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Formation of Benzylic Chlorides by Rearrangement of Cycloheptatrienes with Tellurium Tetrachloride

Michael Albeck,* Tova Tamari, and Milon Sprecher

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel

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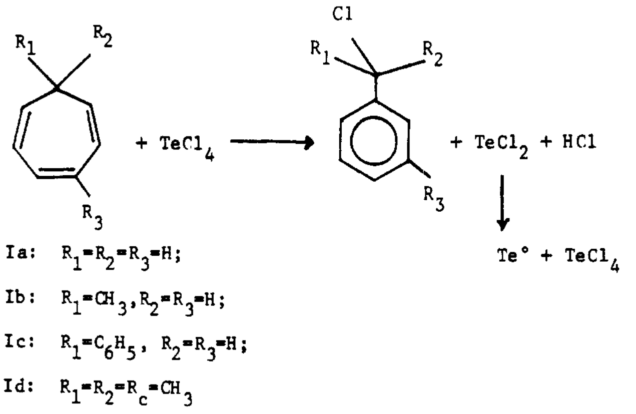
The rearrangement of cycloheptatrienes and alkyl cycloheptatrienes to substituted benzenes has been reported to proceed photochemically, or thermally at higher temperatures.[1] For the latter conditions a radical pathway has been postulated.[2-4] Föhlisch[5] has presented evidence for the operation of ionic pathways in the isomerization and in the solvolysis of chloro- and bromocycloheptatrienes to benzyl halides or ethers, etc. Reaction temperatures of 80–125 °C were found necessary.

In this paper we report the unique and facile rearrangement of various cycloheptatrienes to benzene derivatives accompanied by benzylic halogenation. The reaction is formulated below and involves the use of tellurium tetrachloride as a reagent. It was studied for compounds Ia–d and proceeded at low temperature (0–5 °C) in good yield. Products and reaction times in CCl_4 are listed in Table I. The rate of the reaction is solvent dependent.



Ia: $R_1=R_2=R_3=H$;

Ib: $R_1=CH_3, R_2=R_3=H$;

Ic: $R_1=C_6H_5$, $R_2=R_3=H$;

Id: $R_1=R_2=R_c=CH_3$

In the more polar solvent CH_2Cl_2 the reaction is much faster than in CCl_4. For example, with 3,7,7-trimethylcycloheptatriene (Id) in methylene chloride the reaction was complete after 15 min, whereas in carbon tetrachloride it took 120 min. Only the listed rearrangement products and polymeric products were obtained. The ratio of rearrangement product to polymeric product decreases as the temperature is raised. The polymerization of the benzyl-type halides under such reaction conditions has been reported by us previously.[6] Reactions are terminated and polymerization avoided by the addition of water which hydrolyzes the $TeCl_4$. The action of $TeCl_4$ is not catalytic. When cycloheptatriene reacted with $TeCl_4$ in various molar ratios it was found that the reaction proceeded in a ratio of 1:0.7 cycloheptatriene/$TeCl_4$, and any excess of cycloheptatriene did not react. This ratio is due to the disproportionation of $TeCl_2$ which forms metallic tellurium and $TeCl_4$.

A cationic mode of rearrangement is suggested for the reaction on the following bases. Reactions of $TeCl_4$ with olefins are known to proceed by ionic mechanisms[7,8] involving electrophilic addition of either $TeCl_3^+$ ("telluration") or Cl^+ ("chlorination"). The relative rates of reaction found for the series of cycloheptatrienes studied (see Table I) are those expected for the formation of carbenium ion intermediates. The solvent effect is consistent with an ionic rearrangement.

Furthermore, Id yielded only 3-(2-chloro-2-propyl)toluene and none of the 4-(2-chloro-2-propyl) isomer. This regioselectivity can be rationalized on the basis of the proposed ionic mechanism (vide infra). In contrast, the thermal rearrangement of Id at 300 °C has been reported to give a mixture of *m*- and *p*-cymene (in addition to nonaromatic products).[4]

In view of the known valence tautomerism between the cycloheptatriene and norcaradiene systems one must consider the possibility of rearrangement from either or both structures.

Starting with the cycloheptatriene structure, one may propose Scheme I for the rearrangement.

Of possible sites for electrophilic attack, that on C-6 yields the most stable carbenium ion, it being maximally delocalized and in the case of $R = CH_3$ stabilized by electron release from the C-3 methyl substituent. In such an intermediate the migrating atom would be a tetrahedral carbon rather than a trigonal one, and the resulting product in such a scheme is exclusively the meta isomer, as found in fact.

A possible reservation may be raised in the case of the rearrangement of Ia which would involve the (incipient?) formation of a primary carbenium ion. Such an objection would, of course, fall if all steps prior to aromatization are reversible.

