(0.004 mmol) of di-*tert*-butyl peroxyoxylate in 15 ml of benzene by stirring 10 h at 25 °C. The products were precipitated by the addition of methanol and dried in vacuo to give a solid that softened at about 85 °C and had appreciable solubility in benzene, chloroform, and acetone: IR (KBr) 1776 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.9–2.1 (broad, $CHCH_2$), 1.24 (s, *t*-Bu), and 6.1–7.2 (broad, Ar); mol wt (toluene) 6100.

Anal. Calcd for $(styrene)_{36}(\mathbf{17})_9(O\text{-}t\text{-}Bu)_2$ (mol wt 6004): C, 84.41; H, 7.86. Found: C, 84.00, 85.49; H, 7.43, 7.82.

Attempted CIDNP Experiments. *tert*-Butyl phenylperacetate in CCl_4 was heated to 116 °C in the probe of a Varian A-60 NMR spectrometer. CIDNP signals were noted at δ 2.9 (absorption, CH_3Cl), 3.1 (emission, unknown), 3.7 (absorption, unknown), 4.1 (absorption, $PhCH_2O\text{-}t\text{-}Bu$), 4.7 (emission, $PhCH_2Cl$), and 7.27 (emission, $CHCl_3$). The normal NMR spectrum of **15** was observed at 100 °C but CIDNP signals were absent, and for **17** at 100 °C no NMR signals at all were visible, perhaps because of polymerization.

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Organotellurium Chemistry. 1. Benzyl Tellurocyanate: a Stable Alkyl Tellurocyanate[1] †

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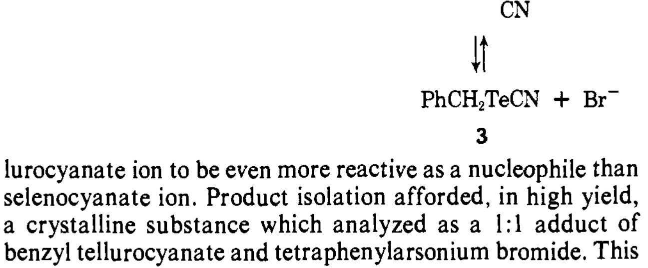
Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174. *Received August 31, 1976*

Abstract: Solutions of alkali-metal tellurocyanates were prepared for the first time and have been employed in the synthesis of benzyl tellurocyanate (**3**). Compound **3**, which represents the first isolable alkyl tellurocyanate, has been physically characterized, and its reactions with selected reagents (oxygen, bromine, hydroxide ion, hypophosphorous acid, and benzyl mercaptan) are reported.

Introduction

Despite the fact that salts of the thiocyanate and selenocyanate ions have been known for more than a century, unsuccessful attempts to prepare the analogous tellurocyanate ion were reported as late as 1964.[2] The first tellurocyanate salt, a dimethylformamide solvate of tetraethylammonium tellurocyanate, was reported by Downs in 1968.[3] Several years later, Austad et al. reported the isolation of solvent-free tetramethylammonium and tetraphenylarsonium tellurocyanates.[4] It appeared that the tellurocyanate anion was stable only adjacent to a large, nonpolarizing cation, at least in the absence of an interposed solvent molecule. In accord with this idea, it has long been known that tellurium dissolves slowly in a liquid ammonia solution of potassium cyanide, but is recovered as elemental tellurium upon evaporation of the solvent.[5] The known tellurocyanate salts are sensitive to air oxidation and are decomposed by water with the liberation of tellurium.[3,4]

The only report of the reaction of tellurocyanate ion with an alkyl halide appeared in 1973.[6] In this study, in which benzyl bromide was reacted with tetraphenylarsonium tellurocyanate (**1**) in acetonitrile, rate measurements showed tellurocyanate ion to be even more reactive as a nucleophile than selenocyanate ion. Product isolation afforded, in high yield, a crystalline substance which analyzed as a 1:1 adduct of benzyl tellurocyanate and tetraphenylarsonium bromide. This material was suggested to be tetraphenylarsonium bromocyanobenzyltellurate (**2**), an example of a four-electron three-



$$\underset{\mathbf{1}}{Ph_4As^+\ TeCN^-} \xrightarrow[MeCN]{PhCH_2Br} \underset{\mathbf{2}}{Ph_4As^+}\ PhCH_2\text{—}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CN}{|}}{Te^-}} \rightleftarrows \underset{\mathbf{3}}{PhCH_2TeCN} + Br^-$$

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† Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

center tellurium compound. Small amounts of tetraphenylarsonium bromide could be recovered by recrystallization of this complex, suggesting the existence of an equilibrium of the three-center anion with bromide ion and benzyl tellurocyanate (**3**); the latter, however, was not isolated or otherwise detected.

