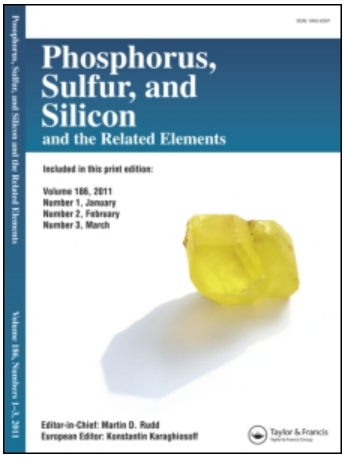

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SYNTHESIS AND PROPERTIES OF COMPOUNDS RELATED TO 1-t-BUTYLACETYLENE-2-PHOSPHONIC ACID AND 1-*t*-BUTYLETHANE-1,2,2-TRIPHOSPHONIC ACID. STERICALLY OVERCROWDED PHOSPHORUS COMPOUNDS, PART I:

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SYNTHESIS AND PROPERTIES OF COMPOUNDS RELATED TO 1-*t*-BUTYLACETYLENE-2-PHOSPHONIC ACID AND 1-*t*-BUTYLETHANE-1,2,2-TRIPHOSPHONIC ACID. STERICALLY OVERCROWDED PHOSPHORUS COMPOUNDS, PART I:

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Dedicated to Professor F. Huber on occasion of his 60th birthday.

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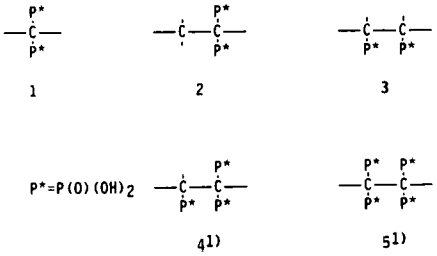
1-*t*-Butylacetylene-2-phosphonic acid diethyl and di-iso-propyl esters, **6a**, **6b** were synthesized via the $NiCl_2$ promoted MICHAELIS-ARBUZOV-type reactions. Ethyl, iso-propyl and methyl esters **7a–7c** of 1-*t*-butylethane-1,2,2-triphosphonic acid were obtained by three routes including the "anomalous MICHAELIS-BECKER-type" reaction. In addition the parent triphosphonic acid **7d** and an anilinium salt **7e** were synthesized. These overcrowded molecules exist at ambient temperature in two different rotameric forms.

Key words: Phosphonic acids; stereochemistry; NMR; intramolecular rotation.

1. INTRODUCTION

Oligophosphonic acids with methane and ethane structures **1** to **5** and related compounds have aroused considerable interest as complexing reagents for



1 2 3

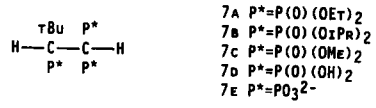
4[1] 5[1]

alkaline earth and transition metals in various chemical and technical fields, in

cosmetics and in pharmacy.[2] Previous experiments showed that the geminal diphosphonic acids **1** and **2** have better chelating abilities than the vicinal analogues **3**.[1,2] Combining both building principles in structures related to **4** and **5** additional influence of molecular conformation on donor properties of corresponding anions is expected.

Here we wish to report on synthetic routes leading to 1-*t*-butyl-acetylene-2-phosphonic acid dialkyl esters **6a** and **6b**,

and on 1-*t*-butylethane-1,2,2-triphosphonic acid and the corresponding derivatives **7a–7e**:

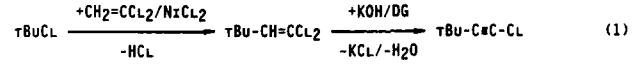


The sterically overcrowded compounds to type **7a–7e** each exhibit two individual rotameric forms stable at room temperature. Special studies concerning the simulation of molecular structures, studies of intramolecular exchange processes and further experimental work in one- and two-dimensional NMR-techniques will be described in subsequent papers of this series.[3]

2. PREPARATIVE STUDIES

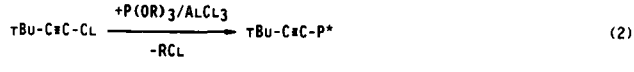
2.1. 1-t-Butylacetylene-2-phosphonic acid dialkyl esters **6**

1-*t*-Butyl-2,2-dichloroethylene **8** is obtained from *t*-butyl-chloride, 1,1-dichloroethylene and anhydrous $AlCl_3$.[4] Dehydrochlorination of **8** with potassium hydroxide in diethylene glycol (DG) yields 1-*t*-butyl-2-chloroacetylene **9**:[4]



8 9

While unsubstituted chloroacetylenes react readily with trialkylphosphites,[5] **9**, a surprisingly stable derivative of chloroacetylene, does not yield easily to MICHAELIS-ARBUSOV-type reactions. In this case activation by anhydrous $NiCl_2$ is required, a method which was introduced by Tavs[6] to study less reactive olefinic, aromatic and heterocyclic halogen derivatives.