The alternative, presented in Scheme II, of rearrangement via the norcaradiene tautomer appears, however, to be more viable, since such a pathway should involve lower energy transition states and intermediates. In the case of Id the methyl substituent at C-3 will facilitate electrophilic attack at C-2 (rather than C-5; see above), leading to the meta isomer found. In all cases the delocalized carbenium ion (X′) formed enjoys both allylic and cyclopropylcarbinyl stabilization. Its steric disposition in this bicyclic system is appropriate for a stereoelectronically controlled cleavage of the C_6–C_7 bond, rather than the C_1–C_6 bond. Such bond cleavage is a further example of the cyclopropylcarbinyl homoallylic-type rearrangement[9] known to occur even in unsubstituted systems (i.e., Ia with $R_1 = R_2 = R_3 = H$).

The conversion of X in Scheme I or X′ in Scheme II to the aromatic end product requires the addition of chloride to the benzyl carbon and elimination of "HE".[6]

In other studies[6] on the reactions of $TeCl_4$ we have found that this reagent yields telluration products in reactions with isolated carbon–carbon double bonds, whereas with conjugated polyenes chlorination products are obtained. Consequently, it is proposed that the electrophilic attack in the present case is one of chlorination (E = Cl), and the aromatization involves the elimination of HCl catalyzed by the $TeCl_4$ present.

The uniqueness of the $TeCl_4$ reagent in its reaction with the cycloheptatriene systems, causing ring contraction and aromatization at low temperatures, is particularly noteworthy. It may be attributed to the Lewis acid character of $TeCl_4$ as well as to the low availability of a chloride ion source in the medium, both of which prevent the termi-

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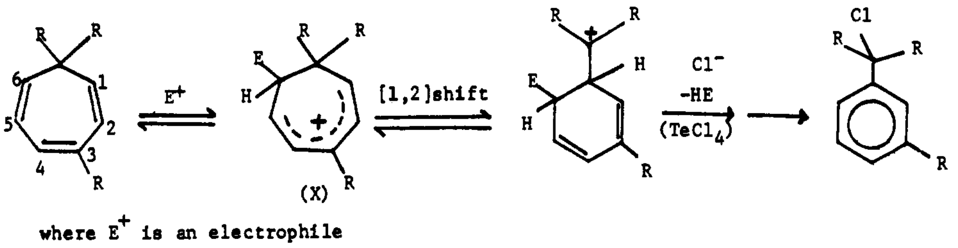
Table I. Reaction of Cycloheptatrienes Ia-d with $TeCl_4$ in CCl_4 at 0-5 °C

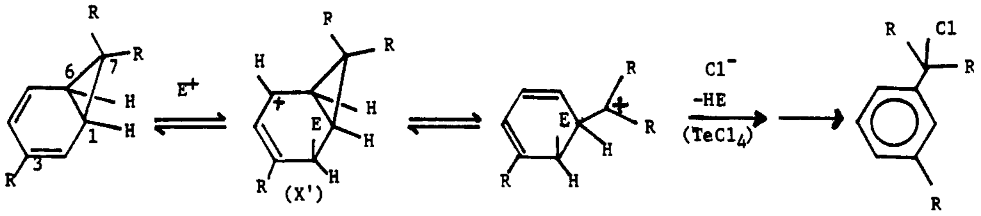
compd	R_1	R_2	R_3	rearrangement product[a]	yield, %	t,[b] h
Ia	H	H	H	benzyl chloride[c]	47	20
Ib	CH_3	H	H	1-chloro-1-phenylethane	63	12
Ic	C_6H_5	H	H	benzyhydryl chloride	70	5
Id	CH_3	CH_3	CH_3	3-(2-chloro-2-propyl)toluene	78	2

[a] In all reactions metallic tellurium precipitated and a polymer was found as byproduct. [b] Time required for complete conversion of reactant. [c] At 25 °C.

Scheme I



Scheme II



nation of the reaction by chloride addition to X and facilitate the conversion of X or X′ to the benzylic halide in the manner indicated. This reactivity contrasts with the reactions of the halogens with cycloheptatriene. Both chlorine[10] and bromine[11] give only simple addition products which eliminate at elevated temperatures to yield (oxidatively) tropylium ion. The latter is also the product reported for the reaction with iodine,[12] as well as with fluorosulfonic acid.[13,14]

Experimental Section

Materials. $TeCl_4$ (CP, Merck, West Germany), cycloheptatriene (technical Merck, West Germany), carvone (AR, Aldrich, U.S.), 4-methylacetophenone (CP, Schuchardt, Germany), 3-methylacetophenone (CP, Schuchardt, Germany), and 2-bromotoluene (CP, Koch-Light, England) were not further purified before use. All solvents were dried by standard procedures.[22]

7-Methylcycloheptatriene was synthesized by the procedure of Conrow[15] from 7-methoxycycloheptatriene and methylmagnesium iodide: ^{1}H NMR ($CDCl_3$) δ 1.36 (3 H, d), 1.40 (1 H, m), 5.15 (2 H, dd), 6.24 (2 H, m), 6.68 (2 H, m). 7-Methoxycycloheptatriene was synthesized[16] from tropylium tetrafluoroborate and methanol. Tropylium tetrafluoroborate was synthesized[17] from cycloheptatriene, PCl_5, and HBF_4.

