Journal of Organometallic Chemistry, 164 (1979) C23–C24

Preliminary communication

AROMATIZATION OF UNSATURATED CYCLOHYDROCARBONS AND HALOCYCLOHYDROCARBONS BY TELLURIUM TETRACHLORIDE

MICHAEL ALBECK and TOVA TAMARY

Department of Chemistry, Bar-Ilan University, Ramat-Gan (Israel)

(Received October 23rd, 1978)

Summary

TeX_4 (X = Cl, Br) brings about aromatization of various unsaturated cyclohydrocarbons and halocyclohydrocarbons by dehydrogenation and dehydrohalogenation, respectively. In some of the cases studied the adducts formed by addition of $TeCl_4$ to the unsaturated hydrocarbons were isolated and identified.

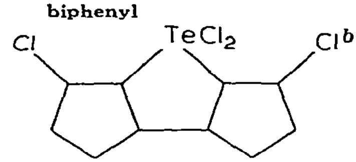
Dehydrogenation of activated acyclic hydrocarbons by selenium dioxide is well known [1]. It was reported recently that polynuclear hydrocarbons are dehydrogenated by the catalytic effect of tellurium [2] and that NaHTe debrominates *vic*-dibromides [3]. We report below the dehydrogenation and dehydrohalogenation of several cyclic hydrocarbons and halogenated cyclic hydrocarbons by $TeCl_4$ and $TeBr_4$ to give the corresponding aromatic compounds. The compounds investigated and products obtained are listed in Table 1.

In all these reactions, metallic tellurium and HCl were formed in addition to the organic products. In order to identify which tellurium species is active in the dehydrogenation and dehydrohalogenation, cyclohexene was treated with TeO_2 and both cyclohexene and cyclohexyl chloride were treated with powdered metallic tellurium, but no reaction took place in all three cases.

In reactions in which aromatic products cannot be formed, for example that with bicyclopentene (other examples have been studied), the product of addition of $TeCl_4$ to the olefinic reagent was the final product. In several cases in which the molar ratio of hydrocarbon to $TeCl_4$ was 1/1 an addition adduct was formed quantitatively. From cyclohexene and with chlorocyclohexane 2-chlorocyclohexyltellurium trichloride was formed, while from 4-methylcyclohexene 2-chloro-4-methylcyclohexyltellurium trichloride was obtained; bicyclohexene gave an addition adduct which has not yet been completely identified. Reaction of the above compounds with an additional 1 molar proportion batch of $TeCl_4$ converted the adducts to the corresponding aromatic end products. In other cases such as with 9,10-dihydroanthracene,

TABLE 1

AROMATIZATION OF CYCLIC HYDROCARBONS AND HALOCYCLOHYDROCARBONS BY $TeCl_4$

Reagent	Solvent	T (°C)	Products[a]
9,10-Dihydroanthracene	$CHCl_3$, CCl_4	25	9,10-dichloroanthracene
	$CHCl_3$, CCl_4	76	9,10-dichloroanthracene
Decalin	neat	200	1,2-dichloronaphthalene, 1-chloronaphthalene and naphthalene
Tetralin	neat	200	1,2-dichloronaphthalene, 1-chloronaphthalene and naphthalene
2,2′-Bicyclohexene	toluene	reflux	biphenyl
	CCl_4	76	biphenyl
	$CHCl_3$	63	biphenyl
2,2′-Bicyclopentene	CCl_4	76	
Cyclohexene[c]	CCl_4, $CHCl_3$, CH_3CN	76	benzene
4-Methylcyclohexene	CCl_4, CH_3CN, benzene	76	toluene
1-Methylcyclohexene	CCl_4	76	toluene
3-Chlorocyclohexene	CH_3CN	25	benzene
	CCl_4	76	benzene
Cyclohexyl chloride[d]	CCl_4	76	benzene
Cyclohexyl bromide	CCl_4	76	benzene
Limonene	CCl_4	76	*p*-cymene

[a]Reaction time was 6 h. [b]Identified by elemental analysis, ^{13}C NMR and ^{1}H NMR spectroscopic measurements. [c]A reaction with $TeBr_4$ gave the same results, though the reaction was much slower. [d]No reaction occurred with $TeBr_4$. Cyclohexene was formed in the first stage followed by aromatization to benzene.

3-chlorocyclohexene, 1-methylcyclohexene, decalin, tetralin and limonene, no addition adducts were detected, only the aromatic products being obtained directly.

References

1 E.N. Trachtenberg, in R.L. Augustine (Ed.), Oxidation Techniques and Applications in Organic Synthesis, Marcel Dekker Inc., N.Y. 1969, p. 166—171 and ref. cited therein.
2 K. Takahashi and Y. Ogino, Chemistry Lett., (1978) 423, 549.
3 K. Ramasamy, S.K. Kalyanasundaram and P. Shanmugam, Synthesis, (1978) 311.