Stable C-Halogenated Arsaalkenes

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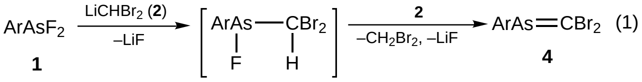
Summary: Stable arsaalkenes (alkylidenearsanes) ***4*−*6****, dihalogenated at the alkene carbon atom, were synthesized in good yields by a one-pot synthesis from n-butyllithium, difluoroarsane* ***1,*** *and, respectively, chloroform, bromoform, and tetraiodomethane.* ***4*** *undergoes nearly quantitative lithium−bromine exchange with n-butyllithium at low temperature to give, after quenching with methanol, the monobrominated arsaalkene* ***10****.*

During the last 20 years, considerable progress has been made in the synthesis of doubly bonded compounds of group 15 elements, particularly derivatives of the type −M=C<. But, while many phosphaalkenes −P=C< have been isolated,[1] only some stable arsaalkenes −As=C< substituted at arsenic and carbon by various alkyl, aryl, silyl, amino, or siloxy groups have been prepared to date.[2] Arsaalkenes halogenated at the alkene carbon atom should be of great interest as synthons for the preparation of functionalized arsaalkenes via halogen−metal exchange with *n*-butyllithium. The first representative of this new class of arsaalkenes to be isolated was $F_3CAs{=}C(F)NR_2$,[2h] whereas $F_3CAs{=}CF_2$[3] was characterized only as a transient species. However, due to the high kinetic stability of the C−F bond, functionalization is not easy in this case. For this reason we have prepared a new class of arsaalkene bearing on the carbon atom chlorine, bromine, or iodine substituents. These should be convertible to the lithium derivatives RAs=C(X)Li.

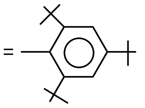
The *C*,*C*-dibromo(2,4,6-tri-*tert*-butylphenyl)arsaalkene **4** was prepared in 46% yield by a one-pot synthesis from 2 equiv of $LiCHBr_2$ (**2**; prepared from bromoform and *n*-butyllithium in THF at −100 °C)[4] and 1 equiv of an aryldifluoroarsane **1**.[5] As in the synthesis of the phosphaalkene $ArP{=}CBr_2$,[4] we suppose that the carbenoid **2** acts first as a nucleophile to afford **3** and then as a base to give the arsaalkene **4**[6] (eq 1).



$$ArAsF_2 \xrightarrow[-LiF]{LiCHBr_2\ (\mathbf{2})} \left[ArAs(F){-}CBr_2(H)\right] \xrightarrow[-CH_2Br_2,\ -LiF]{\mathbf{2}} ArAs{=}CBr_2 \quad (1)$$

1 **3** **4**

Ar =



The *C*,*C*-dichloro- and *C*,*C*-diiodo(2,4,6-tri-*tert*-butylphenyl)arsaalkenes **5**[7] and **6**[7] were prepared by a similar route from **1** and, respectively, $LiCCl_3$[8] and $LiCI_3$.[4] However, in contrast to the synthesis of **4**, in which 2 equiv of $HCBr_3$ was required, only 1 equiv of chloroform and tetraiodomethane was used; the forma-

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(1) For reviews, see: (a) Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur Relat. Elem.* **1986**, *29*, 73. (b) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, **1990**; p 157. (c) Markovski, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019.

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(4) Goede, S. J.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677.

(5) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.

(6) Synthesis of **4**: $LiCHBr_2$ was prepared by addition of a solution of *n*-butyllithium (1.6 M in hexane; 10.5 mL, 16.8 mmol) to a solution of bromoform (4.24 g, 16.8 mmol) in THF (75 mL) cooled to −100 °C. After 1 h of stirring, a solution of **1** (3.00 g, 8.4 mmol) in THF (20 mL) was added slowly via syringe to the solution of **2** at −100 °C; then the reaction mixture was warmed to room temperature, THF and hexane were removed *in vacuo* and replaced by pentane, and the lithium salts were filtered. Cooling the pentane solution to −30 °C gave 1.90 g (46%) of white crystals of **4** (mp 132−134 °C). ^1H NMR ($CDCl_3$): δ 1.32 (s, 9H, *p-t*-Bu); 1.47 (s, 18H, *o-t*-Bu); 7.44 (s, 2H, arom H). ^{13}C NMR ($CDCl_3$): δ 31.65 (*p*-(CH_3)$_3$C); 33.15 (*o*-(CH_3)$_3$C); 35.28 (*p*-*C*(CH_3)$_3$); 38.33 (*o*-*C*(CH_3)$_3$); 122.94 (*m*-CH); 140.47 (As=CBr_2); 145.77 (ipso-C); 151.43 (*p*-C); 152.98 (*o*-C). The assignment of the resonances of *p*-C, ipso-C, *o*-C, and CBr_2 has been made unambiguously by two experiments: the spectrum without proton decoupling shows a singlet for CBr_2 and a triplet for ipso-C, whereas both *p*-C and *o*-C appear as complex signals. Irradiation experiments of the *p-t*-Bu protons with a low decoupling power give a singlet for the signal at 151.43 ppm (attributed to *p*-C), whereas the signal at 152.98 ppm remains a complex multiplet. MS EI: *m/z* 492 (M, 7); 434 (M − *t*-Bu-1, 3); 356 (M − *t*-Bu − Br, 28); 319 (ArAs − 1, 100); 57 (*t*-Bu, 49). Anal. Calcd for $C_{19}H_{29}AsBr_2$: C, 46.53; H, 5.96. Found: C, 46.77; H, 6.04.

