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DIAZO COMPOUNDS—66[1]

5-(DIAZOMETHYL)-5H-DIBENZO[a,d]CYCLOHEPTENES—INTERMEDIATES ON THE WAY TO NEW DIBENZOSEMIBULLVALENE AND DIBENZOCYCLOOCTENE SYNTHESES

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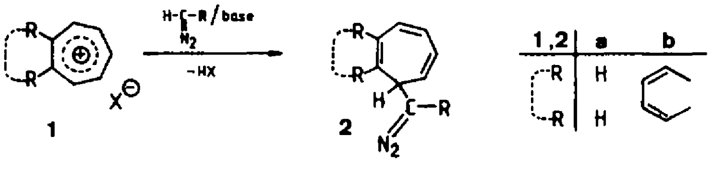
Abstract—Electrophilic diazoalkane substitution of (silver diazomethyl)phosphoryl or mercury bis[(diazomethyl)-carbonyl] compounds (**10a–c** or **12a–c**) with 5-chloro-5H-dibenzo[a,d]cycloheptene (**6**) furnishes the 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes (**8a–c** or **13a–c**). Copper(II) acetylacetonate-catalysed decomposition of these compounds in toluene results, in all cases, in the formation of dibenzosemibullvalenes (**17a–f**). In addition, the dibenzo[a,e]cyclooctenes **16a–e** and, in the case of **13c**, the dibenzoheptafulvene **18f** are formed.

Electrophilic diazoalkane substitution[2] of CO- and PO-substituted diazomethyl compounds with cycloheptatrienylium or benzocycloheptenylium salts (**1a** or **b**) renders the previously rare (diazomethyl)-cycloheptatrienes (**2a**)[3] or (diazomethyl)-benzocycloheptenes (**2b**)[4,5] easily accessible in a one-step reaction. For experimental purposes, the diazomethyl compound is reacted with the Hückel aromatic salt in the presence of an organic amine in order to prevent the acid-catalysed decomposition of the new diazo products. It is also advantageous to react the cycloheptatrienylium or benzocycloheptenylium halides with the very stable silver or mercury derivatives of the diazomethyl compounds, thus avoiding the necessity of adding base.



In the present study, we concerned ourselves with the synthesis of the previously unknown 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes (**8**, **13**) using the same principle and then studied their suitability for opening a new way into the dibenzosemibullvalene (**17**) and dibenzocyclooctene (**16**) series.

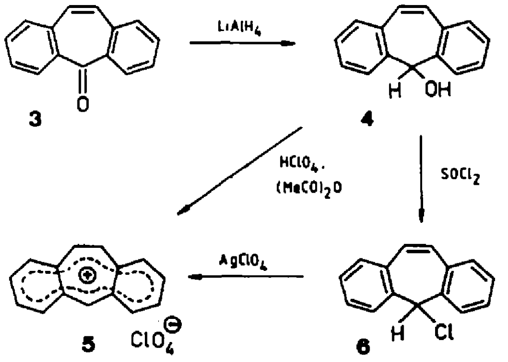
Starting materials for the introduction of the diazomethyl moieties are 5-chloro-5H-dibenzo[a,d]cycloheptene (**6**) and dibenzo[a,d]cycloheptenylium perchlorate (**5**), both of which can be obtained from ketone **3**. Reaction of **3** with sodium borohydride to give alcohol **4**[6] has been reported in the literature. This reaction can also be advantageously performed with lithium aluminium hydride. Reaction of **4** with thionyl chloride to give **6**[6] and subsequent cleavage of chloride from **6** using silver perchlorate[6] provide access to **5**.

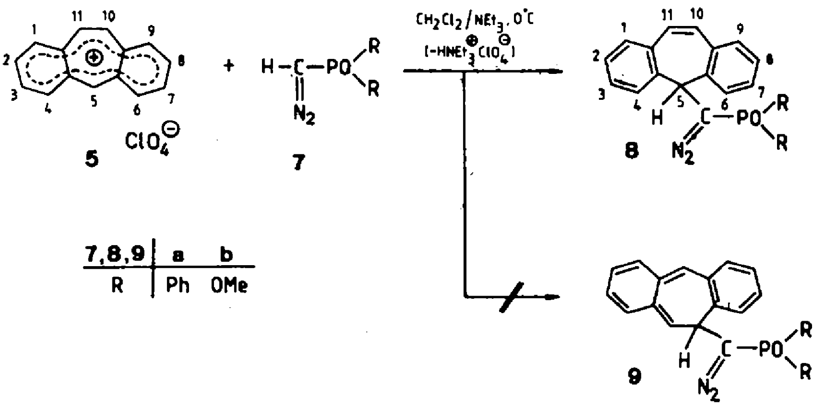
Dibenzocycloheptenylium perchlorate (**5**) can be obtained directly from alcohol **4** in 85% yield by reaction of **4** with perchloric acid in the presence of acetic anhydride. This route to **5** was indicated by Berti[6] and by Heilbronner and co-workers[7] who prepared **5** by comparable methods for UV–vis investigations.