7-Phenylcycloheptatriene was synthesized according to the procedure of Jutz and Voithenleitner[16] from phenylmagesium bromide and 7-methoxycycloheptatriene: ^{1}H NMR ($CDCl_3$) δ 2.66 (1 H, t), 5.30 (2 H, dd), 6.28 (2 H, m), 6.65 (2 H, t), 7.33 (5 H, m).

3,7,7-Trimethylcycloheptatriene was prepared according to the procedure of Adler et al.[18] by the reduction of eucarvone with $LiAlH_4$ in ether and the dehydration of the eucarvol obtained by distillation of the alcohol over $KHSO_4$: ^{1}H NMR ($CDCl_3$) δ 0.95 (6 H, s), 2.02 (3 H, s), 5.20 (2 H, d), 5.86 (2 H, d), 6.20 (1 H, dd). Eucarvone was prepared from carvone by the procedure suggested by Ayer and Browne.[19]

1-Chloro-1-phenylethane was synthesized from 1-hydroxy-1-phenylethane and thionyl chloride.[21] 3-(2-Chloro-2-propyl)toluene was prepared by starting from 3-methylacetophenone and methylmagnesium iodide via 3-(2-hydroxy-2-propyl)toluene by the procedures of Brown et al.[20] The 4-(2-chloro-2-propyl)toluene was prepared in the same way as the meta isomer by starting with p-methylacetophenone.[20]

2-(2-Chloro-2-propyl)toluene was prepared from 2-(2-hydroxy-2-propyl)toluene and thionyl chloride in refluxing benzene.[21] The 2-(2-hydroxy-2-propyl)toluene was prepared by a Grignard reaction of 2-bromotoluene with acetone.[20]

General Procedure. A solution of 10 mmol of the cycloheptatriene and 1.9 g (7 mmol) of $TeCl_4$ in 30 mL of dry CCl_4 or dry CH_2Cl_2 is stirred at 0–5 °C until reaction is complete. The progress of the reaction may be followed by GLC (OV-1, 3%, 2-m column, 110 °C, and SE-30, 20%, 2-m column, 170 °C). Reaction times of compounds Ia–d in CCl_4 solution are listed in Table I. In CH_2Cl_2 solution the reaction times are considerably shorter, e.g., 15 min for Id and 90 min for Ic. Following addition of water, removal of precipitated tellurium compounds by filtration, and evaporation of the solvent from the dried organic layer, the rearrangement product (benzylic halide) may be distilled. The products listed in Table I were identified by GLC and NMR (Varian HA-100) comparison with authentic samples. GLC analysis of the crude product from Id on an Apiezon L (15%) column at 150 °C confirmed the presence of only the meta isomer

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of (2-chloro-2-propyl)toluene. [A synthetic control mixture of ortho, meta, and para isomers of (2-chloro-2-propyl)toluene was shown to be clearly separable on the column.]

Registry No. Ia, 544-25-2; Ib, 4281-04-3; Ic, 1541-11-3; Id, 3479-89-8; $TeCl_4$, 10026-07-0; benzyl chloride, 100-44-7; 1-chloro-1-phenylethane, 672-65-1; benzhydryl chloride, 90-99-3; 3-(2-chloro-2-propyl)toluene, 13240-60-3; 7-methoxycycloheptatriene, 1714-38-1; methylmagnesium iodide, 917-64-6; tropylium tetrafluoroborate, 27081-10-3; phenylmagnesium bromide, 100-58-3; eucarvone, 503-93-5; eucarvol, 503-92-4; 3-methylacetophenone, 585-74-0; *p*-methylacetophenone, 122-00-9; 2-(2-chloro-2-propyl)toluene, 85681-40-9; 2-(2-hydroxy-2-propyl)toluene, 7572-79-4; 2-bromotoluene, 95-46-5; 4-(2-chloro-2-propyl)toluene, 7243-79-0.