We now report an extremely simple method for the preparation of solutions of alkali-metal tellurocyanates, as well as the synthesis and some chemistry of the stable benzyl tellurocyanate (**3**), which represents the first known alkyl tellurocyanate.

Results and Discussion

Alkali-Metal Tellurocyanate Solutions. It was found that stable solutions of potassium or sodium tellurocyanate were readily prepared by stirring together 1 equiv each of powdered tellurium and dry, powdered alkali-metal cyanide in dry dimethyl sulfoxide at 100 °C under an inert atmosphere until all of the tellurium dissolved. The resulting pale-yellow solution decomposed instantly if added to water, with the formation of a jet-black tellurium suspension. Also, attempts to precipitate the alkali tellurocyanates by addition of dry acetone or ether resulted in the formation of a tellurium mirror, showing the salts to be stable only in the Me_2SO solution.

Benzyl Tellurocyanate: Synthesis and Characterization. When a solution of potassium tellurocyanate, prepared as described above, was treated with excess benzyl chloride at room temperature under argon in the dark, most of the tellurocyanate ion had vanished after 2 h. Addition of cold water gave a gray precipitate, which was air dried in the dark and further purified by chromatography or crystallization (see Experimental Section) to give white needles of benzyl tellurocyanate (**3**), mp 126–127 °C; yields were about 60%, based upon the tellurium used. The compound was light sensitive and darkened in the presence of air, particularly in solution; in the dark or under red lights, however, it could be chromatographed on silica and crystallized from hexane–chloroform without decomposition.

Both elemental analysis and mass spectrometry confirmed the composition C_8H_7NTe. The molecular ion was relatively weak (17%), the base peak being the benzyl (or tropylium) cation formed by loss of a TeCN fragment.

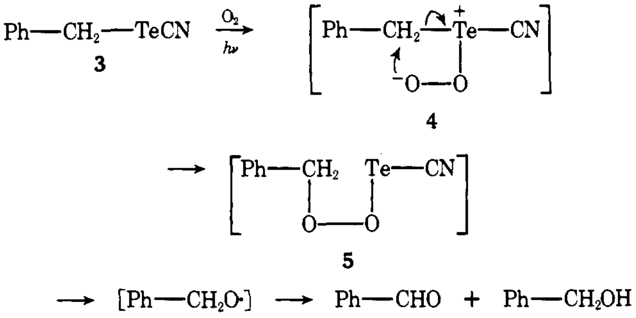
$$\mathrm{KCN} + \mathrm{Te} \xrightarrow{\mathrm{Me_2SO}} \mathrm{KTeCN} \xrightarrow{\mathrm{PhCH_2Cl}} \underset{\mathbf{3}}{\mathrm{Ph\text{-}CH_2TeCN}}$$

The infrared spectrum of **3** in KBr showed the CN absorption band of the tellurocyanate function at 2180 cm^{-1}. The position of this band is almost the same as that (2200 cm^{-1}) observed for the cyano group of benzyl selenocyanate under the same conditions.

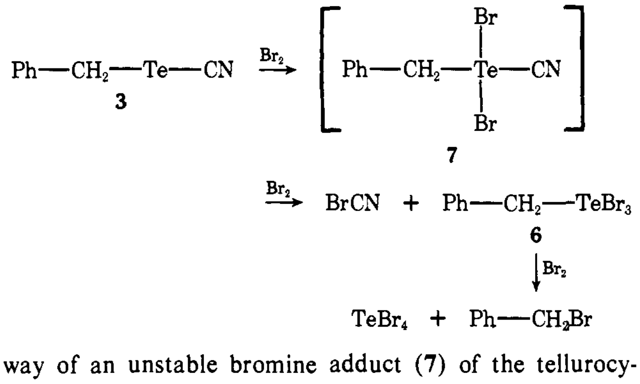
The ^1H NMR spectrum of **3** in $CDCl_3$ consists of a five-proton aromatic singlet at δ 7.38 and a two-proton benzylic singlet at δ 4.52. The corresponding values for benzyl selenocyanate are δ 7.35 and 4.28. Thus the tellurium atom of **3** deshields the adjacent methylene protons considerably more than a selenium atom in the same environment.

