and finally the extent of acidification by X should be sufficient to obviate any need for additional stabilization of the carbanionoid center of *(2)* (as with $X = POX_2$[8]). So far only the nitrosamines *(1a)* have proved to be aminomethylation agents of broad scope[2].

We have now found the thiopivaloyl group to be another substituent permitting quantitative metalation to give stable derivatives (up to −50 °C) of type *(2)*. Thus conversion of *(3)* into the organolithium compound *(4)* can be accomplished under the conditions given in the reaction scheme. Reaction of *(4)* with alkyl halides and carbonyl compounds proceeds *via* C—C linkage to form the products *(5)* (Table 1). Alkylations are more successful than hydroxyalkylations;

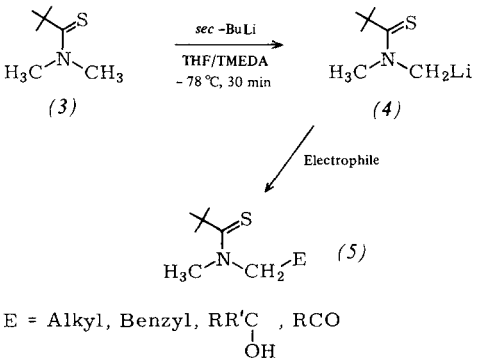

Table 1. Reactions of *(4)* with electrophiles to form products of type *(5)* [a, b].

Electrophile	Yield % spectr. [c]	pure [b]	^{1}H-NMR [d] δ [ppm]
CH_3I	95	80	3.97 (q)
n-$C_5H_{11}I$	91	82	3.86 (br. t)
n-$C_{10}H_{21}Br$	80	79	3.87 (br. t)
$C_6H_5CH_2Br$	48	44	4.08 (m)
C_6H_5CHO	85	70	4.18 (m)
$(C_6H_5)_2CO$	78	63	5.16 (s)
$(CH_3)_2CH$—CHO	80	23	3.73—4.02 (m)
Cyclohexanone	27	17	4.24 (s)
$CH_3CON(CH_3)_2$	56	33	4.71 (s)

[a] NMR data not listed as well as other spectroscopic data (*e.g.* two broad thioamide bands at 1330—1420 and 1450—1510 cm^{-1}) and elemental analyses (within 0.3 %) all accord with the expected structures.
[b] Apart from the adducts with benzaldehyde (m.p. 105 °C), benzophenone (m.p. 150 °C), and cyclohexanone (m.p. 104.5 °C) compounds *(5)* are oils which were purified by chromatography.
[c] From weight of crude product and NMR comparison with analytically pure material.
[d] The α-N-CH_2 signal is given. The *tert*-butyl group appears between 1.38 and 1.46, the methyl group between 3.2 and 3.5 ppm (both singlets). Solvent CCl_4 or $CDCl_3$.

this contrasts with the situation in the case of lithiated nitrosamines which can be described as typical carbonylophiles[2].

The thioamides *(5)* can be smoothly transformed into amides by alkaline H_2O_2[9], as we have demonstrated by preparing compound *(6)* (93 %, m.p. 95.5 °C). Neopentylamines are accessible from *(5)* by desulfuration with $LiAlH_4$[4b,10] (example: *(7)*; 88 %; m.p. 84.5 °C).

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CAS Registry numbers:
(3), 25530-28-3; *(4)*, 58832-32-9; *(6)*, 58832-33-0; *(7)*, 58832-34-1
Table 1. Electrophiles (from top to bottom):
74-88-4; 628-17-1; 112-29-8; 100-39-0; 100-52-7; 199-61-9; 78-84-2; 108-94-1; 127-19-5
Table 1. *(5)* (from top to bottom):
58856-07-8; 58832-24-9; 58832-25-0; 58832-26-1; 58832-27-2; 58832-28-3; 58832-29-4; 58832-30-7; 58832-31-8

