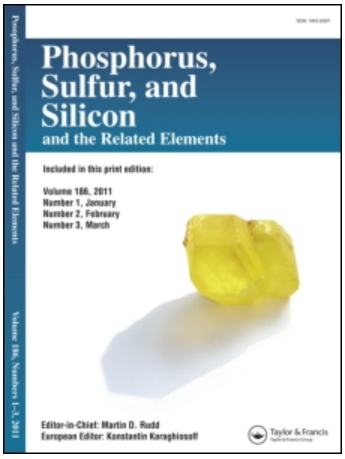


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE FORMATION OF THE BENZO[f]-3-PHOSPHABICYCLO[3.3.0]OCT-6-ENE RING SYSTEM IN THE FRIEDEL-CRAFTS REACTION OF THE ADDUCTS OF 2,5-DIHYDRO-1H-PHOSPHOLE 1-OXIDES WITH DICHLOROCARBENE

György Keglevich[a]; Attila Kovács[b]; Kálmán Újszászy[c]; Gábor Tóth[d]; László Tóke[a]
[a] Department of Organic Chemical Technology, Institute for General and Analytical Chemistry, Technical University of Budapest, Budapest, Hungary [b] Institute for General and Analytical Chemistry, Technical University of Budapest, Budapest, Hungary [c] EGIS Pharmaceuticals, Budapest, Hungary [d] Technical Analytical Research Group of the Hungarian Academy of Sciences, Technical University of Budapest, Budapest, Hungary

To cite this Article Keglevich, György , Kovács, Attila , Újszászy, Kálmán , Tóth, Gábor and Tóke, László(1991) 'THE FORMATION OF THE BENZO[f]-3-PHOSPHABICYCLO[3.3.0]OCT-6-ENE RING SYSTEM IN THE FRIEDEL-CRAFTS REACTION OF THE ADDUCTS OF 2,5-DIHYDRO-1H-PHOSPHOLE 1-OXIDES WITH DICHLOROCARBENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 63: 1, 131 — 141
To link to this Article: DOI: 10.1080/10426509108029436
URL: http://dx.doi.org/10.1080/10426509108029436

Phosphorus, Sulfur, and Silicon, 1991, Vol. 63, pp. 131–141
Reprints available directly from the publisher
Photocopying permitted by license only

THE FORMATION OF THE BENZO[f]-3-PHOSPHABICYCLO[3.3.0]OCT-6-ENE RING SYSTEM IN THE FRIEDEL-CRAFTS REACTION OF THE ADDUCTS OF 2,5-DIHYDRO-1H-PHOSPHOLE 1-OXIDES WITH DICHLOROCARBENE

GYÖRGY KEGLEVICH,[1] ATTILA KOVÁCS,[2] KÁLMÁN ÚJSZÁSZY,[3] GÁBOR TÓTH[4] and LÁSZLÓ TŐKE[1]

[1]*Department of Organic Chemical Technology;* [2]*Institute for General and Analytical Chemistry, Technical University of Budapest, 1521 Budapest, Hungary;* [3]*EGIS Pharmaceuticals, 1475 Budapest, Hungary;* [4]*Technical Analytical Research Group of the Hungarian Academy of Sciences, Technical University of Budapest, 1111 Budapest, Hungary*

(Received February 2, 1991; in final form May 21, 1991)

Depending on the nature of the aromatic substrate the Friedel-Crafts reaction of P-substituted 6,6-dichloro-3-phosphabicyclo[3.1.0]hexane 3-oxides with substituted benzenes may afford two kinds of benzo-phosphabicyclooctene derivatives as well as benzyl-phenyl-hexahydrophosphinine oxides. The formation of the tricyclic products involves the rather rarely occurring opening of the cyclopropane ring, while the benzyl-phenyl-derivatives are formed by ring expansion. Reductive type of Friedel-Crafts reaction is responsible for the formation of a part of the products. In contrast to our earlier proposal the displacement of the two chlorine atoms without the opening of the cyclopropane ring does not take place. The structure of the products was elucidated by ^{13}C, ^{1}H, ^{31}P NMR and mass spectroscopy.

Key words: Dihydrophosphole oxide-dichlorocarbene adduct; Friedel-Crafts reaction; benzo-phosphabicyclooctene oxide; hexahydrophosphinine oxide; reduction, mechanism.

INTRODUCTION

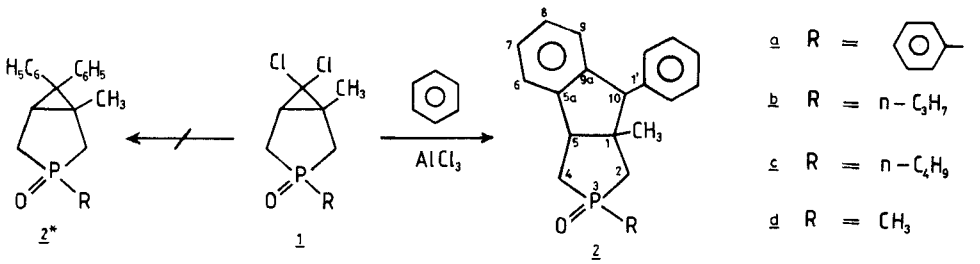
The Friedel-Crafts reactions of the adducts of olefinic compounds with dihalogenocarbene can take place in different ways. Indano-derivatives are formed in the Friedel-Crafts reaction of alkyl-substituted dihalogeno-cyclopropanes,[1] while bicyclic adducts may provide a variety of products depending on the nature of the active agent and the aromatic substrate.[2–4] The Friedel-Crafts reaction of 6,6-dichlorobicyclo[3.1.0]hexane with benzene in the presence of aluminum-trichloride produces a mixture of phenyl- and diphenyl-cyclohexanes,[2] while the similar reaction of the dichloronorcarane (7,7-dichlorobicyclo[4.1.0]heptane) gives benzyl-cyclohexane together with fluorene derivatives.[3] The Friedel-Crafts reaction of other bicyclic cyclopropanes with substituted benzenes has also been studied.[4]