9 6A, 6B, NOT 6C

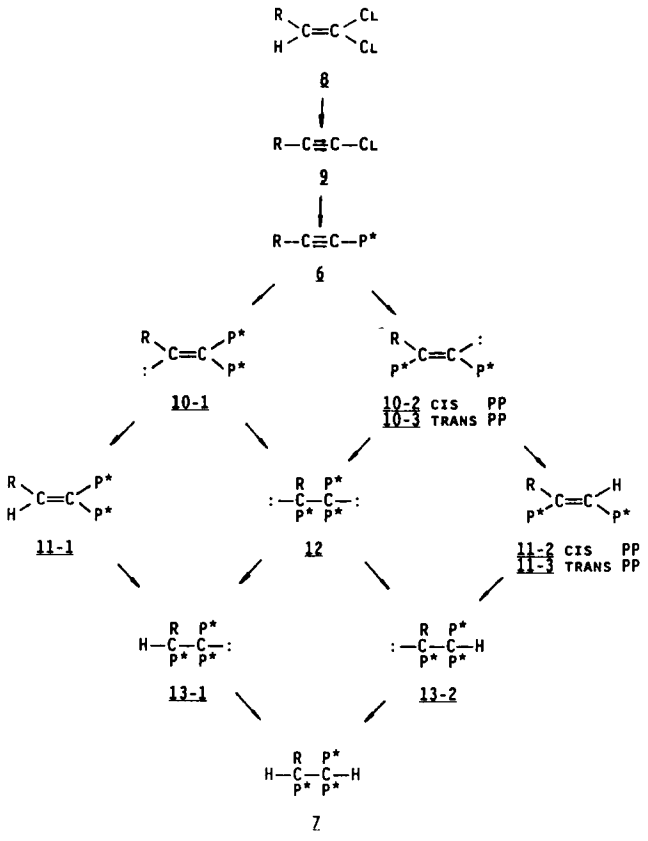
We obtained ethyl and isopropyl esters as colourless liquids, stable at room temperature, in good yields. (**6a** 55%, $\delta_P = -7.415$ ppm, **6b** 75%, $\delta_P = -7.82$ ppm). Attempts to synthesize the methyl ester **6c** according to Equation (2) were not successful. $^{31}P\{^1H\}$-NMR-studies detected basically unreacted trimethylphosphite. A less convenient synthesis for **6b** was described earlier.[10]

2.2. *1-t-Butylethane-1,2,2-triphosphonic acid hexaalkyl esters 7*

We found that sodium dialkyl phosphite, $NaOP(OR)_2$ (R = Et, iPr, Me), henceforth abbreviated as NaP*, is activated by tetrahydrofuran (THF).[1] NaP* reacts via three different routes with

1) 1-*t*-butylactylene-2-phosphonic acid dialkyl ester **6a**, **6b** (R = Et, iPr) or
2) 1-*t*-butyl-2-chloroacetylene **9** (R = Et, iPr, Me) or
3) 1-*t*-butyl-2,2-dichloroethylene **8** (R = Et)

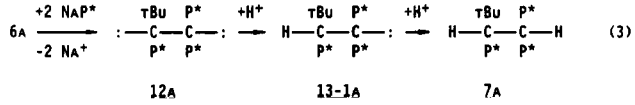
to form the title compounds, 1-*t*-butylethane-1,2,2-triphosphonic acid hexaalkyl esters **7**. These findings are explained by the reaction sequences as shown in Scheme 1:



Details are discussed below.