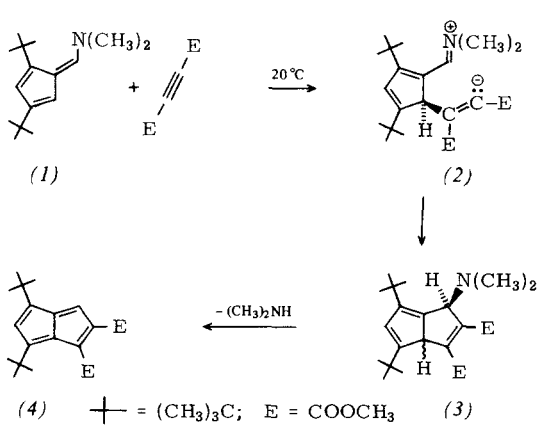
[1] Part of the projected Thesis by *W. L.*, Universität Giessen.
[2] *D. Seebach* and *D. Enders*, Angew. Chem. *87*, 1 (1975); Angew. Chem. Int. Ed. Engl. *87*, 15 (1975); *D. Enders*, Thesis, Universität Giessen 1974.
[3] *B. Bánhidai* and *U. Schöllkopf*, Angew. Chem. *85*, 861 (1973); Angew. Chem. Int. Ed. Engl. *85*, 836 (1973); *R. R. Fraser* and *P. R. Hubert*, Can. J. Chem. *52*, 185 (1974).
[4] a) *D. Enders* and *D. Seebach*, Angew. Chem. *85*, 1104 (1973); Angew. Chem. Int. Ed. Engl. *85*, 1014 (1973); b) *D. Seebach*, *W. Lubosch*, and *D. Enders*, Chem. Ber., in press.
[5] *R. Dach*, unpublished experiments, Universität Giessen (1974/75).
[6] *P. Beak* and *R. Farney*, J. Am. Chem. Soc. *95*, 4771 (1973).
[7] *H. Böhme* and *P. Plappert*, Chem. Ber. *108*, 2827 (1975).
[8] *P. Savignac et al.*, C. R. Acad. Sci. *C279*, 609 (1974); Tetrahedron Lett. *1974*, 2651; J. Organomet. Chem. *57*, C47 (1973); Tetrahedron *31*, 877 (1975).
[9] *H. Vorbrüggen* and *P. Strehlke*, Chem. Ber. *106*, 3039 (1973).
[10] *M. W. Cronyn* and *J. E. Goodrich*, J. Am. Chem. Soc. *74*, 3936 (1952).

[6+2] Cycloadditions of Pentafulvene. A Facile Pentalene Synthesis[**]

By *Klaus Hafner* and *Minoru Suda*[*]

The hitherto known syntheses of pentalene and its derivatives require several reaction steps and frequently the isolation of rather unstable intermediates[1]. We have found that the [6+2]cycloaddition[2] of 6-dimethylaminofulvenes with electron-deficient acetylene derivatives offers a facile synthesis of pentalenes which can be carried out as a "one batch procedure" at 20 °C.

While 6-dimethylaminofulvene undergoes a Michael addition with dimethyl acetylenedicarboxylate at 20 °C in benzene[3], 1,3-di-*tert*-butyl-6-dimethylaminofulvene *(1)*[4] combines with the alkyne under the same reaction conditions, presumably *via* the dipolar intermediate *(2)* and its cyclization product *(3)*, to give the thermally- and air-stable dimethyl 4,6-di-*tert*-butylpentalene-1,2-dicarboxylate *(4)*.