RESULTS AND DISCUSSION

Model experiments designed to substitute the (diazomethyl)phosphoryl compounds **7a** or **b** with the cycloheptenylium perchlorate **5** in dichloromethane in the presence of triethylamine generally resulted in the formation of the desired products **8a** or **b**, albeit in very modest yields (13 or 8%). The C_s symmetry of these products (see later for structural discussions) indicates that the attack of the diazo compounds has occurred at position 5 of cation **5**.

There is no evidence for the formation of the 10(11)-isomers **9a** or **b**. This would have resulted in the loss of aromaticity of one of the benzene rings, as well as loss of





7,8,9	a	b
R	Ph	OMe

conjugation between the two benzene rings, and does not occur for energetic reasons. Variation of the solvent (e.g. acetonitrile) and the base (diisopropylethylamine, 1,5-diazabicyclo[4.3.0]non-5-ene) did not result in any improvement in the yield. Methyl diazoacetate, which is known to possess a less nucleophilic diazo carbon atom than **7a** or **b**, does not react at all with **5** under the above-mentioned conditions.

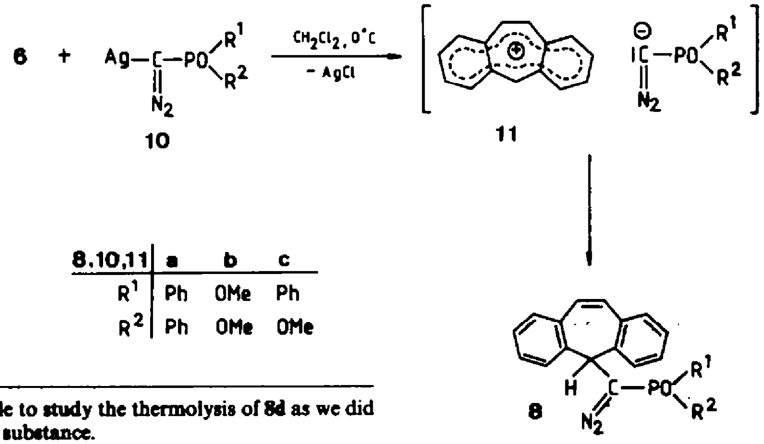
When, however, the chloro compound **6** is used as a potential electrophile with the thermally stable silver derivatives of (diazomethyl)-phosphoryl compounds (**10a–c**), the yellow, crystalline 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes **8a–c** are obtained in 60–70% yields after chromatographic work-up.

Rapid reaction is indicated by the immediate precipitation of silver chloride; the transitory appearance of an intense red colour on dropwise addition of **6** is indicative of the intermediate formation of the dibenzo[a,d]cycloheptenylium cation.[8] The counter ion must now be the strongly nucleophilic diazomethyl anion shown in structure **11**. Combination of both ions leads to the formation of the product. The reasons why the cation develops its electrophilicity solely at position 5 have already been explained.

The carbonylated 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes (**13a–c**) are prepared in 52–59% yields similarly; compound **6** is allowed to react with the mercury derivatives of the (diazomethyl)-carbonyl compounds (**12a–c**). The latter derivatives are preferred as the corresponding silver compounds are thermally unstable and difficult to handle.[9] As precipitation of mercury(II) chloride in dichloromethane is not complete, the reaction mixture is treated with sodium sulfide before chromatographic work-up. The reaction **6** + **14** → **8d** shows that this variation is also suitable for the preparation of phosphorylated 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes. The use of the mercury compound **14** was necessary in this case as we have not yet been able to prepare the di-t-butyl-(silver diazomethyl)-phosphine oxide (**10**, $R^1 = R^2$ = t-Bu).

All the diazo compounds **8a–d**, **13a–c** show the characteristic intense diazo valency vibrations (2045–2080 cm^{-1}) and PO- (1160–1250 cm^{-1}) or CO-absorptions (1615–1685 cm^{-1}) in their IR spectra (Table 1). In the ^1H-NMR spectra of **8a**, **b**, **d** and **13a–c** the protons at C-10 and C-11 are magnetically equivalent and are observed as a 2 proton signal at δ 6.80–7.00 ppm. This is not the case for **8c** which contains a chiral phosphorus: in this compound H-10 and H-11 appear as an AB-system (Table 1). The absorption of the proton at C-5 of **8a–d** and **13a–c** (δ 4.93–5.52 ppm) provides further evidence for the given constitution; in the case of the phosphorylated products, this signal is split into a doublet ($^3J_{H,P} = 4.5–5.9$ Hz).

Diazo compounds of the types **8** and **13** have an unusually high thermal stability.[10] Even on addition of copper(II) acetylacetonate[11] their decomposition in boiling benzene proceeds slowly, thus the decomposition is better carried out in toluene. TLC-monitoring of thermolysis experiments with **8a–c**† or **13a–c** shows complete disappearance of the compounds and the formation of two new products which can be almost completely separated by chromato-