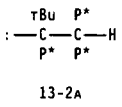
Route 1. 1-*t*-Butylacetylene-2-phosphonic acid diethyl ester **6a** is subject to a nucleophilic attack by the diethyl phosphite anion from NaP* in THF to form an orange-coloured solution. By $^{31}P\{^1H\}$-NMR the carbanionic species **13–1a** was detected which upon addition of H_2O, HCl, or acetic acid was protonated to

1-*t*-butyl-ethane-1,2,2-triphosphonic acid hexaethyl ester **7a**:

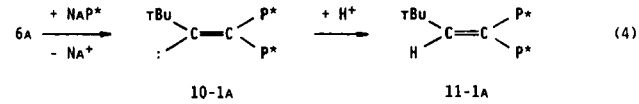


The dicarbanion **12a** is a hypothetical intermediate for which we have no spectroscopic evidence as yet, but a reasonably stable dicarbanion analogous to **12a** was deduced for ethane-1,1,2,2-tetraphosphonic acid octaethyl ester.[1]

No direct NMR-spectroscopic evidence is available at the present time supporting the formation of **13–2a**, a tautomeric form of **13–1a**:



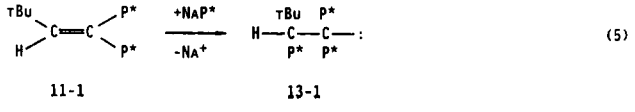
A decrease in the activity of sodium diethyl phosphite towards 1-*t*-butylacetylene-2-phosphonic acid diethyl ester **6a** is observed in ethanolic solutions. Here subsequent addition and reprotonation reactions lead to 1-*t*-butylethene-2,2-diphosphonic acid tetra ethyl ester **11–1a**:



The formation of the vicinal 1-*t*-butylethylene-1,2-cis- or trans-diphosphonic acid tetraethyl esters **11–2a** and **11–3a**

is ruled out by means of $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR-spectroscopy. **11–1a** exhibits the characteristic data $^2J_{PP} = 49.5$ Hz, $^1J_{PC} = 69.3$ Hz (P—C—*t*Bu) and $^1J_{PC} = 59.6$ Hz (P—C—H) resp. The triple bond of **6a** is attacked by the nucleophilic diethyl phosphite anion in beta position with respect to the bulky *t*-butyl group and not, as might be expected, beta to the phosphonate function. Thus steric hindrance arising from the *t*-butyl group predominates over the electronic directing influence of the phosphonate group. Very recently we found that under similar conditions 1-phenylacetylene-2-phosphonic acid diethyl ester yields 1-phenylethene-1,2-trans-diphosphonic acid tetraethyl ester, whose structure is analogous to **11–3a**.[1]

11–1a is an important missing link to explain the reaction mechanism summed up in Scheme 1 above:



Note: Carbanions are indicated by :—C or C—: where the symbol: stands for the negative charge or the lone pair resp.

Analogous procedures following route 1 led to the iso-propyl ester **6b**, which was obtained in 49% yield.

Route 2. A convenient one-pot-synthesis for 1-*t*-butylethane-1,2,2-triphosphonic acid derivatives **7** starts off from 1-*t*-butyl-2-chloro-acetylene **9** and NaP* in THF under reflux conditions leading to **13–1a** and finally by protonation to **7a** in 39.5% yield. Most likely 1-*t*-butylacetylene-2-phosphonic acid diethyl ester **6a** is formed in an initial step by a MICHAELIS-BECKER type reaction.

The hitherto unknown methyl ester **7c** was obtained by route 2 in 64.5% yield.

Route 3. Since strongly basic reagents abstract HCl from chlorinated olefins to form acetylenes we subjected 1-*t*-butyl-2,2-dichloro-ethylene **8** directly to NaP* under conditions described as those of the "anomalous" MICHAELIS-BECKER reaction.[1]

By comparison to the parent compound $CH_2{=}CCl_2$ **8** is deactivated by the bulky *t*-butyl-group. Indeed at room temperature **8** does not react with NaP* in THF with yields of any practical interest. But at elevated temperatures and under pressure **7a** is formed in autoclave reactions. It seems interesting to note that the intermediate 1-*t*-butylethene-2,2-diphosphonic acid tetraethyl ester **11–1a** was obtained as a by-product during the autoclave reaction.

These findings shed additional light onto the mechanism of the anomalous MICHAELIS-BECKER reaction, confirming the formation of acetylenic intermediates **9** and **6** as shown in Equation (6):

$$8 \xrightarrow[-(EtO)_2P(O)H/-NaCl]{+NaP^*} 9 \xrightarrow[-NaCl]{+NaP^*} 6A \xrightarrow{+(EtO)_2P(O)H} 11\text{-}1A \qquad (6)$$

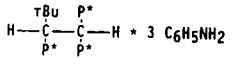
The $^{31}P\{^1H\}$-NMR-data for the title compounds, **7a–7c** are given in Table I below.