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The electronic spectrum of *(4)* (in *n*-hexane) resembles that of 1,3,5-tri-*tert*-butylpentalene[1], except for a bathochromic shift of the longest wavelength maximum by 70 nm [$\lambda_{max}=259$ ($\log\varepsilon=4.29$), 357 (3.71), and 668 nm (2.36)] due to the ester groups. The 60-MHz ^{1}H-NMR spectrum of *(4)* (in $CDCl_3$), which provides proof of structure, consists of six singlets, of which two are assigned to the two ring protons [$\tau=3.85$ (H-3) and 5.07 (H-5)], two to the ester methyl protons ($\tau=6.24$ and 6.36), and two to the *tert*-butyl protons ($\tau=8.96$ and 9.02). The relatively high upfield shift of the H-5 signal indicates the presence of a paramagnetic ring current in *(4)*. The ^{13}C-NMR spectrum of *(4)* (in $CDCl_3$) shows one signal each for the eight ring C atoms at $\delta=129.3$ (C-5), 134.7 (C-3), 135.1, 135.9 (C-1, C-2), 141.6, 143.7 (C-6a, C-3a), 161.7 and 162.9 (C-4, C-6), four signals for the *tert*-butyl C atoms at $\delta=27.9$ and 28.6 (CH_3), 33.0 and 34.9 (quat. C), and four for the ester C atoms at $\delta=51.3$ and 51.9 (CH_3O) and 167.4 and 173.0 (C=O). In contrast to pentalene and its simple alkyl derivatives[5], compound *(4)*, like 1,3,5-tri-*tert*-butylpentalene[1], shows no tendency to dimerize even at elevated temperatures[6].

(5) *(6)*

$\perp\!\!\!\perp$ = $(CH_3)_3C$; R = $COOCH_3$, CHO

Treatment of *(1)* with methyl propiolate or propiolaldehyde affords a *ca.* 40 % yield of the pentalene derivatives *(5)* which are in equilibrium with their dimers *(6)* at room temperature. A study of this equilibrium reaction is in progress.

Dimethyl 4,6-di-tert-butylpentalene-1,2-dicarboxylate (4)

To a solution of *(1)* (1.17 g, 5.0 mmol) in anhydrous benzene (50 mol) is added dimethyl acetylenedicarboxylate (1.50 g, 10.6 mmol) at room temperature. After 2 h, the solvent is removed from the green reaction solution *in vacuo* and the residue chromatographed over silica gel (Kieselgel 60, Merck) with *n*-hexane/ether (10:1). The eluate of the leading blue zone is extensively concentrated at room temperature *in vacuo* and the residue cooled to −70 °C. The fine blue crystals precipitated are filtered off. Compound *(4)* (0.73 g, 44 %) is isolated analytically pure; it is obtained as blue plates, m.p. 120—121 °C, by recrystallization from *n*-hexane.

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CAS Registry numbers:
(1), 58832-18-1; *(4)*, 58832-19-2; dimethyl acetylenedicarboxylate, 762-42-5

[1] *K. Hafner* and *H. U. Süss*, Angew. Chem. *85*, 626 (1973); Angew. Chem. Int. Ed. Engl. *12*, 575 (1973); and references cited therein.

[2] A [6+2] cycloaddition of 6,6-dicyclopropylfulvene with tetracyanoethylene is reported by *A. Cornelis* and *P. Laszlo*, J. Am. Chem. Soc. *97*, 244 (1975). [6+4] cycloadditions of 6-aminofulvenes: *M. Sato*, *S. Ebine*, and *J. Tsunetsugu*, Tetrahedron Lett. *1974*, 2769; *T. Sasaki*, *K. Kanematsu*, and *K. Kataoka*, J. Org. Chem. *40*, 1201 (1975); cf. also *K. N. Houk*, Acc. Chem. Res. *8*, 361 (1975).

[3] *F. Schmidt*, Dissertation, Technische Hochschule Darmstadt 1971; cf. also *K. Hafner*, Pure Appl. Chem. Suppl. Vol. *2*, 1 (1971).

[4] Prepared by analogy with 6-dimethylaminofulvene (Org. Synth. *47*, 52 (1967)) from lithium 1,3-di-*tert*-butylcyclopentadienide and methoxymethylenedimethylammonium monomethyl sulfate in ether/dichloromethane (1:1) at 0 °C: yellow needles of m.p. 116—118 °C; yield 51 % (*H. U. Süss*, Dissertation, Technische Hochschule Darmstadt 1976).