Formation of the products mentioned can be explained by assuming an arylation connected with the opening of the cyclopropane ring to be the first step.[1c–4] To be able to derive certain products a reduction step should also be presumed to exist.[2,3]

In the light of the experiences outlined above we decided to examine how the adducts of 2,5-dihydro-1H-phosphole oxides with dichlorocarbene react with different benzene derivatives in the presence of aluminum-trichloride.

RESULTS AND DISCUSSION

Among the methods[5] suggested by us for the opening of the dichloro-cyclopropane ring in the adducts of 2,5-dihydro-1H-phosphole 1-oxides with dichlorocarbene, procedures using electrophiles (silver-, or mercury salts) have also been described.[6,7] In one of these papers[7] we claimed that the Friedel-Crafts reaction of the P-phenyl adduct (1a) with benzene in the presence of aluminum-trichloride afforded triphenyl-phospabicyclo[3.1.0]hexane derivative 2*a. No chlorine atom was present in the product due to the disubstitution. Structure 2*a was suggested by ^{13}C and ^{1}H NMR and mass spectra. Later, in the course of the detailed re-examination and extension of this kind of Friedel-Crafts reaction, the ^{13}C NMR spectrum of the product obtained by the "Attached Proton Test" (APT)-technique revealed the presence of only one quaternary skeleton carbon atom (at 55.1 ppm) and two CH units (at 51.8 and 60.9 ppm) in the sp^3 region beside the two methylene groups adjacent to the P=O group, indicating that our earlier assignment was not correct. Adding the two quaternary aromatic skeleton carbon atoms suggested by the shifts at 143.9 and 144.6 ppm, one can construct the benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene structure (2a) isomeric with the phenyl-3-phosphabicyclo[3.1.0]hexane (2*a) proposed earlier (Scheme I). ^{13}C NMR data for 2a can be found in Table I.



SCHEME I

TABLE I

^{31}P and ^{13}C NMR data for 10-aryl-1-methyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-oxides (2a–c, $4a_1$ and $4a_2$) in $CDCl_3$

Compound	2a	2b	2c	2d	$4a_1$	$4a_2$
^{31}P	60.7	71.1	71.8		61.8	61.3
C-1	55.1 (8.2)	54.2 (7.2)	54.7 (6.9)	54.8 (7.4)	58.3 (11.0)	55.7 (8.7)
C-2	42.6 (65.1)	39.6 (62.3)	40.5 (62.8)	41.8 (64.4)	37.1 (67.4)	40.5 (69.6)
C-4	33.7 (63.1)	30.4 (59.8)	31.8 (61.7)	32.3 (62.3)	34.0 (61.6)	35.1 (63.1)
C-5	51.8 (7.2)	51.0 (7.2)	51.2 (7.6)	51.8 (7.3)	52.9 (7.3)	52.3 (7.7)
C-5a	143.9*	143.8*	144.1*	144.0*	141.2*	141.2*
C-9a	144.6*	144.1*	144.6*	144.6*	143.9*	145.3*
C-10	60.9 (11.8)	60.7 (10.7)	61.1 (10.4)	61.4 (11.0)	60.9 (11.7)	61.5 (13.2)
C-1′	140.5*	140.1*	140.3*	140.3*	137.2*	137.7*
1—CH_3	23.3	23.3	23.6	23.5	24.7	23.4
Ar—CH_3	—	—	—	—	20.9	21.2
	—	—	—	—	21.3	21.3

*Tentative assignment.

All chemical shifts and couplings match the values expected. The singlet at 4.21 ppm in the ^1H NMR spectrum of 2a is in good accord with the presence of the C(10)H part of product 2a.

Our experiments showed that the same type of product (2) is formed also in the Friedel-Crafts reaction of P-alkyl substituted adducts (1b–d) with benzene (Scheme I). (Accordingly, 2c is obtained from the Friedel-Crafts reaction of 1c, and not 2*c as we suggested earlier.[7]) The ^{13}C and ^1H NMR spectra of the P-alkyl products (2b–d) have the same characteristic features as the phenyl-derivative (2a). The ^{13}C NMR assignments were confirmed by APT-spectra. ^{31}P and ^{13}C NMR spectral parameters for compounds 2b–d are listed in Table I. The results of a detailed NMR study by special NMR techniques suggesting the conformation of the products (2) will be published elsewhere.

Mass spectra of products 2a–d show $m/z = 218$ to be the base peak. This fragment can be deduced by the loss of the (skeleton) methyl group and the departure of the P(0)R part from the molecule. The loss of the phenyl group and the formation of the tropylium cation can also be observed. The mass spectra revealed the presence of no chlorine atom in the molecular ion and in the fragments. Mass spectral (MS) data for compounds 2 were included into Table II. The molecular formulas for 2a–d were confirmed by high resolution MS measurements.