Crystallization of an equimolar mixture of **3** and tetraphenylarsonium bromide afforded pale-yellow needles of the previously described[6] complex **2**, mp 118 °C. The properties of this substance suggested that it is probably a loose molecular complex of its two components, rather than a compound containing an anionic tellurium as previously suggested. Thus, the infrared spectrum of the complex in KBr is virtually identical with spectra of its two derived components mixed in the solid state, and also identical with a composite spectrum of these components. Chromatography of the complex on silica in the dark, using chloroform or acetonitrile as eluent, afforded **3** with a recovery of 90%. Finally, the NMR of the complex in $CDCl_3$ was very similar to that of its derived components, although minor changes were observed, suggesting a loose association of the components in solution. Thus, the benzylic methylene of **3** at δ 4.52 is shifted slightly upfield to δ 4.45 in complex **2**. Also, the aromatic singlet of **3** is split into a multiplet in **2**. The latter splitting effect involves the phenyl of **3** rather than the tetraphenylarsonium cation, since a similar splitting is observed when tetrabutylammonium iodide is added to a solution of **3** in $CDCl_3$. In conclusion, although the three-center tellurate structure for **2** seems unlikely, some type of weak associative force must be operative, the nature of which could be best surmised on the basis of an x-ray crystallographic study.

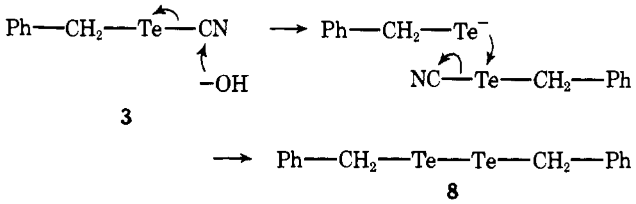
Benzyl Tellurocyanate: Some Chemical Transformations. The most obvious reaction of benzyl tellurocyanate (**3**) is its darkening when exposed to light and air. The compound was surprisingly stable to light alone in the absence of oxygen. Thus, a solution of **3** in $CDCl_3$ in an NMR tube could be irradiated by a Hanovia lamp under nitrogen for 40 h with no decomposition being observed, as indicated by both GC and NMR analysis. Under similar conditions, but under an *oxygen* atmosphere, a black solid precipitated and the solution contained only a mixture of benzaldehyde (60%) and benzyl alcohol (40%). No toluene, diphenylethane, or benzyl chloride were formed in this oxidation. An unpleasant carbylamine-type odor was also noticed, probably as the result of the formation of trace amounts of benzyl isocyanide. The mechanism of the photooxidation of **3** is by no means clear, but it is tempting to speculate that the major reaction pathway may involve singlet oxygen, which could attack the tellurium atom to give the 1,3-dipolar peroxide **4**. Rearrangement of **4** could give an unstable benzylperoxytellurocyanate (**5**), from which benzaldehyde and benzyl alcohol are derivable by way of benzyloxy radicals.



The reaction of tellurocyanate **3** with excess bromine results in loss of the tellurium function and formation of benzyl bromide. A careful NMR study of this reaction revealed the formation of a fairly stable intermediate, which could be isolated when two molecular equivalents of bromine were used. This yellow crystalline compound was shown by complete elemental analysis to be the previously unknown benzyltellurium tribromide (**6**). The formation of **6** from **3** probably proceeds by way of an unstable bromine adduct (**7**) of the tellurocyanate.



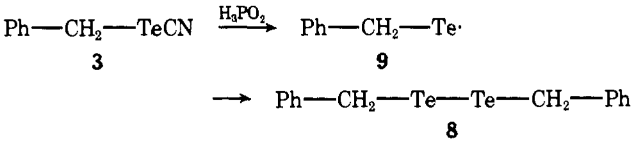
Many diselenides have been prepared by the action of alkali on alkyl or aryl selenocyanates.[7] It was therefore of interest to determine whether or not the same type of reaction was operative in organic tellurocyanate chemistry. It was found, indeed, that the reaction of **3** with methanolic sodium hydroxide under argon afforded, in fair yield (29%), the exceedingly photosensitive dibenzyl ditelluride (**8**). The formation of **8**, which has received brief mention only once in the previous literature,[8] is rationalized as indicated below.