8,10,11	a	b	c
R^1	Ph	OMe	Ph
R^2	Ph	OMe	OMe

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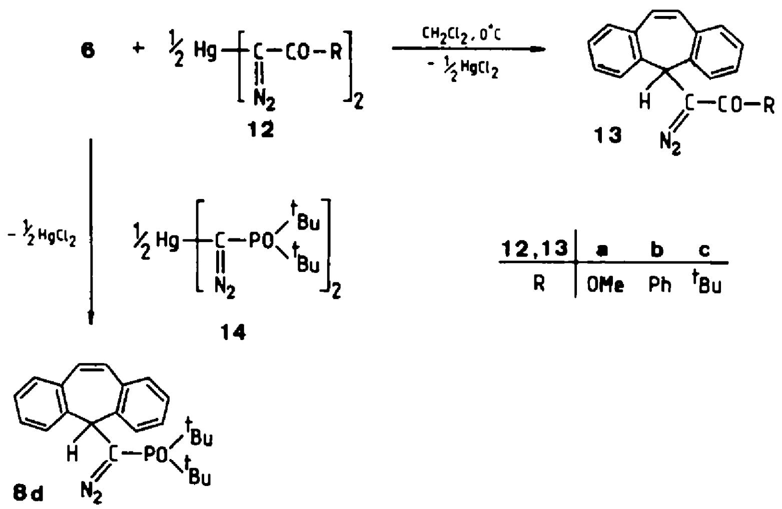
† We were unable to study the thermolysis of **8d** as we did not have sufficient substance.



12,13	a	b	c
R	OMe	Ph	ᵗBu

graphy or fractional crystallization. These products are the dibenzo[a,e]cyclooctenes **16a–e** (9–76%) and the isomeric dibenzosemibullvalenes **17a–e** (5–71%). Only the cyclooctene **16d** could not be isolated in a ^{1}H-NMR spectroscopically pure state; it contains 20% of **17d**. At variance with these results is the thermolysis of **13c** which gives rise to the heptafulvene **18f** (78%). The crude product still contains about 20% of **17f**. Of these compounds, only **17d** has previously been reported in the literature, as the product from the photoisomerization of the isomeric methyl dibenzobarrelen-7-carboxylate.[12]

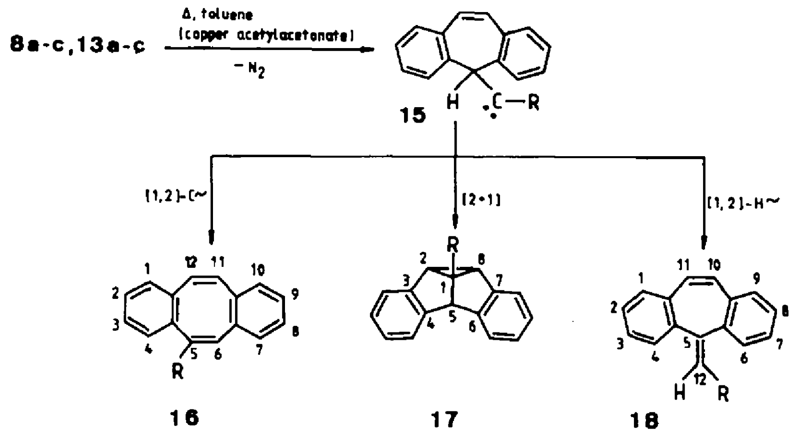
When the product ratios **16**:**17** are considered, the extreme situations in the cases of **8a** (**16a**:**17a** ≅ 15:1) and **8b** (**16b**:**17b** ≅ 1:8) are apparent; for **8c** it is less pronounced (**16c**:**17c** ≅ 3.5:1). Presumably, the rearrangement with introduction of phosphoryl substituents on the benzyl position of the dibenzocyclooctene by a 1,2-C shift starting from carbene **15** (or a corresponding copper carbenoid) is subject to steric hindrance. Whereas the phenyl groups of the phosphoryl moiety can effectively evade interaction with the annellated aromatic system by rotation (formation of **16a**), this is not successful with the dimethoxyphosphoryl group. In this case the spatially favourable intramolecular [2 + 1] cycloaddition to give **17b** is preferred. Evidence for such a steric effect is given by the ^{1}H-NMR spectra of **16b** and **c** which show a line doubling for the methoxy resonances, probably resulting from a hindered rotation. This assumption is supported by dynamic ^{1}H-NMR spectroscopy: in the case of **16b** coalescence is observed at 433 K. The thermolysis results for **13c** also fit into this hypothesis. The formation of **16f** is completely suppressed, **17f** is formed in about 20% yield, while the 1,2-H shift to give **18f** in 78% yield predominates.

From the mechanistic point of view, there is an alternative explanation for the formation of the dibenzosemibullvalenes **17** involving the intramolecular [3+2] cycloadduct **19** as an intermediate. The tendency for diazo dipoles to undergo cycloadditions with non-activated double bonds is not pronounced,[13] but the reaction **20** → **21** → **22** (35%) offers one example of such an intramolecular

Table 1. Spectroscopic data for the 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes **8a–d** and **13a–c**