2.3. *1-t-butylethane-1,2,2-triphosphonic acid* **7d**

The free 1-*t*-butylethane-1,2,2-triphosphonic acid **7d** is obtained from the ethyl ester **7a** via acidolysis with glacial acetic acid (catalyzed by H_2SO_4) or, better, with hydrochloric acid. **7d**, a viscous oil, resisted all attempts at crystallisation. The purity of **7d** was checked by NMR-studies. $^{31}P\{^1H\}$-NMR data are given in Table I below.

A further proof of both the identity and purity of **7d** was obtained by inspection of a 0.1 molar solution of **7d** in a 1 m solution of KOH in D_2O via $^{31}P\{^1H\}$-NMR spectroscopy. It seems well justified, considering the dissociation constants of similar species[7] to assume that **7d**, a hexavalent acid, is fully deprotonated in this strongly alkaline solution, leaving the hexavalent anion, **7e**. $^{31}P\{^1H\}$-NMR-data are given in Table I.

We have not, as yet, succeeded in isolating well defined crystals of alkali or guanidinium salts of **7d** suitable for crystallographic studies. However, a tri-anilinium salt was obtained with analytical data corresponding to **7f**.



7F

TABLE I

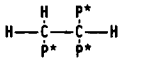
$^{31}P\{^1H\}$-NMR-data of compounds **7a–7d** and **7f**, each in two rotameric forms I and II. Pop.: Population of rotamers. **7e**: Resonances for phosphorus atoms of B- and X-type split into complex multiplets. Not fully understood up to now.[3] Chemical shift values vs. ext. 85% H_3PO_4. n.r. = not resolved

Comp.	δ_P(A) [ppm]	δ_P(B) [ppm]	δ_P(X) [ppm]	J_{PP}(AB) [Hz]	J_{PP}(AX) [Hz]	J_{PP}(BX) [Hz]	Solv.	Conc.	Pop. [%]
7a–I	33.632	27.144	23.106	59.6	n.r.	3.7	CD_3COCD_3	15%	16.5
7b–II	30.257	24.227	25.084	25.9	4.6	1.0			83.5
7b–I	31.80	25.75	20.93	61.1	n.r.	2.3	$CHCl_3$	10%	52
7b–II	27.59	21.91	23.52	28.5	4.5	3.2			48
7c–I	36.111	28.604	24.543	60.0	4.3	n.r.	THF	12%	
7c–II	32.240	25.861	26.457	27.2	4.7	n.r.			
7d–I	29.708	22.720	21.245	34.0	n.r.	n.r.	H_2O	1 m	29
7d–II	25.198	20.431	14.995	50.7	56.0	n.r.			71
7e	26.879	22.909	14.547	49.3	52.4	n.r.	D_2O/KOH	1 m	
7f–I	28.334	23.077	19.593	33.1	n.r.	n.r.	D_2O	1 m	5
7f–II	24.343	222.063	14.251	43.0	48.1	2.4			95

Compound **7f** crystallized in twinned colourless plates.[8] $^{31}P\{^1H\}$-NMR-data for a solution of **7f** in D_2O are given in Table I.

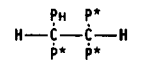
3. SOME REMARKS ON THE $^{31}P\{^1H\}$-NMR-SPECTRA AND MOLECULAR STRUCTURES OF 1-*t*-BUTYLETHANE-1,2,2-TRIPHOSPHONIC ACID DERIVATIVES **7a–7f**

Ethane-1,2,2-triphosphonic acid derivatives **14a–14c** give rise to $^{31}P\{^1H\}$-NMR-spectra of the AB_2-type[1] indicating free rotation around the central ethane C—C bond.



14A P* = P(O)(OR)$_2$
14B P* = P(O)(OH)$_2$
14C P* = P(O)(O$^-$)$_2$

The introduction of a chiral center at carbon C^1 in the 1-phenyl-ethane-1,2,2-triphosphonic acid derivatives **15a–15c**



15A P* = P(O)(OR)$_2$
15B P* = P(O)(OH)$_2$
15C P* = P(O)(O$^-$)$_2$

leads to non-equivalence of the geminal phosphorus atoms thus giving rise to $^{31}P\{^1H\}$-NMR-spectra of the ABC-type which approximate to the ABX-situation.[1] Again free intramolecular rotation is observed for **15a** and **15c**.