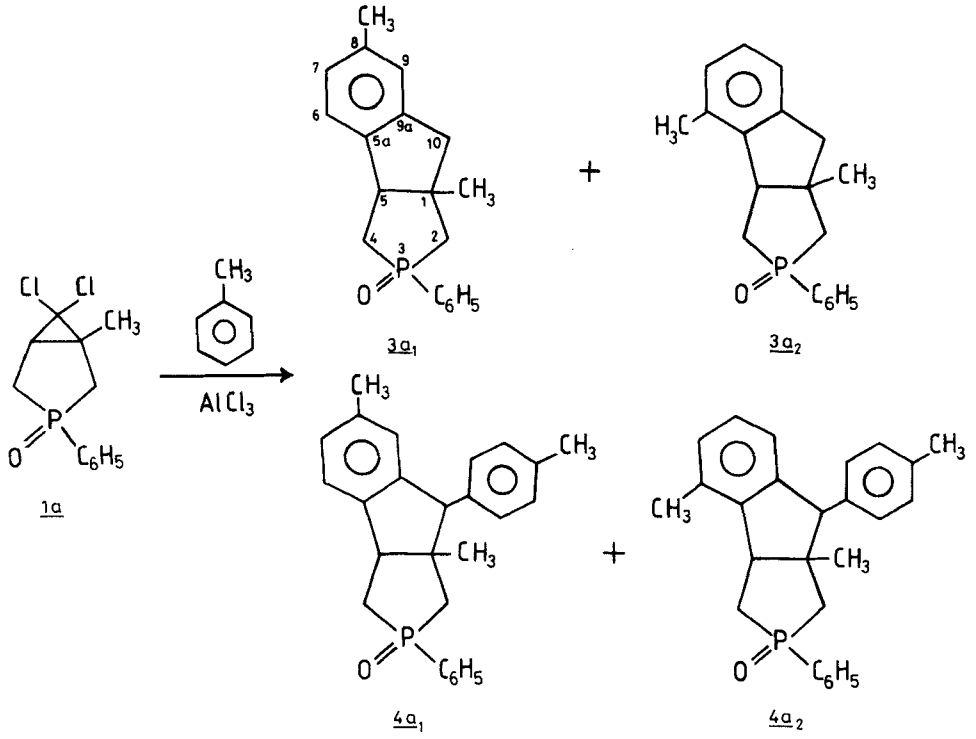
As, according to the literature,[4] the outcome of the Friedel-Crafts reactions may also be influenced by the nature of the aromatic substrate, the effect of substituted benzenes was also tried out. The ^{31}P NMR spectrum of the crude product obtained from the Friedel-Crafts reaction of the phenyl-substituted adduct (1a) with toluene showed the presence of four major components. We could achieve quite good separation of the components of the mixture by means of repeated column chromatography. These samples with a purity of 90–98% were subjected to ^{31}P, ^{13}C and ^1H NMR and GC-MS investigations. Examinations revealed the formation of two kinds of products, among which one is analogous with the phenyl-benzophosphabicyclooctene derivatives (2) mentioned above and can thus be formulated as 4a, while the other product, according to its mass spectrum, contains a hydrogen atom instead of the aromatic ring in position 10 suggesting structure 3a. Moreover both products are formed as two aromatic ring isomers ($3a_1$ and $3a_2$, and $4a_1$ and $4a_2$, respectively) (Scheme II). The isomerism is supported by the fact that the mass spectra of species a_1 and a_2 show the same molecular ion (for 3, $m/z = 296$,

TABLE II

MS data for 10-aryl-1-methyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-oxides (2a–c, $4a_1$ and $4a_2$)

Compound	2a	2b	2c	2d	$4a_1$	$4a_2$
Fragments (m/z)			Relative intensity %			
M^+	74	78	68	63	90	56
$M—CH_3^+$	10	12	6	16	17	15
$M—Ar^+$ (Ar=Ph or tolyl)	63	40	18	48	58[a]	43[b]
$M—CH_3$-$(P(0)R + H)^+$ (218 or 246)	100	100	100	100	100	100
tropylium$^+$ (91 or 105)	91	60	42	35	30	29
aryl$^+$ (+H) (78 or 91)	47	91	82	24	35	30

[a]M-77 (21%).
[b]M-77 (76%).



SCHEME II

TABLE III

^{31}P and ^{13}C NMR data for 1-methyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-oxides (3a$_1$, 3a$_2$, 5a–c and 8a) in $CDCl_3$

Compound	3a$_1$	3a$_2$	5a	5b	5c	8a
^{31}P	63.8	63.9	61.9	72.2	72.8	62.8
C-1	46.3 (12.5)	46.5 (7.3)	48.7 (6.6)	47.7 (6.6)	47.9 (7.4)	51.7 (8.8)
C-2	40.7 (65.9)	40.4 (64.5)	42.2 (64.5)	39.7 (60.9)	39.8 (61.5)	41.5 (65.2)
C-4	34.0 (62.3)	34.0 (63.0)	34.9 (63.7)	32.8 (60.0)	30.8 (61.5)	34.4 (63.0)
C-5	53.5 (8.1)	54.0 (9.5)	54.1 (8.1)	52.9 (7.3)	53.2 (7.3)	53.8 (8.1)
C-5a	141.3 (9.5)	142.1 (9.7)	143.1 (10.5)	143.1 (9.5)	143.3 (9.5)	141.7 (7.3)
C-9a	141.2	141.2	139.5	138.7	139.0	139.0
C-10	51.6 (8.8)	50.5 (8.8)	46.7 (5.8)	45.8 (3.7)	46.0 (3.6)	46.3 (11.8)
1—CH_3	25.9	28.1 (8.1)	29.4 (5.1)	28.8 (7.4)	29.3 (10.3)	26.3
Ar—CH_3	20.8	20.9	18.5	17.9	18.1	19.6
	—	—	18.6	18.1	18.3	19.6