(7) **5** and **6** were prepared by the same procedure: *n*-butyllithium (1.6 M in hexane; 3.3 mL, 5.2 mmol) was slowly added to a mixture of **1** (0.95 g, 2.6 mmol) and $CHCl_3$ (0.30 g, 2.6 mmol) or **1** (0.95 g, 2.6 mmol) and CI_4 (1.35 g, 2.6 mmol) in solution in THF (20 mL) cooled to −100 °C. The reaction mixture turned brown. After removal of solvents *in vacuo*, addition of pentane (50 mL), and filtration of lithium salts, cooling of the pentane solution afforded 0.58 g of white crystals of **5** (56%, mp 136−138 °C) or 0.96 g of yellow crystals of **6** (64%, mp 162−164 °C dec). **5**: ^1H NMR ($CDCl_3$) δ 1.36 (s, 9H, *p-t*-Bu),1.52 (s, 18H, *o-t*-Bu), 7.46 (s, 2H, arom H); ^{13}C NMR ($CDCl_3$) δ 31.47 (*p*-(CH_3)$_3$C), 32.98 (*o*-(CH_3)$_3$C), 35.15 (*p*-*C*(CH_3)$_3$), 38.26 (*o*-*C*(CH_3)$_3$), 122.27 (*m*-CH), 139.48 (ipso-C), 151.19 (*p*-C), 153.68 (*o*-C), 168.78 (As=CCl_2); MS EI: *m/z* 402 (M, 10), 319 (ArAs − 1, 28), 57 (*t*-Bu, 46). Anal. Calcd for $C_{19}H_{29}AsCl_2$: C, 56.59; H, 7.26. Found: C, 56.46; H, 7.41. **6**: ^1H NMR ($CDCl_3$) δ 1.32 (s, 9H, *p-t*-Bu), 1.45 (s, 18H, *o-t*-Bu), 7.46 (s, 2H, arom H); ^{13}C NMR ($CDCl_3$) δ 31.43 (*p*-(CH_3)$_3$C), 33.06 (*o*-(CH_3)$_3$C), 35.20 (*p*-*C*(CH_3)$_3$), 38.17 (*o*-*C*(CH_3)$_3$), 70.62 (As=CI_2), 123.51 (*m*-CH), 151.26 (*o*-C), 151.53 (*p*-C); MS EI: *m/z* 586 (M, 51), 529 (M − *t*-Bu, 7), 459 (M − I, 9), 402 (M − *t*-Bu-I, 29), 319 (ArAs − 1, 100), 57 (*t*-Bu, 21). Anal. Calcd for $C_{19}H_{29}AsI_2$: C, 38.93; H, 4.99. Found: C, 39.12; H, 5.09.

(8) Koebrich, G.; Floy, K.; Fischer, R. H. *Chem. Ber.* **1966**, *99*, 1793

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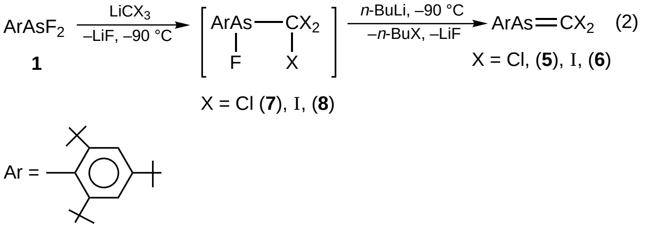
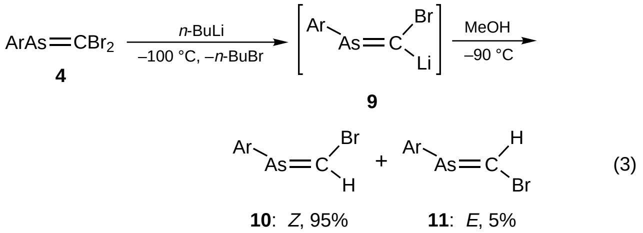
tion of **5** and **6** from the probable intermediates **7** and **8** was effected by addition with a second equivalent of *n*-butyllithium at −90 °C (eq 2).