$^{31}P\{^1H\}$-NMR-spectra of the 1-*t*-butylethane-1,2,2-triphosphonic acid derivatives **7a–7d** and **7f** show two independent ABX-type systems with some ABC-character as shown for the *ethyl* compound **7a** in Figure 1.

Relevant data are given in Table I. They indicate steric hindrance of intramolecular rotation giving rise to two individual rotameric forms, which might have structures as shown in Figure 2. Data corresponding to Figure 2 were

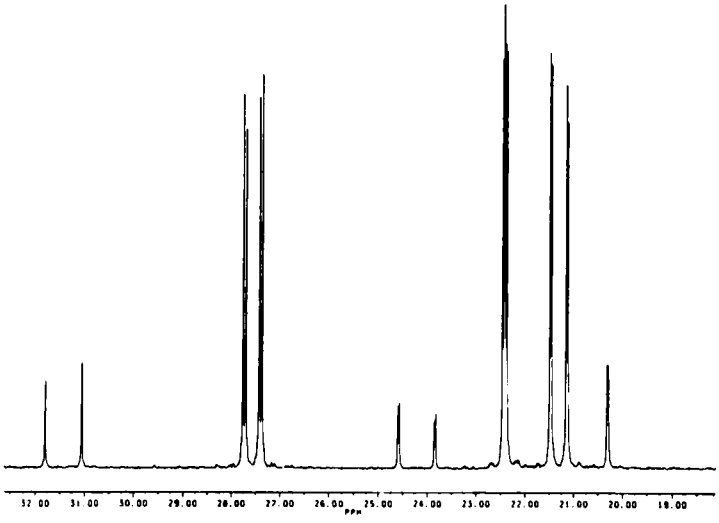


FIGURE 1 81 MHz $^{31}P\{^1H\}$-NMR-spectrum of *ethyl ester* **7a**. 10% in $C_6D_5CD_3$, ambient temperature. Two ABX-type-spectra indicate two rotameric forms of **7a**.

obtained for the *methyl* ester **7c** from calculations[3] based on semi empirical methods using the program system MOPAC.[9]
Further evidence for the existence of two distinct rotamers was drawn from EXSY experiments, which will be described separately.[3]

$^{31}P\{^1H\}$-NMR-spectra of the carbanions **13–1a–13–1c** show strongly coupled ABC-systems indicating single conformers or rapid exchange as demonstrated in Figure 3.

Detailed studies concerning the simulation of molecular structures by MOPAC[9] calculations, the rotational equilibria, details of experimental work in one- and two dimensional NMR techniques involving conventional COSY spectra of the type $^1H,^1H$ and $^{13}C,^1H$, supported by COSY spectra under decoupling conditions like $^1H,^1H\{^{31}P\}$, $^{31}P,^{31}P\{^1H\}$ and $^{31}P,^{13}C\{^1H\}$, will be described in subsequent papers of this series.[3]

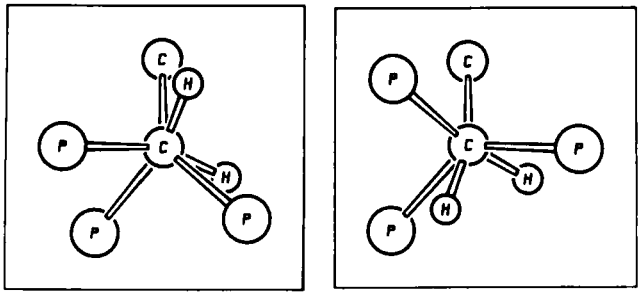


FIGURE 2 Two rotameric forms of *methyl ester* **7c**. Calculated[3] by semi empirical methods using the program system MOPAC.[10] View through the C—C axis of the ethane skeleton.