π Participation and Stereoselectivity. Solvolysis Rates of (*E*)- and (*Z*)-1-Aryl-5-heptenyl Chlorides

Mirko Orlović, Eugenio Polla, and Stanko Borčić*

Faculty of Pharmacy and Biochemistry, University of Zagreb, 41001 Zagreb, Yugoslavia

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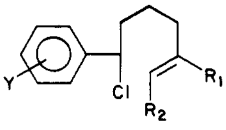
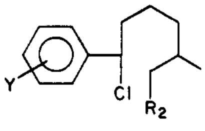
We have reported[1,2] that the solvolysis rates of most chlorides of the series U are enhanced relative to those of the corresponding series S.[3]



U



S

1, $R_1 = R_2 = H$
2, $R_1 = CH_3; R_2 = H$
(*E*)-3, $R_1 = H; R_2 = CH_3$
4, $R_1 = R_2 = CH_3$

$Y = p\text{-}OCH_3, p\text{-}CH_3, H, p\text{-}Br, m\text{-}Br$

There is no rate acceleration in the following cases: (a) when the aliphatic double bond is substituted with only one alkyl group as in series **1U**, (b) when the terminal double bond in **1U** is replaced by a cyclopropane ring,[4] and (c) in all cases when the substituent on the phenyl ring is the very electron-donating *p*-methoxyl. All other chlorides of the U series react faster than the corresponding chlorides of the S series, and the k_U/k_S ratio increases as the electron-donating ability of the substituent Y decreases; i.e., the largest rate enhancements are observed when Y = *m*-Br.[2] The relevant k_U/k_S values given in Table I have a puzzling feature: rate enhancements observed with (*E*)-**3U** are somewhat *larger* than those of **2U**.

This observation is not consistent with a participation mechanism involving charge-localized carbenium-ion-like transition states. If such were the case, then **2U** and (*E*)-**3U** would react by way of a tertiary and a secondary carbenium ion, respectively, and since the former is more stable then the latter, rate enhancements with **2U** could be expected to be much more important than those with (*E*)-**3U**, which is contrary to observation.

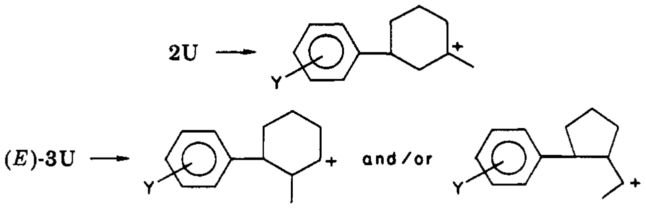
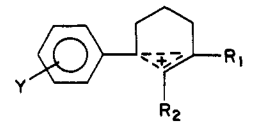


Table I. Solvolysis of 1-Arylalkyl Chlorides and 1-Aryl-5-alkenyl Chlorides: Relative Rates at 25 °C

Y^a	solvent^b	k_U/k_S			
		2	(*E*)-**3**	(*Z*)-**3**	**4**
p-OCH_3	95E	1.07	0.89	1.25	1.08
p-CH_3		1.50	2.42	0.95	3.22
	80E	1.13	1.43	1.52	2.23
H		2.57	5.93	2.75	16.1
	97T			3.95	
p-Br		3.05	6.18	5.17	18.9
m-Br		5.73	10.3	17.5	58.2

^{a} Substituent on the phenyl ring. ^{b} 95E and 80E are 95 and 80 vol % aqueous ethanol, respectively; 97T is 97 wt % aqueous 2,2,2-trifluoroethanol.

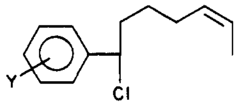
It was pointed out[2] that these results are not easily accommodated by a bridged, carbonium ion **5** like transition state. Although **5** is consistent with a small reactivity difference between **2U** and (*E*)-**3U**, nevertheless the expectation is again that the former should be more reactive than the latter.



5

A relevant analogy is the observation that while in acid-catalyzed hydration isobutene is about 10^4 times more reactive than *trans*-2-butene,[5,6] it is still 3 times more reactive in bromine addition,[7,8] a reaction proceeding by way of bridged bromonium ions.

It appears that there must be a factor, possibly steric in origin and not immediately obvious from formula **5**, which is responsible for an additional rate enhancement of (*E*)-**3U** and/or for a rate deceleration of **2U**. In this respect it seemed of interest to measure the solvolysis rates of the geometric isomers of (*E*)-**3U**, i.e., the series (*Z*)-**3U**.



(*Z*)-3U

The results of this investigation are summarized in Table II. Using previously[2] measured values for k_{3S}, the $k_{(Z)\text{-}3U}/k_{3S}$ ratios were calculated and are shown in column five of Table I. If the rate enhancements of the two geometrically isomeric series of structure **3U** are compared, it can be seen (Table I) that the stereochemistry of the participating double bond has very little influence on the reaction rates. Both series of chlorides **3U** react at very similar rates, and the rate enhancements tend to be of the same magnitude or larger than those measured with **2U** relative to **2S**. In fact, in the case of *m*-Br-substituted derivatives, where the participation is the most pro-

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