TABLE IV

MS data for 1-methyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-oxides (3a$_1$, 3a$_2$, 5a–c and 8a

Compound	3a$_1$	3a$_2$	5a	5b	5c	8a
Fragments (*m/z*)	Relative intensity %					
M^+	47	32	57	52	36	38
M—CH_3^+	10	5	15	20	10	6
M—CH_3-(P(0)R + H)$^+$ (156 or 170)	100	100	100	100	100	100

while for 4, m/z = 386) and the a_1 and a_2 pairs of products 3 and 4 display similar fragmentation and possess similar ^{13}C NMR features. The ^{13}C NMR and MS characteristics for isomers $4a_1$ and $4a_2$ are rather similar to those for the C-phenyl-derivatives (2) as can be seen from Table I and Table II, respectively.

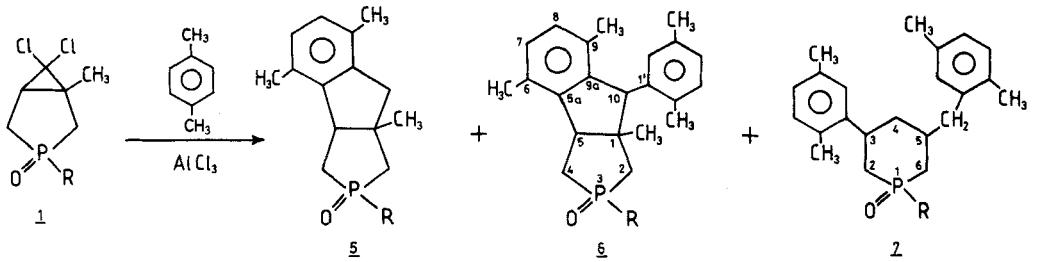
Beside the MS data, the ^{13}C NMR spectra obtained by the APT-technique also confirm structures $3a_1$ and $3a_2$ by showing the presence of three skeleton methylene signals. The ^{13}C NMR and MS data for the two isomers (a_1 and a_2) of 3 are provided in Table III and Table IV, respectively.

We should like to mention that the position of the methyl group in the fused aromatic ring in products 3a and 4a was substantiated on the basis of the orientation rules (as will be shown in the section dealing with the mechanism). As the position of the methyl group in the fused aromatic ring could only be confirmed in the case of the a_1 isomer, the position of the methyl substituent in the a_2 isomer should be regarded to be tentative. A reduction step must be assumed to exist to explain the formation of products $3a_1$ and $3a_2$, as we shall show in a later section.

The Friedel-Crafts reaction of the dihydro-1H-phosphole oxide-dichlorocarbene adducts (1a–c) with 1,4-xylene was also investigated. Three products, namely benzo-phosphabicyclooctene derivatives 5 and 6, and benzyl-phenyl-hexahydrophosphinine oxide 7 could be separated from the mixture by means of column chromatography (Scheme III).

The ^{13}C NMR and MS features of products 5a–c are similar to those of the isomers of 3a, as it can be seen from Table III and Table IV, respectively. A fragmentation involving the departure of the P(0)R part and the loss of the (skeleton) methyl group results the base peak in the mass spectra of both 3a and 5a–c. The singlet at ~2.8 ppm in their ^1H NMR spectra justifies the $C(10)H_2$ part of the skeleton.

The NMR data of compounds 6b,c are in accord with the structure proposed. The ^{13}C NMR spectra obtained by APT-technique refer to the same structural elements that can be found in products 2 and 4a (Table V). The C(10)H unit in compounds 6b,c is confirmed by the singlet at ~4.1 ppm in their ^1H NMR spectra. The mass spectra for products 6b and 6c reveal the appropriate molecular ion (m/z = 380 and 394, respectively) and display a fragmentation very similar to that of analogous derivatives (2 and 4a). The only difference is that a new fragment (m/z = 170) coming from the joint loss of the xylyl-ring, methyl group and the P(0)R part can also be observed in their spectra which happens to appear as the base peak (Table VI). The preferred superposition of the fragmentations may be



SCHEME III

TABLE V

^{31}P and ^{13}C NMR data for 10-aryl-1-methyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-oxides (6b and 6c) in $CDCl_3$

Compound	6b	6c
^{31}P	75.6	76.4
C-1	52.1 (5.2)	52.2 (5.2)
C-2	35.3 (61.5)	35.3 (62.3)
C-4	31.5 (60.8)	29.3 (60.8)
C-5	55.2 (8.1)	55.4 (8.1)
C-5a	142.8*	143.0*
C-9a	143.2*	143.2*
C-10	57.4 (2.2)	57.6 (3.6)
C-1′	141.7*	142.0*
1—CH_3	33.0	33.2
Ar—CH_3	17.9	18.2
	18.1	18.4
	20.3	20.6
	19.7	20.0

*Tentative assignment.