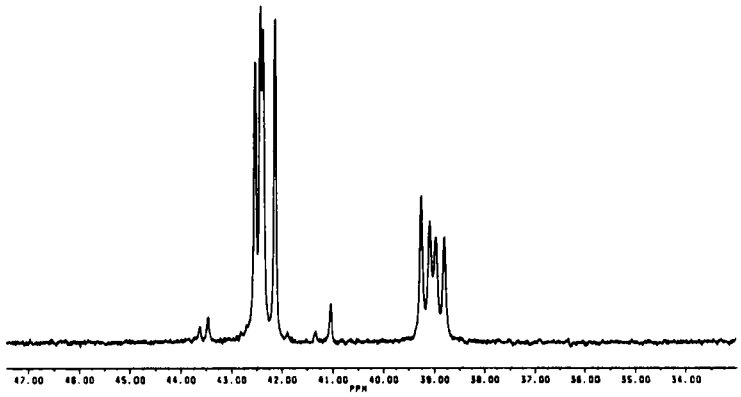


FIGURE 3 81 MHz $^{31}P\{^1H\}$-NMR-spectrum of carbanion **13–1a**. Ca. 1 m in THF, ambient temperature. One ABC-type spectrum indicating one rotameric form only or rapid exchange.

4. EXPERIMENTAL

General remarks

If not otherwise indicated NMR spectra were run on a BRUKER AM 200 spectrometer operating at 200 MHz for ^1H-, at 50.294 MHz for ^{13}C- and at 81.015 MHz for ^{31}P-NMR. Samples were not sealed. Solvents and concentrations are specified in the subsequent sections.

1-t-Butyl-2,2-dichloroethylene **8**.[4] ^1H-NMR (C_6D_6): 1.1765 (9H, *t*Bu, $^4J_{HH} = 0.76$ Hz), 5.8980 (1H, =CH—, $^4J_{HH} = 0.76$ Hz) [ppm].
$^{13}C\{^1H\}$-NMR (C_6D_6): 29.24 ($\underline{C}H_3)_3C$), 33.57 ($(CH_3)_3\underline{C}$), 119.24 (CH), 138.69 (CCl_2) [ppm].

1-t-Butyl-2-chloroacetylene **9**.[4] ^1H-NMR ($CDCl_3$): 1.2177 ppm (9H, *t*Bu) $^{13}C\{^1H\}$-NMR (C_6D_6): 29.31 ($\underline{C}H_3)_3C$), 56.75 ($(CH_3)_3\underline{C}$), 67.75 (C-CCl), 77.20 (C-$\underline{C}$Cl) [ppm].

Sodium dialkylphosphite NaOP(OR)$_2$ NaP[1].* $^{31}P\{^1H\}$-NMR (1 molar solution in THF): R = Et: 150.81 ppm, R = iPr: 152.95 ppm, R = Me: 151.1 ppm. All reactions with sodium dialkyl phosphite were carried out with dry THF in an atmosphere of dry nitrogen.

1-t-Butylacetylene-2-phosphonic acid diethyl ester **6a**. A mixture of 81.9 g (0.703 mol) **9**, 140 g (0.844 mol) $P(OEt)_3$ and 2.3 g anhydrous $NiCl_2$ was warmed up rapidly to and held for 25 h at reflux temperatures. (110°C increasing to 160°C).

Work-up procedure (1): Rapid distillation of the reaction mixture in vacuo yielded 111.5 g (73%) of the ester **6a**. Colourless liquid. B.p. 60°C/6.7 Pa. $n_D^{20} = 1.4416$. $C_{10}H_{19}O_3P_{19}$ (218.26): C found 55.2 (calc. 55.1), H 9.29 (8.72), p 13.9 (14.2).

Work-up procedure (2). The reaction mixture was dissolved in 500 ml ether, extracted with 50 ml 0.05 m HCl and finally with 200 ml H_2O. The dried (Na_2SO_4) ether solution was concentrated and fractionated as shown above. Identification by NMR-Methods: ^1H-NMR (C_6D_6): 1.050 (9H, *t*Bu, $^5J_{PH} = 0.4$ Hz), 1.142 (6H, $OCCH_3$, $^3J_{HH} = 7.08$ Hz, $^4J_{PH}$ not resolved), 4.088 (4H, OCH_2, $^3J_{HH} = 7.08$ Hz, $^3J_{PH} = 9.06$ Hz) [ppm]. $^{31}P\{^1H\}$-NMR (C_6D_6): −5.64 ppm.