Diazo Compound	IR(KBr) [cm^{-1}] C=N_2	P=O	C=O	^{1}H-NMR($CDCl_3$, δ in ppm, J in Hz) 5-H ($^3J_{P,H}$)	10-H/11-H	Aromatic H	Other signals
8a	2055	1195	—	5.27 (5.5)	6.90	7.05-7.68	—
8b	2080	1250	—	4.93 (5.0)	6.80	7.23-7.50	3.39 (d, 6H, $^3J_{P,H}$ = 12.0, P-OMe)
8c	2060	1225	—	4.98 (4.5)	6.75[a]	6.94-7.55	3.49 (d, 3H, $^3J_{P,H}$ = 11.5, P-OMe)
8d	2045	1160	—	5.03 (5.9)	6.88	7.2 - 7.55	1.08 (d, 18 H, $^3J_{P,H}$ = 14.5, P-ᵗBu)
13a	2080	—	1685	5.15 (—)	6.95	7.25-7.55	3.62 (s, 3H, OMe)
13b	2060	—	1615	5.52 (—)	7.00	7.20-7.65	—
13c	2070	—	1618	5.28 (—)	6.90	7.25-7.60	1.02 (s, 9H, ᵗBu)

[a] As a result of the presence of the chiral phosphorus atom, an AB-system is observed, δ_A = 6.85, δ_B = 6.65, $J_{A,B}$ = 11.3 Hz.



15-18	a	b	c	d	e	f
R	POPh$_2$	PO(OMe)$_2$	PO(OMe)Ph	COOMe	COPh	CO^{t}Bu

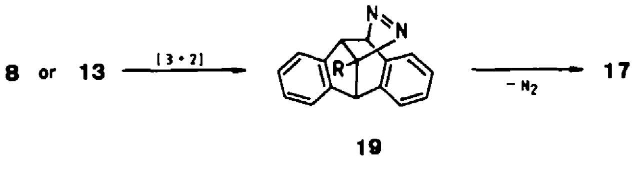
cycloaddition step.[14] However, as solutions of 8 or 13 even on warming show no spectroscopic changes which could be attributed to the formation of 19, there is no basis for the postulation of the Δ^1-pyrazoline as an intermediate.

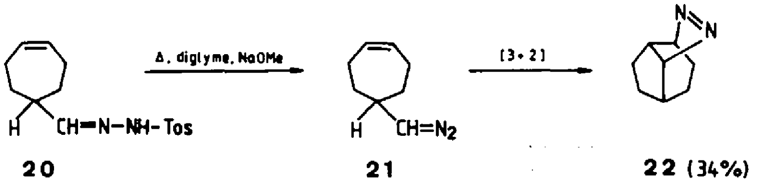
With the exception of the PO- and CO-absorptions (see Tables 2 and 3), the IR spectra of 16 and 17 contain only few bands of diagnostic value such as, e.g. the C=C bond of 16 (1575–1628 cm^{-1}). As a result of the substitution at C-5, the protons H-11 and H-12 appear in the ^{1}H-NMR spectra of 16 as an AB system with δ 6.46–6.82 and a vicinal coupling constant of 11–12 Hz. The resonance of the proton H-6 is structurally more informative. It is adjacent to an acceptor substituent, takes over the benzyl position, and thus resonates at unusually low field (δ 7.81–8.05).† In the spectra of 16b and c, the structurally typical cis $^3J_{H,P}$ coupling of 19 or 22 Hz, respectively, is observed. The ^{1}H-NMR spectrum of 16c displays an interesting phenomenon: each proton resonance appears as two signals. This is presumably the result of a hindered rotation of the chiral phosphoryl group on the boat conformation of the dibenzocyclooctene ring[13] (see also Table 2).

In contrast to products 16, the dibenzosemibullvalenes 17 possess a plane of symmetry which is responsible for the magnetic equivalence of the protons H-2 and H-8. Both cyclopropane hydrogen atoms experience a strong paramagnetic shift by the immediately adjacent benzene nuclei (δ 3.58–3.97) and, if appropriate, the resonances are split by coupling with phosphorus. In this series as well the phosphinate 17c is a special case. The C_s symmetry is cancelled out by the chirality of the phosphorus so that the two protons on the three-membered ring are no longer magnetically equivalent and now resonate as the AB part of an ABX system (X = ^{31}P) (Fig. 1). The third proton of 17 bound to an sp^3 hybridized carbon atom (H-5) is, as to be expected, shifted to even lower field (δ 4.54–4.97) and, in the cases of 17a–c, additionally split by phosphorus (see Table 3).

The ^{13}C-NMR spectra of 17b and e were recorded as models for the compound type. In both spectra, the resonances for the two identical cyclopropane carbon atoms C-2 and C-8 are observed at the same field (δ 42.40 or 48.10, respectively); the assignment is confirmed by the coupling with hydrogen (> 170 Hz). The carbon atoms C-1 of both dibenzosemibullvalenes resonate at δ 51.86 or 69.92, respectively and, in the case of 17b the signal is split (197.4 Hz) by coupling with phosphorus. Finally, the carbon atoms C-5 resonate in the typical benzyl region (δ 54.87 or 56.57, respectively) (Experimental).