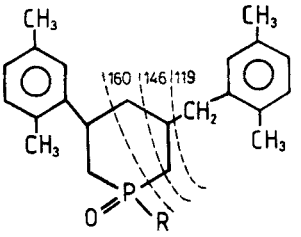
TABLE VI

MS data for 10-(2,5-dimethylphenyl-)1,6,9-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-oxide (6b and 6c)

Compound	6b	6c
Fragments (*m/z*)	Relative intensity %	
M^+	49	50
M—CH_3^+	28	22
M-xylyl$^+$ +H	29	16
M—CH_3-(P(0)R + H)$^+$ (274)	42	33
M—CH_3-xylyl-P(0)R$^+$ (170)	100	100

due to the difference in configuration at C_{10}. The ^{13}C NMR spectral parameters seem to confirm this assumption. Further NMR study on the stereostructure of products 6b,c is in progress.

The formation of the benzyl-phenyl-hexahydrophosphinine oxides (7a-c) was substantiated on the basis of ^{31}P and ^{1}H NMR and mass spectroscopy. The mass spectra reveal the appropriate molecular ions and characteristic fragmentations like the loss of the diMeBz group (M-119) and the departure of diMeBzC_2H_3 and diMeBzC_3H_5 (M-146 and M-160, respectively) (Figure 1). The latter type of fragmentation observed also for other phospinine oxide derivatives[6] refers to structure 7. The ^{31}P NMR chemical shifts of 33.4–41.6 ppm are also affirmative as match the range characteristic for phosphinine oxides.[8] The lack of the skeleton methyl group in products 7a–c is obvious from their ^{1}H NMR spectra. The relative ^{1}H NMR intensity of the xylyl-methyl groups and the aromatic protons has the expected value. It can also be seen from the mass spectra that the benzyl-phenyl-derivatives (7a–c) are accompanied by the homologues containing an additional or a missing methyl group in a quantity of about 30%. These impurities may come from intermolecular methyl-migration but the intramolecular migration is also probable on



7a-c

FIGURE 1

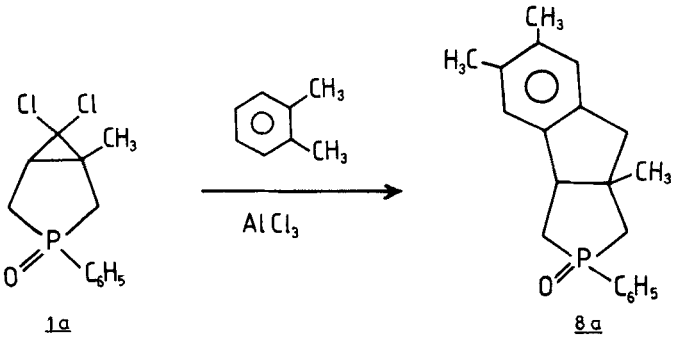
the basis of the rather complex ^{13}C NMR spectra of the products (7). Alkyl-migration in the course of the Friedel-Crafts reaction is a known process.[9]

In the last case 1,2-xylene was the reagent in the Friedel-Crafts reaction of the phenyl-substituted adduct (1a). Benzo-phosphabicyclooctene 8a could be prepared from the mixture after column chromatography (Scheme IV). The ^{13}C NMR spectrum of the product shows also the presence of a small amount of the aromatic ring isomers. The ^{13}C NMR features for main isomer 8a are shown in Table III, while the MS data are listed in Table IV.

Benzo-phosphabicyclooctene oxides prepared are all new compounds. An indeno-dihydrophosphole-derivative having a somewhat similar framework was described earlier by Quin et al.[10]

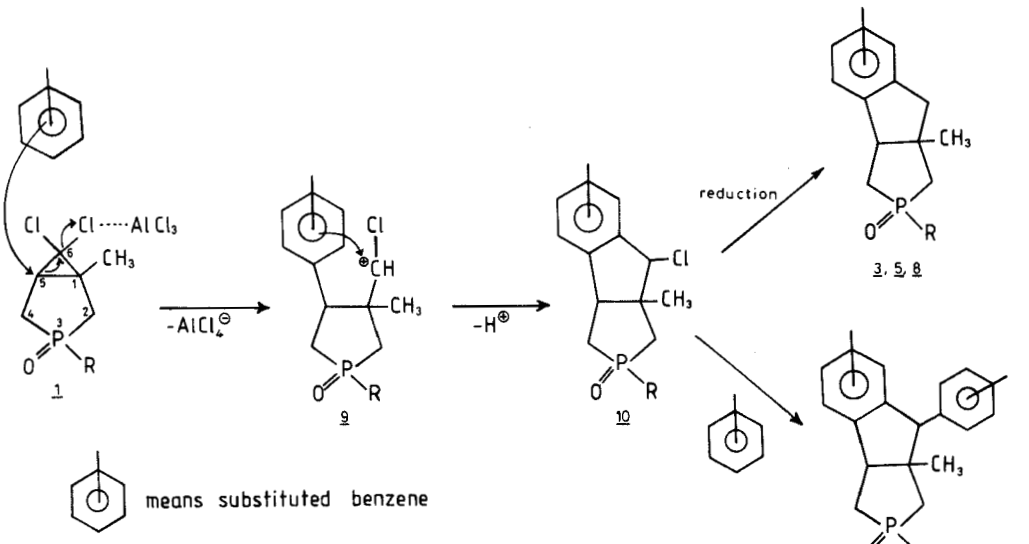
Finally it should be considered how the products prepared can be formed in the course of the reaction. We have already mentioned that the arylation accompanied by the opening of the cyclopropane ring is the first step in the Friedel-Crafts reaction of dihalogeno-cyclopropanes with aromatic substrates.[1-4] Theoretically the cyclopropane ring can open up in three ways. In the case of bicyclic-derivatives one of these routes involving the fission of the bridging bond leads to ring expanded products,[2] while the other two kinds of opening occur rather rarely.[3,11] According to Scheme V and Scheme VI both the rather unusual ring opening and the one resulting ring expansion occur in the Friedel-Crafts reaction of dihydro-1H-phosphole oxide-dichlorocarbene adducts (1) with substituted benzenes.