1-t-Butylacetylene-2-phosphonic acid di-iso-propyl ester **6b**. 230 g (1 mol) $P(OiPr)_3$ and 4 g (0.03 mol) freshly dried $NiCl_2$ was warmed up slowly to and held for 2 hrs. At 130°C. After cooling to ambient temperature 100 g (0.86 mol) **9** were added dropwise and the mixture heated to 120°C for 2 hrs. Distillation in vacuo using a 40 cm Vigreux column led to 160 g (75%) **6b**. Colourless liquid. B.p. 76–77°C/1.3 Pa. $^{31}P\{^1H\}$-NMR (neat): −7.82 ppm. ^1H-NMR (5% in $CDCl_3$): 1.28 (9H, *t*Bu, s), 1.36 (6H, $OC(CH_3)_2$, s), 4.71 (sp, d, 6.2 Hz $^3J_{HH}$, 9.3 Hz $^3J_{POCH}$) [ppm].

1-t-Butylethane-1,1,2-triphosphonic acid hexaethyl ester **7a**. *Route 1-1:* Reaction of **6a** with NaP* in THF: A mixture of 10.9 g (0.05 mol) **6a** and 150 ml of a 1 M solution of NaP* [$NaOP(OEt)_2$] (0.15 mol) in THF was kept for 24 h at room temperature.

$^{31}P\{^1H\}$-NMR control: Carbanionic species **13–1a** in THF (reaction mixture) ABC-system: 42.79 ppm (A), 42.05 ppm (B), 39.22 ppm (C), $J_{AB} = 88.1$ Hz, $J_{AC} = 7.5$ Hz, $J_{BC} = 28.2$ Hz; NMR parameters were not refined by iteration.

By addition of glacial acetic acid the pH value of the reaction mixture was adjusted to about 5. (External test: few drops of the mixture on wet pH-paper). THF was driven off in vacuo, and the residual oil was dissolved in 100 ml dichlorométhane. The CH_2Cl_2 phase was washed with 100 ml H_2O, separated from water and then dried with Na_2SO_4. CH_2Cl_2 was removed in vacuo and the remaining product was purified by vacuum fractionation at 145–150°C, 2.7 Pa. 20.2 g (82%) **7a**. Colourless oil. Practically pure compound from NMR. Within a few weeks slow crystallization at room temperature started. Best synthesis for **7a**.

$^{31}P\{^1H\}$-NMR (C_6D_6): see Table 1.

Derivatization of **7a**: Equimolar amounts of **7a** and NaH in THF formed quantitatively pure carbanion **13–1a** as shown by NMR. Best synthesis of **13–1a**.

Route 1-2: Reaction of **6a** with NaP* in ethanol: A mixture of 43.6 g (0.2 mol) **6a** and 63.5 g (0.46 mol) of diethylphosphite was warmed up to 70°C. After addition of 8 ml of a saturated solution of C_2H_5ONa in C_2H_5OH an increase in temperature to 112°C was observed. Subsequently, the temperature was maintained at 110°C for 3 h. Fractionation in vacuo yielded 51.4 g (52.4%) **7a**, b.p. 133–139°C/6.7 Pa.

$C_{18}H_{41}O_9P_3$ (494.51): C 44.1 (43.7), H 9.56 (8.30), P 18.2 (18.8). Identification by NMR: $^{31}P\{^1H\}$ (C_6D_6) ABX System:

30.21 (A, CHtBuP), 24.09 (B, CHP_2), 24.81 (X, CHP_2) [ppm], $J_{AB} = 27.3$ Hz, $J_{AX} = 4.2$ Hz, J_{BX} = not resolved. Products from routes 1–1 and 1–2 were identical.

Route 2-1: Reaction of **9** with NaP* in THF. A mixture consisting of 58 g (0.5 mol) **9** and 200 ml of a 1 m solution of NaP* [$NaOP(OEt)_2$] (0.2 mol) in THF was kept for 16 hrs at room temperature and refluxed for 8 hrs. After adjustment of the pH value to 5 with acetic acid the reaction mixture was worked up as shown above. Short path distillation at 95°C/2.7 Pa yielded 97 g (39.5%) **7a** (pure by $^{31}P\{^1H\}$-NMR).

Route 2-2: Reaction of **9** with NaP* in THF, identification of by-product **11–1a**. Identical procedure as described under route 2–1. Fine fractionation of volatile components led to 39.1 g **11–1a**, b. p. 144–152/6.7 Pa, colourless oil.