[5] *K. Hafner*, *R. Dönges*, *E. Goedecke*, and *R. Kaiser*, Angew. Chem. *85*, 362 (1973); Angew. Chem. Int. Ed. Engl. *12*, 337 (1973).

[6] An X-ray structural analysis of *(4)* is being performed by Prof. *H. J. Lindner* (Darmstadt).

(Dichloromethylene)triphenylphosphorane

By *Rolf Appel*, *Fritz Knoll*, and *Harald Veltmann*[*]

(Dichloromethylene)triphenylphosphorane *(3)* is obtained from triphenylphosphane and dichlorocarbene, which is generated from chloroform and potassium *tert*-butoxide[1] during the reaction. On reaction of triphenylphosphane with carbon tetrachloride the species *(3)* also arises as a short-lived intermediate[2], which resists isolation—just as in the preparation according to ref. [1]—and can only be detected by Wittig reaction with carbonyl compounds.

The first indications of a possible isolation were provided by attempted preparations of *(3)* by dechlorination of (trichloromethyl)triphenylphosphonium chloride *(1)* and dehydrochlorination of (dichloromethyl)triphenylphosphonium chloride *(5)* with an excess of bis(triphenylphosphoranylidene)methane according to equations (a) and (b), respectively[3].

$$\underset{(1)}{[Ph_3P{-}CCl_3]^{\oplus}\,Cl^{\ominus}} + \underset{(2)}{C(=PPh_3)_2} \longrightarrow \quad (a)$$

$$\underset{(3)}{Ph_3P{=}CCl_2} + \underset{(4)}{[Ph_3P{=}CCl{=}PPh_3]^{\oplus}\,Cl^{\ominus}}$$

$$\underset{(5)}{[Ph_3P{-}CHCl_2]^{\oplus}\,Cl^{\ominus}} + \underset{(2)}{C(=PPh_3)_2} \longrightarrow \quad (b)$$

$$\underset{(3)}{Ph_3P{=}CCl_2} + \underset{(6)}{[Ph_3P{=}CH{=}PPh_3]^{\oplus}\,Cl^{\ominus}}$$

During the reactions, which were performed in acetonitrile and dichloromethane, respectively, a singlet appeared in the ^{31}P-NMR spectrum (85 % H_3PO_4 as external standard) at −21.6 ppm which was not observed in any of the other preparations; it disappeared immediately upon addition of benzaldehyde. Thereafter triphenylphosphane oxide and β,β-dichlorostyrene could be detected.

This signal also gradually disappears in the absence of benzaldehyde, thus suggesting a deprotonation reaction of the ylide *(3)* with solvents. In order to record the ^{13}C-NMR spectrum the salt *(5)* bearing a ^{13}C label at the alkyl carbon atom was therefore treated with *(2)* in a deuteriobenzene suspension. The signal of the ylidic C atom which is split into a doublet by phosphorus coupling is seen at $\delta=-73.9$ ppm ($J_{P,^{13}C}=72.3$ Hz; minus sign indicates downfield shift). It was established by ^{13}C-NMR spectroscopy that hydrolysis of *(3)* affords only dichloromethane and triphenylphosphane oxide (TMS as internal standard).

Preparative scale isolation of the pure salt-free ylide *(3)* synthesized according to eq. (b) depends crucially upon the use of an aprotic solvent with which the strongly basic ylide is unable to form a corresponding acid-base pair. A suitable solvent system proved to be a mixture of chlorobenzene and toluene in which *(3)* displays adequate solubility. On removal of the solvent it remains behind as a yellow substance decomposing between 115 and 122 °C, which can be stored for several days. In contrast, solutions of *(3)* can only be stored for limited periods; they turn darker and darker while depositing a coating on the wall of the vessel. Apart from the ^{13}C-NMR spectrum, elemental analysis and cryoscopic molecular mass

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