18 (**a** oder **b**): Smp. 181° (Hexan), Ausb. 1,3 g (89,5%). – NMR.: δ 0,28 (*s*, 12 H, Si—CH_3); 0,45 (*s*, 12 H, Si—CH_3); 0,62 (*s*, 12 H, Si—CH_3); 2,11 (*s*, 6 H, —CH_3); 2,16 (*s*, 6 H, —CH_3); 7,28 (*s*, 2 H, arom. H).

$C_{28}H_{50}O_3Si_6$ (603,2) Ber. C 55,75 H 8,35% Gef. C 55,61 H 8,50%

Zur Darstellung von **15** wird 1 g (2,3 mmol) **9** in 80 ml abs. Methanol (nach Zugabe von Natrium) unter Ausschluss von Feuchtigkeit während *ca.* 50 Std. unter Rückfluss gekocht, schwerlösliches **15** (1,1 g, 78,8%) abfiltriert und durch Kristallisation gereinigt. – Aus Hexan (lösungsmittelfrei): Smp. 256° (Zers.). – NMR.4): δ 0,35 (*s*, 36 H, Si—CH_3); 2,92 (*s*, 18 H, O—CH_3).

$C_{24}H_{54}O_6Si_6$ (607,2) Ber. C 47,47 H 8,96% Gef. C 47,53 H 9,03%

Aus Cyclohexan (mit einer Molekel Lösungsmittel): Smp. 258–261° (Zers.). – NMR.4): δ 0,30 (*s*, 36 H, Si—CH_3); 1,41 (*s*, 12 H, H-aliph.); 3,10 (*s*, 18 H, O—CH_3).

$C_{30}H_{66}O_6Si_6$ (691,4) Ber. C 52,12 H 9,62% Gef. C 51,80 H 9,61%

Die Darstellung von **16** erfolgt durch längeres Kochen (*ca.* 35–40 Std.) von **15** (0,72 g, 1,2 mmol) in 20 ml Methanol/Wasser 4:1. Man filtriert von eventuell nicht umgesetztem **15** und bringt **16** durch langsames Abdampfen des Methanols im N_2-Strom bei 25° zur Kristallisation. Smp. 255–256°, Ausb. 0,43 g (77%). Mol.-Gew. (osmometr. in CH_2Cl_2): 472. – NMR.: δ 0,42 (*s*, Si—CH_3).

$C_{18}H_{36}O_3Si_6$ (469,0) Ber. C 46,10 H 7,74% Gef. C 46,01 H 7,84%

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4) Lösungsmittel $CDCl_3$ (0,1 M).

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111. The Stereochemistry of Fragmentation Products Formed in the Lead Tetraacetate and Related Oxidations of Alcohols1). Part I. *β*-Fragmentation of *cis*- and *trans*-4-*t*-Butylcyclohexanemethanol

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(15. X. 73)

Summary. The stereochemistry of *β*-fragmentation products formed in the oxidation of *cis*- and *trans*-4-*t*-butylcyclohexanemethanol with lead tetraacetate and with lead tetraacetate-metal chloride combinations, under various reaction conditions, has been investigated, and the results compared with those obtained, under similar conditions, in the oxidative decarboxylation of *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acid with the same reagents. It was found that all four substrates afford, under comparable conditions, identical *cis*-*trans* proportions of the respective fragmentation products, and that, therefore, so far as steric course is concerned, both

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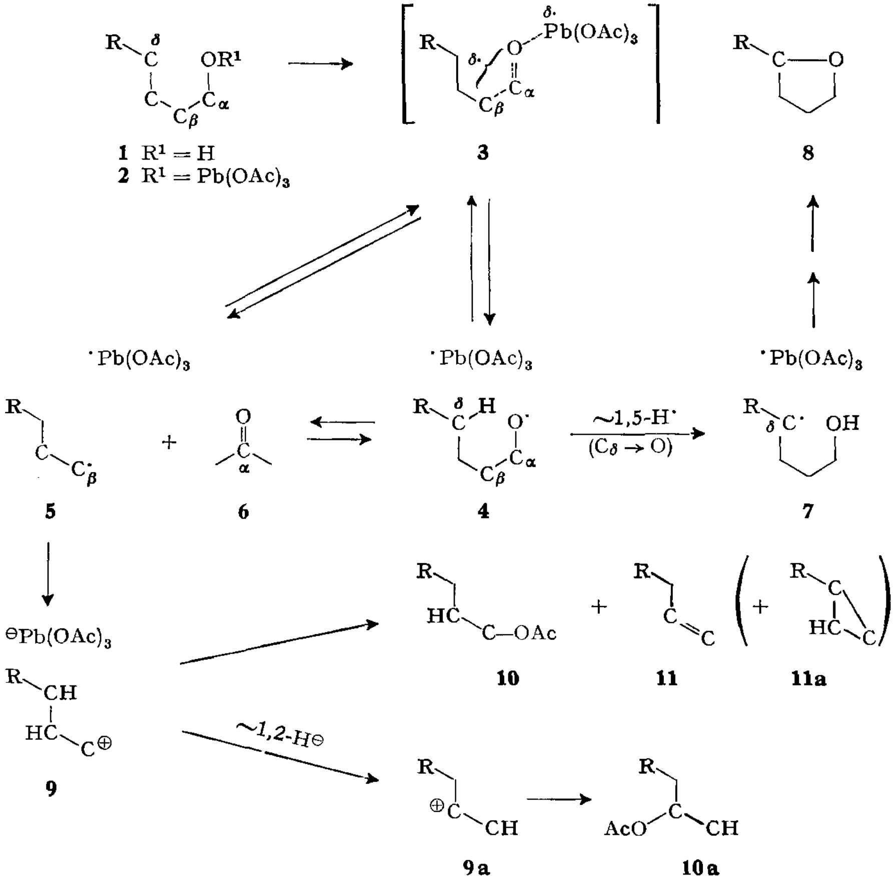
the initial homolytic and subsequent heterolytic processes involved in the lead tetraacetate fragmentation reaction are independent of the nature and configuration of the starting material.