Identification by NMR:

300 MHz 1H-NMR ($CDCl_3$): 1.325 (9H, *t*Bu), 1.35 (6H, $OCCH_3$), 4.07 (4H, OCH_2), 7.61 (1H, =CH—, $^2J_{PH}^{cis} = 32.5$ Hz, $^3J_{PH}^{trans} = 52$, 5 Hz) [ppm]. $^{31}P\{^1H\}$-NMR (C_6D_6): 19.62 ppm, (CP_2), 13.31 ppm (CtBuP), $^3J_{PP} = 49.1$ Hz. $^{13}C\{^1H\}$-NMR: 122.06 ppm (CP_2, d, d, $^1J_{PC} = 69.3$ Hz, $^1J'_{PC} = 59.6$ Hz).

Chemical identifications. Equimolar amounts of **11–1a** and a 1 m solution of NaP* [$(NaOP(OEt)_2)$] were combined. The carbanionic species **13–1a** was formed immediately in quantitative yield. Identical $^{31}P\{^1H\}$-NMR-data as given under route 1–1.

Route 3: Autoclave reactions of **8** with NaP*

Route 3-1: Isolation of **7b**. A mixture of 22.8 g (0.15 mol) **8** and 450 ml of 1 m solution of NaP* [$NaOP(OEt)_2$] in THF (0.45 mol) was heated for 14 hrs at 140°C and 12 atm. The reaction mixture was worked up as described above to yield, after short path distillation, at 100°C 6.7 Pa 46 g of a colourless liquid consisting of 86% of **7b**, according to $^{31}P\{^1H\}$-NMR. Purification as above.

By-product: **11–1a**. See below.

Route 3-2. Identification of by-product **11–1a** Analogous reaction, 5 hrs, 120°C, 8 atm. Short path distillation. Fine fractionation at 127°C/1.3 Pa. 16.0 g (30%) **11–1a**. Colourless liquid. Identification by NMR:

$^{31}P\{^1H\}$-NMR (pure): AB-System: 18.900 ppm (A), 12.847 ppm (B), $^3J_{PP} = 49.6$ Hz.

1-t-Butylethane-1,1,2-triphosphonic acid hexa-iso-propyl ester **7b**

Route 1. To 300 ml of a 1 m solution of NaP* [$NaOP(OiPr)_2$] (0.3 mol) in THF were added dropwise 19 g (0.077 mol) **of 6b**. After an incubation period of about 10 min the colourless solution turned

yellow and then brown. To prevent polymerisation of the acetylenic compound 10 g (0.06 mol) of diiso-propylphosphite were added. The reaction was completed by heating to reflux temperatures for 2 hrs. Work-up as above. Volatile compounds were driven off by short path distillation at 80°C/13 Pa. The remaining 22 g of non-volatile liquid were analyzed by $^{31}P\{^1H\}$-NMR and shown to consist of 93% **7b**.

1-t-Butylethane-1,1,2-triphosphonic acid hexamethyl ester **7c**
Route 2. Compound **9** (20 g; 0.172 mol) was added dropwise to 1000 ml of a 0.5 m solution of NaP* [$NaOP(OMe)_2$] (0.5 mol) in THF with stirring at reflux temperature. This temperature was maintained fro 2 hrs. Work-up as above. Volatile components were driven off by short path distillation at 80°C/13 Pa. The remaining 20 g of non volatile liquid were analysed by $^{31}P\{^1H\}$-NMR: 75% **7c**.

1-t-Butylethane-1,2,2-tris-phosphonic acid **7d**. 10 g (0.02 mol) **7a**, 75 ml glacial acetic acid and 1 ml H_2SO_4 conc. were refluxed for 5 hrs. After evaporation a viscous oil remained, practically pure **7d** according to $^{31}P\{^1H\}$-NMR. For NMR data see Table I. Attempts to crystallize **7d** failed. Analogous results for the acidolysis in conc. HCl. Purity 97%. Titration vs. NaOH: equivalence points at 2 and 3 acidic H.

1-t-Butylethane-1,2,2-tris-phosphonic acid trianilinium salt **7f**. To a solution of 38 g (0.12 mol) **7d** (as prepared above) in 200 ml methanol were added 11 g (0.12 mol) aniline. After evaporation of the solvent the remaining oil was super-layered with acetone. After one to two days a solid deposit was formed which was purified by crystallization from water. 36 g (58%). **7e**. Colourless platelets. M.p. 237.5°C (decomposition). $C_{24}H_{38}O_9N_3P_3$ (605.57): C 47.0 (47.60), H 6.4 (6.32), N 6.6 (6.94), P 16.5 (15.36). DTA/DTG: At 187°C 15.4% (15.3%) loss of one mol of aniline.

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