Like their phosphorus homologues,[4,9] the arsaalkenes **4**−**6** are stable at room temperature and are not air and moisture sensitive. They have been characterized by mass spectrometry, C, H analysis, and their ^{1}H and ^{13}C NMR spectra. In their ^{13}C NMR spectra, the resonances of the carbon doubly bonded to arsenic were observed at δ (ppm) 168.78 (X = Cl), 145.77 (X = Br), and 70.62 (X = I), in the same range as those obtained by Bickelhaupt[4] and Appel[9] for $\mathrm{ArP{=}CX_2}$.

Addition of butyllithium to **4** at low temperature followed by methanolysis at −90 °C affords the new arsaalkenes **10**[10] and **11** in the ratio 95/5 (eq 3).



Only the major isomer was isolated. However, the attribution of the *Z* or *E* structure can be made on the basis of the alkene CH chemical shifts. NOE experiments show that, by irradiation of the *o*-*t*-Bu protons, the intensity of the As═CH signal at lower field increases in relation to that at higher field. Thus, the signal at 8.39 ppm in the ^{1}H NMR spectrum corresponds to the ethylenic hydrogen of the *Z* isomer, whereas the signal at 8.74 ppm is due to the *E* isomer. A similar assignment has been made by Bickelhaupt in the phosphaalkene ArP═C(H)I.[4]

Mechanistic arguments also support the preponderant formation of **10**. The halogen−metal exchange by attack by *n*-butyllithium at bromine should occur from the least hindered side, leading to carbenoid intermediate **9**. Its carbenoid homologue ArP═C(Li)Br[4,11] is configurationally stable; therefore, we can suppose that this also is true for the carbenoid ArAs═C(Li)Br. Thus, intermediate **9** is protonated by methanol to give (*Z*)-**10**.

The ratio **10**/**11** was still the same after the isomer mixture had been kept for 1 week in solution at room temperature. After 1 h of photolysis at 254 nm, a new *Z*/*E* ratio (60/40) was observed and some unidentified products were formed. This new ratio was unchanged after the solution had been kept for some days at room temperature, confirming the configurational stability of **10** and **11**. The complete isomerization to **11** was not possible, since a further 5 h of irradiation caused complete disappearence of starting **10** and **11**.

In conclusion, arsaalkene **4**, and very likely dichloro- and diiodoarsaalkenes **5** and **6**, will be useful new synthons in doubly bonded arsenic chemistry since substitution of halogen by a functional group, with retention of the As═C bond, appears to be potentially easy via the lithium carbenoids ArAs═C(Li)X. Studies on **4**−**6** are in progress.

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[9] Halogenated phosphaalkenes have also been obtained by Appel et al. by another route: (a)Appel, R.; Immenkeppel, M. *Z. Anorg. Allg. Chem*. **1987**, *553*, 7. (b) Appel, R.; Casser, C.; Immenkeppel, M. *Tetrahedron Lett.* **1985**, *26*, 3551.

[10] Synthesis of **10**: A solution of *n*-butyllithium (1.6 M in hexane; 1.4 mL, 2.2 mmol) was added dropwise to a solution of **4** (1.09 g, 2.2 mmol) in $\mathrm{Et_2O}$ (20 mL) cooled to −100 °C. After 1 h of stirring at −90 °C, 1.5 equiv of methanol was added to the orange reaction mixture at this temperature. The mixture was slowly warmed to room temperature, turning gradually to yellow. Solvents were removed *in vacuo*, 50 mL of pentane was added, and the lithium salts were filtered. ^{1}H NMR showed the formation of **10** and **11** in the ratio 95/5. Recrystallization from $\mathrm{Et_2O}$/MeOH (1/3) led to 0.72 g of colorless crystals of **10** (78%, mp 86−88 °C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.33 (s, 9H, *p*-*t*-Bu); 1.47 (s, 18H, *o*-*t*-Bu); 7.45 (s, 2H, H arom); 8.39 (s, 1H, ═CHBr). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 31.44 (*p*-($\mathrm{CH_3})_3$C); 32.87 (*o*-($\mathrm{CH_3})_3$C); 35.06 (*p*-*C*($\mathrm{CH_3})_3$); 38.13 (*o*-*C*($\mathrm{CH_3})_3$); 122.33 (*m*-CH), 141.36 (ipso-C); 150.30 (*p*-C); 153.22 (As═*C*HBr); 153.48 (*o*-C). MS EI: *m*/*z* 412 (M, 2); 356 (M − *t*-Bu + 1, 4), 319 (ArAs − 1, 11); 276 (M − *t*-Bu − Br, 100); 57 (*t*-Bu, 54). Anal. Calcd for $\mathrm{C_{19}H_{30}AsBr}$: C, 55.22; H, 7.32. Found: C, 55.28; H, 7.39.

[11] Van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174.