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THE REACTION OF DIARYL TELLURIDES WITH VIC-DIBROMIDES

A NEW AGENT OF DEBROMINATION

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THE fact that aryltellurides (I) are very easily transformed into the corresponding diaryl tellurium dihalides (III) led us to study their reactive with ethylene bromides in order to obtain ethylenes (IV).

Actually refluxing a solution of diphenyl telluride (I: $Ar=Ar=C_6H_5$) in ethylene bromide for about two hours the corresponding tellurium dibromide was obtained in good yield. Several diaryl tellurides (I) and vic-dibromides (II) were used and the compounds of type III and IV (when solids) obtained in these experiments have been identified by mixed melting point with authentic samples. The results are given in Table 1.

Performing the reaction of diphenyl telluride and ethylene bromide under mild conditions (gently refluxing during 30 min) the ethylene bis

¹ K. Lederer, <u>Ber. 49</u>, 334 (1916); K. Lederer, <u>Ann. 391</u>, 326 (1912); H. Rheinboldt and G. Vicentini, <u>Ber. 89</u>, 624 (1956).

diphenyl telluronium bromide (V) was obtained in 74% yield. (m.p. 259-263°; Found: Te, 33.7. $^{\text{C}}_{26}{}^{\text{H}}_{24}{}^{\text{Br}}_{2}{}^{\text{Te}}_{2}$ requires Te, 33.96). This compound is the first that contains two tellurium atoms in the same molecule.

A solution of compound V in ethylene bromide being vigorously refluxed gave rise to yellow crystals of diphenyl tellurium dibromide (m.p. 199-202°). The same transformation was observed when compound V was recrystallized from glacial acetic acid.

$$V \xrightarrow{\text{BrCH}_2-\text{CH}_2\text{Br}} \xrightarrow{\hspace{1cm}} 2(\text{C}_6\text{H}_5)_2\text{TeBr}_2 + 2\text{CH}_2=\text{CH}_2$$

$$V \xrightarrow{\hspace{1cm}} \text{HOAc} \xrightarrow{\hspace{1cm}} (\text{C}_6\text{H}_5)\text{TeBr}_2 + \text{CH}_2-\text{CH}_2 + (\text{C}_6\text{H}_5)_2\text{Te}$$

Whether or not the telluronium bromides of type V are necessarily intermediate in these debromination reactions is under investigation.

It was also shown that a solution of diphenyl telluride in allyl bromide heated at 180° in a sealed tube for 3 hr gives rise to a diphenyl tellurium dibromide and probably diallyl.

$${^{\text{C}}_{6}}^{\text{H}}_{5}{^{\text{TeC}}}_{6}^{\text{H}}_{5} + {^{\text{2CH}}}_{2}{^{\text{=CH-CH}}}_{2}{^{\text{-Br}}} \longrightarrow {^{\text{(C}}_{6}}^{\text{H}}_{5})_{2}^{\text{TeBr}}_{2} + {^{\text{(CH}}}_{2}{^{\text{=CH-CH}}}_{2})_{2}$$

No reaction occured when a mixture of n-butyl bromide and diphenyl telluride was heated in a sealed tube at 180° for two days. Under the same experimental conditions methyl iodide gave rise to the corresponding telluronium iodide. In this connexion it is interesting to point out

LABLE 1.

Reaction of Diaryl Tellurides with vic-Dibromides

Yield		1	1	1	948	100b	1	58ª	93 ^e		
Yield Ethylenes (IV) Yield $\frac{\pi}{2}$		•	1	•	C _{6H5} CH=CHC _{6H5} (trans)	сен ₅ сн≖снсоон	ı	Cholesterol	Cholesterol		
Yield		99	70	98	85	74	84°	77	17		
Diaryl tellurium dibromides (III)	Ar'	b.p.solv. 8-CloH7 p-CH30-C6H4	b.p.solv. a-GloH7 p-GH20-G6H4	$c_{\rm H_5}$	C6H5	C ₆ H ₅	C ₆ H ₅	c _H 5	cens	.46-149°.	
Diaryl dibrom	Ar ,	8-c10H7	$^{a-c}_{10^{\rm H}7}$	C ₆ H ₅	c ₆ H ₅	6,45°	c _e H ₅	ce ^H 5	c ₆ H ₅	ter, m.p. 1	
•dwa1		b.p.solv.	b.p.solv.	b.p.solv,	150°	011	b.p.solv.	b.p.solv.	950	23°. . 128-133°. rom ethanol/was, m.p. 133-14	
Solv.		II	Ħ	Ħ	1	ı	Ħ	xilene	ŧ	p. 118-12 tter, m.p. twice fr solvents	
Vic-dibromides (II)		Broh ₂ -oh ₂ Br	BroH2-cH2Br	BrCH2-CH2Br	o ₆ 15 chbr. chbro ₆ 15	CeH5CHBr.CHBrCOOH	CH2-CH2 CH2-CH2 CHBr. CHBr	Dibromo cholesterol xilene	Dibromo cholesterol	a Crude product: recrystallization from ethanol m.p. 118-123°. b Crude product: recrystallization from ethanol/water, m.p. 128-133°. c Impure product. d Crude product: rec.from glacial acetic acid then twice from ethanol/water, m.p. 146-149°. e Very impure product: several rec. from different solvents, m.p. 133-146°. 4 H. Rheinboldt and G. Vicentini, Ber. 89, 624 (1956).	
Diaryl tellurides (I)	Ar'	8-C10H7 p-CH30-C6H4 BrcH2-CH2Br	a-c10H7 p-CH30-C6H4	c ₆ H _S	C6H5	C ₆ H ₅	c _e H _S	c ₆ H ₅	06H5	a Crude product: recrysta b Crude product. c Impure product. d Crude product: rec.from e Very impure product: se f H. Rheinboldt and G. Vi.	
Diaryl t	Ar	8-C10H7	a -C10H7	C _e H ₅	c ₆ H ₅	c ₆ H ₅	06H5	c ₆ H ₅	c _{6H5}	a Crude b Crude c Impure d Crude e Very it	

that Lederer has shown that the reaction of methyl iodide² and a-bromo acids and esters³ with tellurides, when performed at room temperature gives rise to the corresponding telluronium halides, but even at higher temperature debromination of the alkyl halide was never observed.

Since diary! tellurides may be recovered quantitatively by treating the diaryl tellurium dihalides with sodium sulphite⁵ they are suitable debromination agents.

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² K. Lederer, <u>Ann.</u> 399, 262 (1913).

³ K. Lederer, <u>Ber.</u> 46, 1362 (1913).

⁴ See Table 1 on page 7.

⁵ L. Reichel and E. Kirschbaum, <u>Ber.</u> 76, 1105 (1943).