Scheme V shows the possible way for the formation of the benzo-phosphabicyclooctene derivatives. Three elemental steps may take place in the first stage of

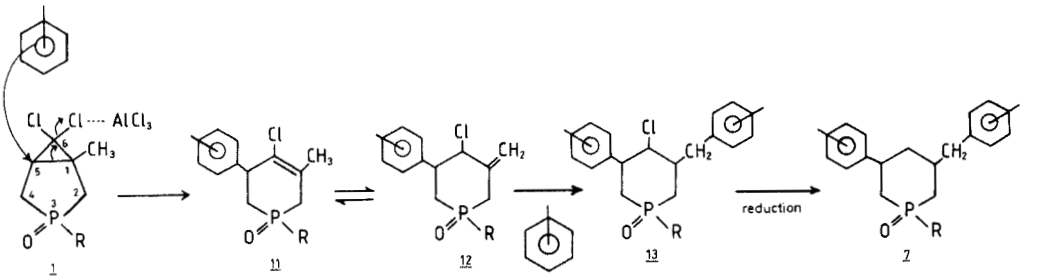


1a 8a

SCHEME IV



SCHEME V



SCHEME VI

the reaction: the aluminum-trichloride promoted departure of the appropriate chlorine atom, the opening of the cyclopropane ring by the rarely occurring rupture of the C_5—C_6 bond and the nucleophilic attack of the aromatic substrate on C_5 to give intermediate 9. This species may take part in an intramolecular arylation reaction producing chloro-derivative 10, which may react with a second molecule of (substituted) benzene to yield benzo-phosphabicyclooctenes 2, 4 or 6. Intermediate 10 may also be the subject of reduction resulting products 3, 5 or 8.

Another way involving the fission of the C_1—C_5 bond of adduct 1 in the first step can also be realized to yield ring expanded product 11 (Scheme VI). Phospinine oxide 11 is then isomerized to intermediate 12 under the circumstances of the reaction. Chloro-derivative 13 is obtained on arylation of species 12 to give benzylphenylphosphinine oxide 7 after reduction. This kind of product could only be prepared in the reaction with 1,4-xylene.

The substitution on the aromatic ring takes place according to the orientation rules to provide the two isomers (a_1 and a_2) of products 3 and 4.

The formation of benzo-phosphabicyclooctene derivatives 3, 5 and 8 and benzylphenylphosphinine oxide 7 can only be explained by assuming a reduction.

Similar reductive type of Friedel-Crafts reaction was observed during the arylation of 6,6-dichloro-bicyclo[3.1.0]hexane[2] and the dichloronorcarane.[3] At the present stage of our work we can not establish the origin of the hydrogen.

EXPERIMENTAL

^{31}P, ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 100 MHz instrument operating at 40.26, 100.0 and 25.0 MHz, respectively. Chemical shifts are downfield relative to 85% phosphoric acid and to tetramethylsilane, respectively, and have a positive sign. All coupling constants are given in Hertz. Infrared spectra were taken on a SPECORD 75 spectrometer. Mass spectra were obtained on a MS 25-RFA instrument at 70 eV.

The adducts of 2,5-dihydro-1H-phosphole 1-oxides with dichlorocarbene (1a–d) were prepared as described earlier.[12,5]

3,10-Diphenyl-1-methyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (2a). The mixture of 0.9 g (3.27 mmol) of 1a and 1.31 g (9.81 mmol) of aluminum-trichloride in 30 ml of benzene was stirred at the boiling point for 4 hours. After cooling to room temperature, 30 ml of benzene and 10 ml of ice-water was added and the mixture was stirred for a short period of time. The organic phase was dried over sodium sulfate and the solvent was evaporated to give crude product which was purified by repeated column chromatography on silica gel using chloroform-methanol (98:2) and acetone as the eluants. 0.6 g (51%) of 2a was obtained after recrystallization from n-pentane-acetone 3:2; mp. 182-3°C; ^{31}P and ^{13}C NMR, Table I; ^{1}H NMR ($CDCL_3$) δ 1.10 (s, 3H, C_1—CH_3), 1.9–2.2 (m, 2H, C(2)H_2), 2.4–2.7 (m, 2H, C(4)H_2), 3.5–3.9 (m, 1H, C(5)H), 4.15 (s, 1H, C(10)H), 6.8–7.5 (m, 14H, ArH); MS, Table II; IR (KBr disc) 2920, 1580, 1430, 1180, 730 cm^{-1}; M^{+}_{found} = 358.1500, $C_{24}H_{23}OP$ requires 358.1487.

