensed at the cold end of the system (410 mg) and no volatile materials were condensed in the traps. Chromatography of the thermolyzed material on alumina gave 230 mg (57% yield) of tetrachloroanthracene[13b] and 125 mg of recovered **3a**.

REFERENCES

[1a] B. R. O'Connor, *J. Org. Chem.* 33, 1991 (1968); [b] L. Brandsma, E. Harryvan and J. F. Arens, *Rec. Trav. Chim.* **87**, 1238 (1968).

[2] A. Messeguer, J. Rivera and F. Serratosa, *Tetrahedron Letters* 2895 (1973).

[3a] B. P. Stark and A. J. Duke, *Extrusion Reactions*, Pergamon Press, Oxford, 1967; [b] E. J. Corey and W. L. Mock, *J. Am. Chem. Soc.* **84**, 685 (1962); [c] G. J. D. Peddle, D. N. Roark, A. M. Good and S. G. McGeachin, *Ibid.* 91, 2807 (1969); D. N. Roark and G. J. D. Peddle, *Ibid.* **94**, 5837 (1972); [d] H. Gilman, S. G. Cottis and W. H. Atwell, *Ibid.* **86**, 1596 (1964); [e] R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197 (1964).

[4] O. Diels and W. E. Thiele, *Ber.* 71, 1173 (1938); however the method has recently been questioned by F. E. Herkes and H. E. Simmons, *Synthesis* 166 (1973).

[5a] O. Diels and K. Alder, *Ber.* **62**, 2337 (1924); [b] G. D. Weiss, *J. Org. Chem.* **27**, 3692 (1962); [c] C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.* **82**, 1515 (1960); *Ibid.* **83**, 3428 (1961).

[6] An entire Chapter by R. W. Hoffmann is devoted to benzynes, in *Chemistry of Acetylenes* (Edited by H. G. Viehe). Marcel Dekker, New York (1969).

[7] J. P. N. Brewer, I. F. Eckhard, H. Heaney and B. A. Marples, *J. Chem. Soc.* (*C*), 664 (1968); H. Heaney and J. M. Jablonski, *Ibid.* 1895 (1968); H. Heaney ankd B. A. Marples, *J. Chem. Educ.* **45**, 801 (1968).

[8] The preparation of these naphthalenes will be reported in a separated paper, *Anales de Quim.* in preparation.

[9] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, pp. 78–82. Verlag Chemie-Academic Press, New York (1970).

[10] *Annual Reports B*, **69**, 324 (1972). see also, G. Sugowdz, P. J. Collin and W. H. F. Sasse, *Austral. J. Chem.* **26**, 147 (1973).

[11a] M. E. Kuehne, *J. Am. Chem. Soc.* **84**, 837 (1962); [b] H. H. Wassermann and J. Solodar, *Ibid.* **87**, 4002 (1965); [c] T. Matsuda and T. Mitsuyasu, *Bull. Chem. Soc. Japan* **39**, 1342 (1966); [d] I. Tabushi, R. Oda and Okazaki, *Tetrahedron Letters* 3743 (1968); [e] L. Friedman, R. J. Osiewcz and P. W. Rabidean, *Ibid.* 5735 (1968).

[12] *c.f.* B. Hankinson and H. Heaney, *Tetrahedron Letters* 1335 (1970).

[13a] J. Font, F. Serratosa and L. Vilarrasa, *Tetrahedron Letters* 4743 (1969); [b] J. Font, F. Serratosa and L. Vilarrasa, *Ibid.* 4105 (1970); [c] F. Serratosa and P. Solá, *Ibid.* 821 (1973).

[14a] J. Sauer, B. Schroeder and R. Weimer, *Chem. Ber.* **100**, 306 (1967); J. Sauer, B. Schroeder and A. Milelert, *Ibid.* **100**, 351 (1967); [b] See also M. C. Kloetsel, *Organic Reactions* **4**, 1 (1948).

[15] J. F. King, P. de Mayo, C. L. McIntosch, K. Piers and O. J. M. Smith, *Can. J. Chem.* **48**, 3704 (1970).

[16a] A. Maccoll in *Modern Aspects of Mass Spectrometry* (Edited by R. I. Reed), pp. 143–68. Plenum Press, New York (1968); [b] T. W. Bentley and R. A. W. Johnstone, *Adv. Phys. Org. Chem.* **8**, 151 (1970); [c] R. C. Dougherty, *Fortschr. Chem. Forsch.* **45**, 93 (1974).

[17] R. C. Dougherty, *J. Am. Chem. Soc.* **90**, 578 (1968).

[18] F. W. McLafferty, D. J. McAdoo and J. S. Smith, *Ibid.* **91**, 5400 (1969).

[19] T. DoMinh, H. E. Gunning and O. P. Strausz, *Ibid.* **89**, 6785 (1967); O. P. Strausz, T. DoMinh and J. Font, *Ibid.* **90**, 1930 (1968); O. P. Strausz, G. J. A. Kennepohl, F. X. Garneau, T. DoMinh, B. Kim, S. Valenty and S. Skell, *Ibid.* **96**, 5723 (1974).

[20a] J. Strating, B. Zwanenburg, A. Wagenaar and A. C. Udding, *Tetrahedron Letters* 125 (1969); [b] R. C. Haddon, *Ibid.* 3897 (1972); [c] J. Fleischhauer, M. Beckers and H. D. Scharf, *Ibid.* 4275 (1973).

[21] F. Serratosa, *J. Chem. Educ.* **50**, 402 (1973).

[22] Dr. S. Olivella, private communication.

[23] M. J. S. Dewar, A. Harget and E. Hasselbach, *J. Am. Chem. Soc.* **91**, 7521 (1969).

[24] E. Winterfield and G. Giesler, *Angew. Chem. Internat. Edn.* **5**, 579 (1966).