Lastly, evidence for the structure of the dibenzo-





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† The same is also true for 6-acceptor substituted benzocyclooctenes.[4,5]

Table 2. Spectroscopic data for the 5-substituted dibenzo[a,e]cyclooctenes **16a–e**

Dibenzo[a,e]-cyclooctene	IR(KBr) [cm^{-1}]			^{1}H-NMR(CDCl$_3$, δ in ppm, J in Hz)			
	C = C	P = O	C = O	6-H ($^3J_{P,H}$)	11-H 12-H ($J_{A,B}$) [δ_A, δ_B]	Aromatic H	Other Signals
16a	1620 1588	1185	—	a	6.74 (11.7) [6.79, 6.69]	6.8 - 8.0	—
16b	1625	1248	—	7.83 (22)	6.79 (11.7) [6.85, 6.74]	6.9 - 7.4	3.69, 3.76 (each d, 6H, $^3J_{P,H}$ = 11, P-OMe)
16c	1620 1588	1222	—	7.81 (20)	6.46 (12.0) [6.58, 6.32]	6.8 - 7.7	3.71 (d, 3H, $^3J_{P,H}$ = 10.5, P-OMe)
				7.94 (19)	6.68 (~11) [6.76, 6.60]		3.74 (d, 3H, $^3J_{P,H}$ = 10.5, P-OMe)
16d	1575	—	1725	8.05 (—)	6.82 (12) [6.72, 6.92]	6.9 - 7.4	3.79 (s, 3H, OMe)
16e	1628 1592	—	1655	a	6.74 (11.7) [6.79, 6.69]	6.9 - 7.9	—

[a] The resonance of H-6 is masked by the aromatic proton resonances.

heptafulvene **18f** is necessary. It is at first surprising that this compound is colourless whereas heptafulvene itself (red oil)[16] and benzoheptafulvene (yellow solid)[17] are both characterized by intense colourations. In contrast to this and in accord with our results is the fact that the unsubstituted dibenzoheptafulvene (**18**, R = H) is colourless.[18] This compound thus possesses olefin and not fulvene characteristics.

In the ^{1}H-NMR spectrum of **18f**, a three proton signal at δ 6.85 is especially conspicuous and has to be assigned to H-10, H-11, and H-12. This phenomenon can be explained by the idea that the ring protons and the exocyclic proton fortuitously resonate at the same field and that the t-butoxycarbonyl group no longer has an effect on the chemical shifts of H-10 and H-11. Thus, **18f** is clearly different from the possible dibenzocyclooctene isomer **16f** for which one would expect to observe an AB spin system and a clearly separated one proton signal (see also Table 2). The ^{13}C-NMR spectrum of **18f** does not provide any further structurally relevant information as the signals for the aromatic and olefinic carbon atoms cannot be unequivocally assigned.

EXPERIMENTAL

M.ps (not corrected): Mettler FP 61 m.p. apparatus (heating rate: 2° min^{-1}). Elemental analyses: Perkin–Elmer Analyzer 240. IR spectra: Beckman Acculab, Perkin–Elmer 397. ^{1}H-NMR spectra: Varian EM 390, Bruker WP 200 (TMS as internal standard). Column chromatography: Macherey and Nagel kiesel gel (0.06–0.2 mm). The separations were monitored on ready made TLC plates (DC-Fertigplatten Alugram SIL G-UV$_{254}$) using the same solvents as for the column chromatography. All solvents were anhyd and distilled before use.

Starting materials. Compound **4** was prepared by reduction of **3** with NaBH$_4$;[6] we used LAH in place of NaBH$_4$. The following compounds were prepared according to lit. methods: **6**;[6] **7a**,[19] **7b**;[20] **10a**,[19] **10b**,[20] **10c**;[21] **12a**,[22] **12b**,[23] **12c**[24] and **14**.[25]

Dibenzo[a,d]*cycloheptenylium perchlorate* (**5**). A soln of 3.13 g (15.00 mmol) **4** in 30 ml of Ac$_2$O is stirred at 0° and treated with 2.85 g (20.00 mmol) of 70% perchloric acid. After addition

Table 3. Spectroscopic data for the 1-substituted dibenzosemiobullvalenes **17a–e**

Dibenzosemibullvalene	IR(KBr) [cm^{-1}]		^{1}H-NMR(CDCl$_3$, δ in ppm, J in Hz)			
	P = O	C = O	2-H/8-H ($^3J_{P,H}$)	5-H ($^3J_{P,H}$)	Aromatic H	Other signals
17a	1195	—	3.58 (10.8)	4.54 (9.0)	6.9 - 7.7	—
17b	1250	—	3.59 (12.5)	4.63 (10.0)	6.9 - 7.3	3.58 (d, 6H, $^3J_{P,H}$ = 11, P-OMe)
17c	1225	—	3.66[a] (11.0)	4.61 (9.0)	6.9 - 7.9	3.62 (d, 3H, $^3J_{P,H}$ = 10.5, P-OMe)
17d	—	1710	3.78 (—)	4.97 (—)	6.9 - 7.3	3.68 (s, 3H, OMe)
17e	—	1660	3.97 (—)	4.87 (—)	7.0 - 7.7	—

[a] As a result of the presence of the chiral phosphorus atom, the AB-part of an ABX-system is observed, δ_A = 3.76, δ_B = 3.55, $J_{A,B}$ = 7.5 Hz.