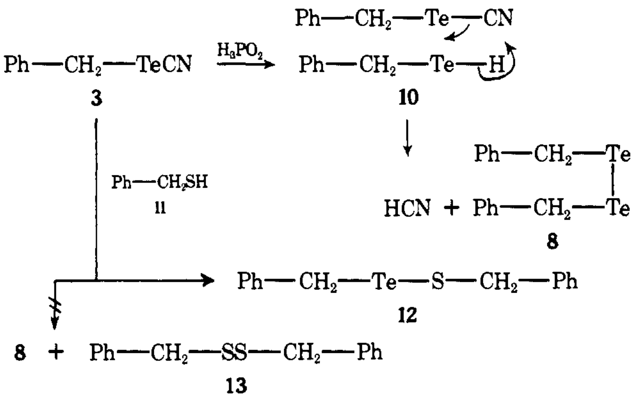
Treatment of **3** with warm hypophosphorous acid proved to be a superior method for the conversion of **3** into **8**, the latter being obtained very cleanly and almost quantitatively.[9] NMR experiments did not reveal a detectable intermediate in this reaction. We have considered two mechanisms for this reaction (Scheme I). In mechanism a, tellurocyanate **3** is reduced to the benzyltellurium radical **9**, which undergoes subsequent dimerization to ditelluride **8**. In mechanism b, **3** is reduced first to the extremely reactive tellurol intermediate **10**, which then undergoes a four-center condensation with **3** to give **8** and hydrogen cyanide. Indirect evidence favoring the latter mechanism was found by investigating the reaction of **3** with benzyl mercaptan (**11**) in CCl_4 solution. NMR showed the disappearance of both **3** and **11** and the formation of a single new product. Isolation afforded yellow prisms of the previously unknown dibenzyl thiotelluride (**12**), and neither **8** nor dibenzyl disulfide (**13**) were produced as by-products.

Scheme I

Mechanism a



Mechanism b



The results described above clearly indicate the potential utility of the easily prepared potassium tellurocyanate in organotellurium chemistry. Further synthetic applications of this reagent are under investigation in our laboratory.

Experimental Section

All reactions were run under red lights in an inert atmosphere unless otherwise stated. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Mass, infrared (KBr), and ultraviolet (hexane) spectra were determined using Perkin-Elmer 270B, 137, and 202 spectrometers, respectively. All tellurium containing mass peaks are reported for ^{130}Te. NMR spectra were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Benzyl Tellurocyanate (3). A mixture of freshly crushed and finely ground tellurium (3.19 g, 0.025 mol) and powdered potassium cyanide (1.63 g, 0.025 mol) in dry dimethyl sulfoxide (Me_2SO, 25 ml) was heated at 100 °C with stirring until all the Te dissolved (~1 h). To the resulting pale-yellow solution, cooled to room temperature and diluted with more dry Me_2SO (50 ml), was added dropwise with stirring a solution of benzyl chloride (6.33 g, 0.05 mol) in Me_2SO (25 ml). After stirring for 2 h at room temperature the mixture was poured into cold water (250 ml). The gray solid was filtered, dried, and washed by decantation with hot petroleum ether. The insoluble residue was crystallized from hexane-chloroform (9:1) to yield 3.77 g (61.0%) of **3** as white needles: mp 126-127 °C; IR 2180 cm^{-1}; NMR 4.52 (s, 2 H), 7.38 (br s, 5 H); mass spectrum *m/e* (relative intensity) M^+ 247 (17), 91 (100). Anal. Calcd for C_8H_7NTe: C, 39.25; H, 2.88; N, 5.72; Te, 52.13. Found: C, 39.00; H, 2.85; N, 5.66; Te, 52.07.

A solution of sodium tellurocyanate was prepared similarly from NaCN (2.45 g) and Te (6.4 g) in Me_2SO (40 ml) and reacted with benzyl chloride under the same conditions as above to yield 57.4% of **3**.

