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HYPERVALENT IODINE IN SYNTHESIS XXVI: A CONVENIENT SYNTHESIS OF ACETYLENIC TELLURIDES

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Abstract: Acetylenic tellurides have been prepared by the reaction of sodium arenetellurolates with alkynylphenyliodonium tosylates in DMF.

There is considerable current interest and research activity in tricoordinate iodine (II) compounds. The latest members of the family of multicoordinate iodine species, alkynylphenyliodonium tosylates, have become valuable reagents in organic synthesis⁽¹⁾. Following our finding that alkynylphenyliodonium tosylates are efficient electrophilic alkynylating agents for sodium areneselenolates⁽²⁾, we investigated the possibility of extending this alkynylating reaction to sodium arenetellurolates since tellurium is an element homologous with selenium. Such reaction would provide an effective method for the preparation of acetylenic tellurides which are synthetic intermediates of great potential. They can function as either nucleophilic or electrophilic tellurium centers. Moreover, they can be easily transformed into vinylic tellurides by reaction with sodium borohydride⁽³⁾.

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In this communication we report a convenient method for the synthesis of acetylenic tellurides. Analogous to Se-alkynylation of sodium areneselenolates⁽²⁾, alkynylation of the sodium arenetellurolates (1), prepared by reduction of diaryl ditellurides with sodium borohydride, with alkynylphenyliodonium tosylates (2) readily occurred in a single step to afford acetylenic tellurides (3).

ArTeNa +	RC≡CI+Ph [−] OTs	DMF 70-80 C	ArTeC=CR		
(1) (2)			(3)		
Ar=Ph	R=Ph		Ar	R	
$C_{10}H_8$	t-Bu	а	Ph	Ph	
p-CH ₃ C ₆	₅ H ₄	b	$C_{10}H_8$	Ph	
p-BrC ₆ H	[4	с	$p\text{-}CH_3C_6H_4$	Ph	
		d	$p-BrC_6H_4$	Ph	
		e	Ph	t-Bu	
		f	$C_{10}H_{8}$	t-Bu	

Simple stirring the sodium arenetellurolates (1) with alkylnylphenyliodonium tosylates (2) in dimethylformamide at 70-80 °C gave, after workup and isolation, the desired acetylenic tellurides (3) in good yields, as shown in Table 1.

The products were characterized by ¹H-NMR, IR, MR spectra and m. p. as summarized in the Table.

In literature some methods to prepare acetylenic tellurides were developed, such as the reaction of the lithium acetylides with elemental tellurium, followed by trapping the intermediate lithium tellurolates with alkyl halides or by the reaction of the corresponding lithium acetylide with aryltellurium bromides,⁽³⁾⁽⁴⁾ treatment of haloacetylenes with lithium organyltellurolates,⁽⁵⁾ reaction of appropriate terminal alkyne with phenyltellurium bromide in the presence of cuprous iodied⁽⁶⁾, treatment of arenetellurenyl halides with Grignard reagents⁽⁷⁾ and the reaction of arenetellurenamides with terminal acetylenes⁽⁸⁾. However, these methods are deficient in some respects, such as low yields, expensive, toxic or not readily available reagent, strict reaction conditions, or difficulties with isolation of the product and limited scope.

The present method has the advantages of accessible starting materials, mild reaction conditions, convenient manipulation and moderate yield.

General procedure for the preparation of acetylenic tellurides(3): A mixture of the appropriate diaryl ditelluride (1 mmol) and sodium borohydride (2. 2 mmol) in DMF (10 ml) was stirred under an N₂ atmosphere at 50-60 C until the solution was clear. The mixture was allowed to cool to room temperature, an appropriate alkynylphenyliodonium tosylate (2) (2 mmol) and DMF (10 ml) were added and stirring was continued at 70-80 C under N₂. The course of the reaction was followed by TLC. When the reaction was completed, the mixture was cooled, diluted with water (15 ml) and the product was extracted with petroleum ether (3×10 ml). The combined extracts were washed with water, and dried with MgSO₄. After removal of the solvent, the residue was chromatographed on a column of silica gel using methylene chloride as eluent to give the acetylenic telluride. All relevant data are summarized in the Table.

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MR(M^+) or elemental analysis found (calcd.)%	308	358	322	C:43.42(43.71) H:2.24(2.36)	C:50.52(50.42) H:4.86(4.94)	C:57.12(57.04) H:5.18(5.09)
IR,v(cm ⁻¹)	3080, 2940, 2150, 1580, 1480, 1440, 1020, 750, 725, 675	3080, 2940, 2150, 1580, 1450, 1440, 1020, 750, 790, 690	3085, 2940, 2140, 1580, 1490,1450,1010,750,685	3040, 2940, 2120, 1585, 1480, 1020, 810, 750, 730, 690	3020, 2940, 2150, 1569, 1470,1035,1009,750,690	3010, 2940, 2150, 1570, 1480,1010,790,750
¹ H-NMR (ppm) (CCl ₄ /TMS)	7.67-7.17(m,10H)	7.60-7.30(m,12H)	7.70-7.00(m,9H)	7.50-7.17(m,10H)	7. 10-7. 50(m,5H) 1. 23(s,9H)	7.20-7.51(m,7H) 1.25(s,9H)
m. p(°C)	oil	oil	71	33	oil	lio
Yield (%)	51%	20%	53%	49%	49%	48%
Reaction Time(hr)	~	5	т	4	4	4
Product	3a	3b	3c	3d	3e	3£

Table 1 Acetylenic tellurides (3) prepared

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