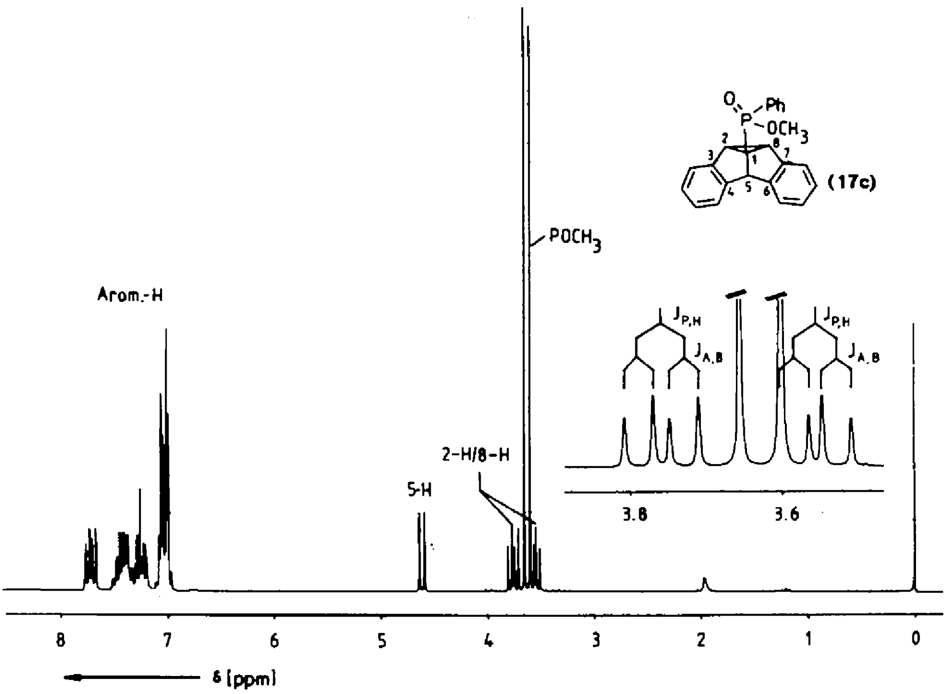

Fig. 1. ^{1}H-NMR spectrum (200 MHz, $CDCl_3$) of **17c**.

of 50 ml of ether, the product is filtered by suction and washed with ether to give **5**, yield 3.70 g (85%), red crystalline powder m.p. 134–138 (dec) (lit.[6] 135) (Found: C, 61.4; H, 3.86. Calc for $C_{15}H_{11}ClO_4$ (290.70): C, 61.97; H, 3.81%.)

Reaction of dibenzo[a,d]*cycloheptenylium perchlorate* (**5**) *with the (diazomethyl)-phosphoryl compounds* **7a** *and* **b**. A soln of 1.21 or 0.75 g (5.00 mmol) of **7a** or **b**, respectively, and 0.50 g (5.00 mmol) of Et_3N in 25 ml of CH_2Cl_2 is stirred at 0° and treated dropwise within 30 min with a suspension of 1.46 g (5.00 mmol) of **5** in 25 ml of CH_2Cl_2 whereupon the red colour of **5** disappears. The mixture is allowed to warm to room temp, is then shaken twice with water (15 ml each time), and dried with Na_2SO_4. The yellow soln is concentrated at 25°/20 Torr. Chromatography of the residual resin on 180 g kiesel gel (column: 150 × 2.8 cm) with 800 ml EtOAc gives unreacted **7a** or **b** together with **8a** [0.28 g (13%)] or **8b** [0.13 g (8%)] as yellow oils which crystallize on trituration with EtOAc. For decomposition temps and analytical data, see Table 4; for IR and ^{1}H-NMR spectroscopic data, see Table 1.

*General procedure for the reaction of 5-chloro-*5H-*dibenzo*[a,d]*cycloheptene* (**6**) *with the silver (diazomethyl)-phosphoryl compounds* **10a–c**. To a soln of 5.00 mmol of **10a–c** in 30 ml of CH_2Cl_2 is added dropwise with stirring within 20 min at 0° a soln of 1.13 g (5.00 mmol) of **6** in 30 ml of the same solvent. As the ppt of AgCl cannot be completely filtered, the mixture is stirred for a further 10 min at room temp, is then concentrated, and the residue chromatographed on 160 g kiesel gel (column: 120 × 2.8 cm) with 800 ml of EtOAc. Concentration at 25°/15 Torr and trituration of the oily residue furnishes the crystalline **8a–c**. For yields, decomposition temp, and analytical data, see Table 4; for IR and ^{1}H-NMR spectroscopic data, see Table 1.

*General procedure for the reaction of 5-chloro-*5H-*dibenzo*[a,d]*cycloheptene* (**6**) *with the mercury bis[diazomethylcarbonyl] compounds* **12a–c** *or* **14**. To a soln of 2.50 mmol of **12a–c** or **14** in 30 ml of CH_2Cl_2 is added dropwise with stirring at 0° a soln of 1.13 g (5.00 mmol) of **6** in 30 ml of CH_2Cl_2. The mixture is then filtered and the yellow filtrate is stirred for 20 min with 40 ml of sat Na_2S aq. The organic phase is separated, dried with Na_2SO_4, and evaporated at 25°/20 Torr. The dirty yellow residue is chromatographed on 120 g of kiesel gel (column: 80 × 2.8 cm) with 600 ml of CH_2Cl_2 to give **13a–c** or **8d** as yellow oils which crystallize on trituration with ether. For yields, decomposition temps, and analytical data, see Table 4; for IR and ^{1}H-NMR spectroscopic data, see Table 1.