Tetraphenylarsonium Bromide–Benzyl Tellurocyanate Complex (2). Saturated solutions of **3** (0.49 g) and tetraphenylarsonium bromide[10] (0.93 g) in MeCN were mixed, cooled, and diluted with ether to turbidity. After chilling overnight, the yellow crystals which separated were filtered and recrystallized from MeCN-Et_2O to give adduct **2**: mp 118 °C (lit.[6] mp 118 °C); mass spectrum *m/e* (relative intensity) 247 (17), 91 (100). Chromatography of **2** on silica using $CHCl_3$ or MeCN as eluent regenerated **3** (90% recovery).

Photochemical Decomposition of 3. A solution of **3** (50 mg) in $CDCl_3$ (0.5 ml) in an NMR tube was irradiated in the presence of oxygen, using a Hanovia lamp, until no more tellurium deposited. The suspension was filtered, and the filtrate was analyzed by NMR spectroscopy showing it to contain benzaldehyde (60%) and benzyl alcohol (40%). This was further confirmed by GC analyses.

Irradiation of $CDCl_3$ solutons of **3** in the presence of nitrogen for 40 h led to no decomposition and the NMR spectrum remained unchanged.

Benzyltellurium Tribromide (6). A solution of **3** (0.50 g, 0.002 mol) in dry CH_2Cl_2 was treated dropwise with a solution of bromine (0.33 g, 0.002 mol) in CH_2Cl_2. After stirring for ½ h, the mixture was filtered and concentrated at a low temperature to the crystallization point. The yellow clumps of crystals were filtered to give **6**: mp 150 °C (dec, turns gray at 135-138 °C); NMR 4.60 (s, 2 H), 7.42 (m, 5 H). Anal. Calcd for $C_7H_7Br_3Te$: C, 18.34; H, 1.54; Br, 52.29. Found: C, 18.49; H, 1.51; Br, 52.43.

Dibenzyl Ditelluride (8). a. Action of Alkali on 3. A solution of **3** (0.49 g, 0.002 mol) in MeOH was treated with a methanolic solution of NaOH (0.160 g, 0.004 mol). After 5 min stirring, the mixture was diluted with water and the product was filtered. Crystallization of the dry red precipitate from petroleum ether yielded dibenzyl ditelluride (**8**) as red-brown plates (0.125 g; 29%): mp 80-81 °C (lit.[8] mp 78.4-79 °C); NMR 4.25 (s, 4 H), 7.22 (br s, 10 H), λ_{max} 224 nm (log ϵ 4.41), 280 (3.79), 412 (2.00), mass spectrum M^+ 442. Anal. Calcd for $C_{14}H_{14}Te_2$: C, 38.43; H, 3.22; Te, 58.33. Found: C, 38.27; H, 3.30; Te, 58.33.

b. Action of Hypophosphorous Acid on 3. A mixture of finely powdered **3** (1.0 g) and H_3PO_2 (12 ml, 50%) was warmed gently with stirring. After 3 h the brown solid was filtered, dried and crystallized from petroleum ether to yield **8** (0.81 g, 91%), mp 80-81 °C.

Dibenzyl Thiotelluride (12). A solution of **3** (0.123 g) and benzyl mercaptan (0.062 g) in CCl_4 was stirred for 20 min. The solvent was removed and the residue was crystallized from petroleum ether to give yellow prisms of **12**: mp 68-69 °C; NMR 3.92 (s, 2 H), 4.10 (s, 2 H) and 7.25 (m, 10 H); mass spectrum *m/e* (relative intensity) M^+ 344 (99), 91 (100). Anal. Calcd for $C_{14}H_{14}STe$: C, 49.17; H, 4.13; S, 9.37; Te, 37.31. Found: C, 49.27; H, 4.09; S, 9.50; Te, 37.09.

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Metalation Reactions. 19. Selectivity in the Metalation of Polymethylbenzenes

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Contribution from the Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel.