1-Methyl-10-phenyl-3-n-propyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (2b) *was prepared on a similar way from* 1b. Yield 60%; ^{31}P and ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 3H, C_1—CH_3), 1.6–2.0 (m, 2H, C(2)H_2), 2.1–2.4 (m, 2H, C(4)H_2), 3.4–3.8 (m, 1H, C(5)(H), 4.15 (s, 1H, C(10)H), 6.8–7.5 (m, 9H, ArH); MS, Table II; IR (neat) 2920, 1590, 1440, 1160, 740 cm^{-1}; M^{+}_{found} = 324.1670, $C_{21}H_{25}OP$ requires 324.1643.

3-n-Butyl-1-methyl-10-phenyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (2c) *was prepared on a similar way from* 1c. Yield 65%; ^{31}P and ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 0.81 (*t*, 3H, C(4')H_3), 0.97 (s, 3H, C_1—CH_3), 3.4–3.8 (m, 1H, C(5)H), 4.10 (s, 1H, C(10)H), 6.8–7.5 (m, 9H, ArH); MS, Table II; IR (neat) 2940, 1600, 1450, 1160, 740 cm^{-1}; M^{+}_{found} = 338.1825, $C_{22}H_{27}OP$ requires 338.1800.

1,3-Dimethyl-10-phenyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (2d) *was prepared in a similar way from* 1d. Yield 21%; ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 3H, C_1—CH_3), 1.23 (d, 3H, P—CH_3, $^{2}J_{PH}$ = 13), 4.04 (s, 1H, C(10)H), 6.6–7.6 (m, 9H, ArH); MS Table II; IR (neat) 2950, 1580, 1430, 1160, 720 cm^{-1}; M^{+}_{found} = 296.1320, $C_{19}H_{21}PO$ requires 296.1330.

1,8- and 1,6-Dimethyl-10-(4-methylphenyl-)3-phenyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (4a_1 *and* 4a_2) *and 1,8- and 1,6-Dimethyl-3-phenyl-benzo[f]-3-phosphabicyclo-[3.3.0]oct-6-ene 3-Oxide* (3a_1 *and* 3a_2). The reaction of 0.9 g (3.27 mmol) of 1a, 1.31 g (9.81 mmol) of aluminum-trichloride and 30 ml of toluene was carried out at 80°C as that of 1a with benzene. Repeated column chromatography of the crude product using chloroform-methanol (97:3) and benzene-acetone (4:6) afforded 0.15 g (12%) of 4a_1, 0.06 g (5%) of 4a_2, 0.15 g (16%) of 3a_1 and 0.07 g (7%) of 3a_2.

4a_1: ^{31}P and ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3H, C_1—CH_3), 2.34 (s, 6H, Ar—CH_3), 4.20 (s, 1H, C(10)H), 6.8–7.5 (m, 12H, ArH) MS, Table II; M^{+}_{found} = 386.1811, $C_{26}H_{27}OP$ requires 386.1800.

4a_2: ^{31}P and ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 1H, C(10)H); MS, Table II;

3a_1: ^{31}P and ^{13}C NMR, Table III; ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 3H, C_1—CH_3), 2.33 (s, 3H, Ar—CH_3), 2.91 (s, 2H, C(10)H_2), 6.75–7.5 (m, 8H, ArH); MS, Table IV; M^{+}_{found} = 296.1350, $C_{19}H_{21}OP$ requires 296.1330.

3a_2: ^{31}P and ^{13}C NMR Table III; ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 2H, C(10)H_2); MS, Table IV;

10-(2,5-Dimethylphenyl-)3-n-propyl-1,6,9-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (6b), *3-n-Propyl-1,6,9-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide* (5b) *and 5-(2,5-*

dimethylbenzyl-)3-(2,5-dimethylphenyl-)-1,2,3,4,5,6-hexahydro-1-n-propylphosphinine 1-Oxide (7b). The reaction of 0.79 g (3.27 mmol) of 1b and 30 ml of 1,4-xylene in the presence of 1.31 g (9.81 mmol) of aluminum-trichloride was carried out and the mixture was worked up as in the earlier cases to give 0.15 g (12%) of 6b, 0.23 g (25%) of 5b and 0.11 g (9%) of 7b.

6b: ^{31}P and ^{13}C NMR, Table V; ^1H NMR ($CDCl_3$) δ 4.11 (s, 1H, C(10)H), 6.1–7.2 (m, 5H, ArH); MS, Table VI; M^+_{found} = 380.2297, $C_{25}H_{33}OP$ requires 380.2269.

5b: ^{31}P and ^{13}C NMR, Table III; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3H, C_1—CH_3), 2.21 and 2.27 (s, 6H, Ar—CH_3), 2.76 (s, 2H, C(10)H_2) 6.5–7.1 (m, 2H, ArH); MS, Table IV; M^+_{found} = 276.1706, $C_{17}H_{25}OP$ requires 276.1643.

7b: ^{31}P NMR ($CDCl_3$) δ + 41.4; ^1H NMR δ 2.25 (s, 12H, Ar—CH_3), 6.7–7.2 (m, 6H, ArH); MS, *m/z*: 382, 263, 235, 221; IR (neat) 2920, 1600, 1440, 1145 cm^{-1}; M^+_{found} = 382.2445, $C_{25}H_{35}OP$ requires 382.2425.

3-n-Butyl-10-(2,5-dimethylphenyl-)1,6,9-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (6c), *3-n-Butyl-1,6,9-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide* (5c) *and 1-n-Butyl-5-(2,5-dimethylbenzyl-)3-(2,5-dimethylphenyl-)1,2,3,4,5,6-hexahydrophosphinine 1-Oxide* (7c) *were prepared as the n-propyl-derivatives.*

6c: Yield 10%; ^{31}P and ^{13}C NMR, Table V; ^1H NMR ($CDCl_3$) 4.16 (s, 1H, C(10)H), 6.1–7.1 (m, 5H, ArH); MS, Table VI; M^+_{found} = 394.2451, $C_{26}H_{35}OP$ requires 394.2426.