*General procedure for the thermolysis of the 5-(diazomethyl)-*5H-*dibenzo*[a,d]*cycloheptenes* **8a–c** *or* **13a–c**; *preparation of the dibenzo*[a,e]*cyclooctenes* **16a–e**, *the dibenzosemibullvalenes* **17a–e**, *and the dibenzoheptafulvene* **18f**. A soln of 3.00 mmol of **8a–c** or **13a–c** in 30 ml of toluene is heated in a preheated oil bath at 110° and treated with 40 mg of copper(II) acetylacetonate. The mixture is heated under reflux until the starting material **8** or **13** can no longer be detected by TLC (20–30 min). The mixture is allowed to cool, concentrated under reduced pressure, and the residue filtered. For **8a–c**, the filtrate is chromatographed on 120 g kiesel gel (column: 80 × 2.8 cm) with 800–1200 ml of ethyl acetate to give isomers **17** and **16**. For **13a** and **b**, chromatography on 50 g of kiesel gel (column: 50 × 2.0 cm) with 200–300 ml of CH_2Cl_2 give mixtures of **16** and **17** which can be separated by fractional crystallization. In the case of **13c**, product **18f** is purified by chromatography on 50 g kiesel gel with 250 ml of toluene. For IR and ^{1}H-NMR spectroscopic data of **16** and **17**, see Tables 2 and 3.

Thermolysis of **8a**

By column chromatography are obtained successively: (a) 60 mg (5%) of *(dibenzotricyclo*[3.3.0.0^{2,8}]*octa - 3,6 - dien - 1 - yl) - diphenylphosphine oxide* (**17a**) as colourless needles with m.p. 180–181° (from CH_2Cl_2–ether). (Found: C, 82.8; H, 5.36. Calc for $C_{28}H_{21}OP$ (404.44): C, 83.15; H, 5.23%.) (b) 0.92 g (76%) of (dibenzo[a,e]cycloocten-5-yl)-diphenylphosphine oxide (**16a**) as colourless prisms with m.p. 185° (from CH_2Cl_2–EtOAc). (Found: C, 83.0; H, 5.28. Calc for $C_{28}H_{21}OP$ (404.44): C, 83.15; H, 5.23%.)

Thermolysis of **8b**

By column chromatography are obtained successively: (a) 84 mg (9%) of *dimethyl dibenzo*[a,e]*cyclooctene-5-phosphonate* (**16b**) as a colourless powder with m.p. 92–93° (from CH_2Cl_2–ether). (Found: C, 69.3; H, 5.62. Calc for $C_{18}H_{17}O_3P$ (312.30): C, 69.22; H, 5.48%.) (b) 0.67 g (71%) of *dimethyl dibenzotricyclo*[3.3.0.0^{2,8}]*octa - 3,6 - diene - 1 - phosphonate* (**17b**) as a colourless powder with m.p. 118–119° (from EtOAc–

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Table 4. Analytical data for the 5-(diazomethyl)-5H-dibenzo[a,d]cycloheptenes 8a–d and 13a–c

Compounds	Yield (%)	m.p. (dec.) °C (recryst. from)	Molecular formula	Elemental analyses			
					C	H	N
[Diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)-methyl]-diphenylphosphine oxide (**8a**)	60	145° (EtOAc)	$C_{28}H_{21}N_2OP$ (432.45)	calc.	77.76	4.89	6.47
				found	77.7	5.04	6.5
Dimethyl [diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)-methanephosphonate (**8b**)	64	119-120° (EtOAc/ether)	$C_{18}H_{17}N_2O_3P$ (340.31)	calc.	63.52	5.03	8.23
				found	63.4	5.02	8.2
Methyl [diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)methyl]-phenylphosphinate (**8c**)	70	86-87° [a] (ether)	$C_{23}H_{19}N_2O_2P$ (386.38)	calc.	71.49	4.95	7.25
				found	71.2	5.06	7.2
Di-tert-butyl-[diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)-methyl]-phosphine oxide (**8d**)	15	155-158° (EtOAc)	$C_{24}H_{29}N_2OP$ (392.47)	calc.	73.44	7.44	7.13
				found	72.4	7.41	7.2
Methyl diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)-acetate (**13a**)	52	122-123° (CH_2Cl_2/ether)	$C_{18}H_{14}N_2O_2$ (290.32)	calc.	74.46	4.86	9.64
				found	74.5	4.91	9.6
Diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)-methyl phenyl ketone (**13b**)	59	120-122° (CH_2Cl_2/ether)	$C_{23}H_{16}N_2O$ (336.39)	calc.	82.12	4.79	8.32
				found	82.4	4.99	8.3
tert-Butyl diazo-(5H-dibenzo[a,d]cyclohepten-5-yl)-methyl ketone (**13c**)	53	121° (CH_2Cl_2/ether)	$C_{21}H_{20}N_2O$ (316.40)	calc.	79.71	6.37	8.85
				found	80.0	6.51	8.9

[a] Melting without decomposition.

ether). ^{13}C-NMR ($CDCl_3$): δ 42.40 (dd, $^1J_{C,H} = 171.3$ Hz, $^2J_{C,P} = 1.90$ Hz, C-2/C-8), 51.86 (d, $^1J_{C,P} = 197.4$ Hz, C-1), 52.5 (dq, $^1J_{C,H} = 148.0$ Hz, $^2J_{C,P} = 5.0$ Hz, $PO\underline{C}H_3$), 54.87 (dd, $^1J_{C,H} = 148.0$ Hz, $^2J_{C,P} = 7.84$ Hz, C-5), 120.88–149.70 (aromatic C). (Found: C, 69.4; H, 5.48. Calc for $C_{18}H_{17}O_3P$ (312.30): C, 69.22; H, 5.48%.)