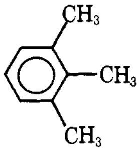
Received January 19, 1976

Abstract: The metalation of 1,2,3- and 1,2,4-trimethyl- and 1,2,4,5-tetramethylbenzene with butyllithium–TMEDA gave bis-1,2- and -1,3-lithiomethyl compounds and that of 1,2,3,5-tetramethylbenzene led to bis-1,2- and -1,3-lithiomethyl and to tris-1,3,5-lithiomethyl derivatives. No bis-1,4-lithiomethyl compounds were obtained with this reagent. The last compounds were formed using butyllithium–potassium *tert*-butoxide as metalating agent. With this reagent also tetrametalation of 1,2,3,5-tetramethylbenzene was observed. The lithium compounds were characterized by their ^1H NMR spectra and by their reaction with trimethylchlorosilane. Their reaction with borane led to benzylic alcohols. The directive effects of methyl and lithiomethyl groups and their possible reasons are discussed.

We have found recently[1] that *o*- and *m*-xylene and mesitylene can be di- and trilithiated with butyllithium–TMEDA at room temperature to bis- and tris(lithiomethyl)benzene, respectively. However *p*-xylene gave under similar conditions a product that was dilithiated at the same benzylic carbon. It was concluded[1] that metalation with butyllithium was favored to proceed in such a manner that charge alternation was maintained in the delocalized carbanion.

The selectivity of dimetalation of polymethylbenzenes can be studied only when more than two methyl substituents are located on the ring. However, the only trimethylbenzene studied previously was mesitylene, in which all the methyls are equivalent by its symmetry and cannot be distinguished in the metalation. Other tri- and tetramethylbenzenes have therefore been submitted to the metalation with butyllithium.

The treatment of 1,2,3-trimethylbenzene (I) with butyllithium in hexane in the presence of tetramethylethylenediamine (TMEDA) gave (Table I) a 2:1 mixture of 2,3- (II) and 2,6-dimethylbenzyllithium (III) and one dilithium derivative exclusively, the bis(1,2-lithiomethyl)-3-methylbenzene (IVa).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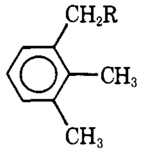
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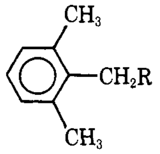
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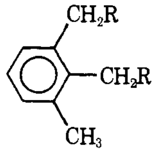
IV

a, R = Li c, R = K

b, R = $Si(CH_3)_3$ d, R = $OCOCH_3$

The composition of the products of metalation was determined by treatment of the reaction mixture with trimethylchlorosilane and isolation of the corresponding trimethylsilyl derivatives IIb–IVb. The disilyl derivative was separated and characterized by its ^1H NMR spectrum (Table II). The ratio of the monosilyl compounds IIb and IIIb has been determined by the ^1H NMR of their mixture, the symmetrical IIIb being easily distinguished from IIb. IIIb was characterized by a singlet at 2.21 ppm (6 H) corresponding to the two equivalent methyls and by a singlet at 2.11 ppm of the methylene (2 H) α to the trimethylsilyl group. IIb was characterized by a singlet at 2.24 ppm (3 H) corresponding to one benzylic methyl and a singlet at 2.11 ppm ascribed to the other benzylic methyl and the methylene α to the trimethylsilyl group. The assignment of the signals was verified when samples of different isomeric ratios were compared. The reduction of the amount of IIb was accompanied by the lowering of the signal height at 2.11 ppm and in samples where IIIb was the major product, the spectrum was composed of a sharp singlet at 2.21 and a lower singlet at 2.11 ppm.

The lithium derivatives IIa–IVa have been identified in the hexane solution by their ^1H NMR spectrum and particularly in the aromatic region. After short metalation times, the protons para to the lithiomethyl groups were found at 5.5–5.73 ppm and the ortho-meta protons at 6.07–6.43 ppm. The signals of IIIa were particularly clear in THF solution, where the para proton appeared as a triplet at 5.53 and the meta protons as a doublet at 6.18 ppm. Longer metalation intervals in hexane–TMEDA led to IVa, which exhibited a multiplet of the two protons para to the lithiomethyl groups at 5.43–5.53 and one proton para to the methyl as a doublet of doublets at 6.06 ppm.

Metalation of I was also carried out with various amounts of butyllithium and potassium *tert*-butoxide according to the procedure of Schlosser.[2] The reaction mixture was treated with trimethylchlorosilane and the composition of the silylated products determined. A ratio of IIb and IIIb was obtained (Table I) after short metalation times that was similar to that