5c: Yield 16%, ^{31}P and ^{13}C NMR, Table III; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3H, C_1—CH_3), 2.16 and 2.23 (s, 6H, Ar—CH_3), 2.76 (s, 2H, C(10)H_2), 6.6–7.1 (m, 2H, ArH); MS, Table IV; M^+_{found} = 290.1810, $C_{18}H_{27}OP$ requires 290.1800.

7c: Yield 10%; ^{31}P NMR ($CDCl_3$) δ + 41.6; ^1H NMR δ 2.24 (s, 12H, Ar—CH_3), 6.65–7.18 (m, 6H, ArH); MS, *m/z*: 396, 277, 249, 235; IR (neat) 2920, 1600, 1440, 1150 cm^{-1}; M^+_{found} = 396.2600, $C_{26}H_{37}OP$ requires 396.2582.

3-Phenyl-1,6,9-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (5a) *and 5-(2,5-Dimethylbenzyl-)3-(2,5-dimethylphenyl-) 1,2,3,4,5,6-hexahydro-1-phenylphosphinine 1-Oxide* (7a) *were prepared as the n-propyl- and the n-butyl-derivatives* (5b *and* 5c).

5a: Yield 18%; ^{31}P and ^{13}C NMR, Table III; ^1H NMR ($CDCl_3$) δ 1.47 (s, 3H, C_1—CH_3), 2.17 and 2.23 (s, 6H, Ar—CH_3), 2.2–2.4 (m, 2H, C(2)H_2), 2.89 (s, 2H, C(10)H_2), 3.6–3.9 (m, 1H, C(5)H), 6.8–7.8 (m, 7H, ArH); MS, Table IV; IR (neat) 2910, 1580, 1420, 1190, 730 cm^{-1};

7a: Yield 9%; ^{31}P NMR ($CDCl_3$) δ + 33.4; ^1H NMR δ 2.24 (s, 12H, Ar—CH_3), 6.68–7.84 (m, 11H, ArH); MS, *m/z*: 416, 297, 269, 255; IR (neat) 2920, 1605, 1440, 1170 cm^{-1}.

3-Phenyl-1,7,8-trimethyl-benzo[f]-3-phosphabicyclo[3.3.0]oct-6-ene 3-Oxide (8a). The reaction of 0.9 g (3.27 mmol) of 1a and 30 ml of 1,2-xylene in the presence of 1.31 g (9.81 mmol) of aluminum-trichloride was carried out and the mixture was worked up as in the earlier cases to give 0.41 g (40%) of the product with main component 8a. ^{31}P and ^{13}C NMR, Table III; ^1H NMR ($CDCl_3$) δ 1.60 (s, 3H, C_1—CH_3), 2.24 (s, 6H, Ar—CH_3), 2.89 (s, 2H, C(10)H_2), 3.4–3.8 (m, 1H, C(5)H), 6.7–7.5 (m, 7H, ArH); MS, Table IV.

ACKNOWLEDGEMENT

The authors are grateful to the Hungarian Academy of Sciences for financial support of the NMR measurements.

REFERENCES

1. (a) J. Buddrus and F. Nerdel, *Tetrahedron Lett.*, **36**, 3197 (1965); (b) J. Buddrus, *Chem. Ber.*, **101**, 4152 (1968); (c) L. Skattebol and B. Boulette, *J. Org. Chem.*, **31**, 81 (1966); (d) Ch. Müller and P. Weyerstahl, *Tetrahedron*, **31**, 1787 (1975).
2. S. R. Sandler, *Chem. and Ind.* (London), 565, (1970).
3. J. Arct and A. Prawda, *Pol. J. Chem.*, **52**, 209 (1978).
4. D. Reinhard and P. Weyerstahl, *Chem. Ber.*, **110**, 138 (1977).
5. Gy. Keglevich, B. Androsits and L. Tőke, *J. Org. Chem.*, **53**, 4106 (1988).
6. Gy. Keglevich, G. Tóth, I. Petneházy, P. Miklós and L. Tőke, *J. Org. Chem.*, **52**, 5721 (1987).
7. Gy. Keglevich, F. Janke, I. Petneházy, Á. Szöllösy, P. Miklós, G. Tóth and L. Tőke, *Phosphorus Sulfur*, **36**, 61 (1988).
8. L. D. Quin, in "The Heterocyclic Chemistry of Phosphorus"; Wiley: New York, 1981; p. 213.

9. (a) J. March, in "Advanced Organic Chemistry; Reactions, Mechanisms, and Structure"; McGraw-Hill, 1977; p. 512; (b) R. M. Roberts and D. Shiengthong, *J. Am. Chem. Soc.*, **86**, 2851 (1964).
10. L. D. Quin, A. N. Hughes, H. F. Lawson and A. L. Good, *Tetrahedron*, **39**, 401 (1983).
11. C. B. Reese and R. D. Stebles, *Tetrahedron Lett.*, **43**, 4427 (1972).
12. Gy. Keglevich, I. Petneházy, P. Miklós, A. Almásy, G. Tóth, L. Tőke and L. D. Quin, *J. Org. Chem.*, **52**, 3983 (1987).