Thermolysis of **8c**

By column chromatography are obtained successively: (a) 0.56 g (52%) of *methyl (dibenzo*[a,e]*cycloocten-5-yl)-phenylphosphinate* (**16c**) as colourless crystals with m.p. 135–136° (from EtOAc–ether). (Found: C, 77.0; H, 5.51. Calc for $C_{23}H_{19}O_2P$ (358.37): C, 77.08; H, 5.34%.) (b) 0.16 g (15%) of *methyl (dibenzotricyclo*[3.3.0.0^{2,8}]*octa - 3,6 - dien - 1 - yl) - phenylphosphinate* (**17c**) as colourless needles with m.p. 169–170° (from ether). (Found: C, 77.0; H, 5.43. Calc for $C_{23}H_{19}O_2P$ (358.37): C, 77.08; H, 5.34%.)

Thermolysis of **13a**

By column chromatography is obtained 0.60 g (76%) of a colourless resin consisting of **16d** and **17d** in a ratio of 60:40 (according to the ^1H-NMR spectrum). The resin is taken up in 3 ml of CH_2Cl_2–ether (1:1), triturated, and cooled to −20° to give, after 24 h, 0.15 g (19%) of *methyl (dibenzotricyclo*[3.3.0.0^{2,8}]*octa - 3,6 - dien - 1 - yl) - carboxylate* (**17d**) as colourless crystals with m.p. 165–166° (lit.[12] 169.5–170.5°). ^1H-NMR comparison with the product described in lit.[12] (Found: C, 82.0; H, 5.45. Calc for $C_{18}H_{14}O_2$ (262.30): C, 82.42; H, 5.37%.) All attempts to obtain *methyl (dibenzo*[a,e]*cycloocten-5-yl)-carboxylate* (**16d**) in the pure state from the filtrate of **17a** were unsuccessful.

Thermolysis of **13b**

By column chromatography is obtained 0.68 g (74%) of a colourless resin consisting of **16e** and **17e** in a ratio of 60:40 (according to the ^1H-NMR spectrum). The resin is taken up in 4 ml of CH_2Cl_2–EtOAc (1:1), triturated, and cooled to −20° to give, after 24 h, 0.32 g (35%) of *dibenzo*[a,e]*cycloocten-5-yl phenyl ketone* (**16e**) as colourless cubes with m.p. 154° (from CH_2Cl_2–EtOAc). (Found: C, 89.5; H, 5.39. Calc for $C_{23}H_{16}O$ (308.38): C, 89.58; H, 5.22%.) Evaporation of the filtrate and trituration of the oily residue with a little ether gives 0.18 g (19%) of *dibenzotricyclo*[3.3.0.0^{2,8}]*octa-3,6-dien-1-yl phenyl ketone* (**17e**) as colourless prisms with m.p. 149–150° (from CH_2Cl_2–ether). ^{13}C-NMR ($CDCl_3$): δ 48.10 (d, $^1J_{C,H} = 171.3$ Hz, C-2/C-8), 56.57 (d, $^1J_{C,H} = 145.2$ Hz, C-5), 69.92 (s, C-1), 121.3–150.14 (aromatic C), 199.72 (CO). (Found: C, 89.5; H, 5.39. Calc for $C_{23}H_{16}O$ (303.38): C, 89.58; H, 5.22%.)

Thermolysis of **13c**

The crude product consists of a 4:1 mixture of **18f** and **17f** (according to the ^1H-NMR spectrum [**17f**: δ 1.17 (s, 9H, $(H_3C)_3C$), 3.79 (s, 2H, H-2/H-8), 5.06 (s, 1H, H-5)]. Column chromatography of this mixture gives 0.68 g (78%) of t-*butyl dibenzo*[a,d]*heptafulven-12-yl ketone* (**18f**) as colourless prisms with m.p. 89–90° (from ether). IR (KBr): 1670 (CO), 1625 cm^{-1} (C=C); ^1H-NMR ($CDCl_3$): δ 1.10 [s, 9H, $(H_3C)_3C$], 6.85 (s, 3H, H-10, H-11, H-12), 7.0–7.3 (m, 8H, aromatic H); ^{13}C-NMR ($CDCl_3$): δ 27.78 [q, $^1J_{C,H} = 123.6$ Hz, $(H_3\underline{C})_3C$], 44.31 [s, $(H_3C)_3\underline{C}$], 125.27–146.44 (aromatic C/olefinic C, an exact assignment is not possible), 21.37 (s, CO). (Found: C, 87.3; H, 6.85. Calc for $C_{21}H_{20}O$ (288.39): C, 87.46; H, 6.99%.)

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