1. Introduction. – The β-fragmentation reaction, which consists of the homolytic C_α–C_β bond cleavage, is a well established mode of stabilization of alkoxy radicals in general [2]. For the β-fragmentation reaction as one of the characteristic processes in the thermal and photolytic lead tetraacetate (hereafter referred to as LTA) oxidation of alcohols **1** [3–8], several mechanisms starting from the initially formed alkoxy-lead(IV)-acetate **2** have been envisaged, involving either heterolytic decomposition [4] [9], decomposition *via* a cyclic transition state [4] [10–11], or homolytic decomposition [3] [5–8] [12].

Most of the data now available strongly support the homolytic mechanism, shown in *Scheme 1*, in the first stages of the LTA β-fragmentation of alcohols **1**, *i.e.* the initial carbon radical character of the β-fragment **5** (*e.g.* "reversible fragmentation", **4** ⇌ **5** + **6** [3–8] [12–14], detection of radicals derived from **5** [15], formation of saturated hydrocarbons [16], dimeric compounds [17–18] and oxygenated products

Scheme 1



[19] corresponding to **5**), and indicate that this reaction and intramolecular homolytic 1,5-hydrogen transfer (**4** → **7**), leading usually (in the presence of LTA) to cyclic ethers **8**, are competitive processes which proceed through a common transition state with alkoxy radical character **3** and/or a more or less fully developed alkoxy radical **4** [3] [5–7] [12] [20] [21].

However, the usual and predominant fragmentation products in the LTA reaction of alcohols **1** are acetates **10** and olefins **11** [3–7]. That these compounds are in major part not formed directly from the carbon radical fragment **5**, but rather upon its one-electron oxidation (*i.e.* by transfer of an electron from carbon to lead) to the corresponding carbonium ion **9**, is substantiated by a number of observations (*e.g.* [6] [22–23]), particularly by the isolation, in some cases, of rearranged fragmentation acetates (of type **10a**) [17–18a] [20] [24], of cyclopropane-containing fragmentation hydrocarbons (such as **11a**) [25], etc.

In contrast to this large amount of mechanistic evidence, relatively little attention has been so far devoted to the steric course of the LTA β-fragmentation of alcohols. Thus, beside the known configurations of the isomeric and diastereomeric cyclic ethers and other products resulting from 'reversible fragmentation' of alcohols [3–8] [12–14], the stereochemistry of the 'substitution' fragmentation products (of type **10**) has been established only in a few (thermal) LTA reactions of steroid and related alcohols [16] [22] [26–31]. Because of considerable steric hindrance to attack from one side, these polycyclic systems undergo C_α–C_β bond cleavage giving exclusively or predominantly one epimeric fragmentation product[3]).

Even less is known about the LTA β-fragmentation of alcohols in the presence of metal halides [33–35] or carbon tetrachloride [18b]; thus the stereochemistry of the fragmentation chloro-products obtained in the reaction of three steroidal substrates of the 5α-androstan-17β-ol series [34][4]) and 5α-pregnan-20-ol series [35][5]) with LTA and cupric chloride in (refluxing) benzene has not been determined.

As regards the thermal and photolytic LTA decarboxylation of carboxylic acids (without or in the presence of catalysts and additives), evidence available from numerous studies [19] [38–47][6]) strongly supports a free-radical chain mechanism involving the intermediacy of carbon radical fragments of type **5** (*Scheme 1*) (which were also detected by ESR. spectroscopy [15] [42] [49]) and of the corresponding, (from **5** by one-electron oxidation) subsequently formed carbonium ions of type **9**. The stereochemistry of the fragmentation products, derived from **5** and **9**, has been investigated in the thermal and photolytic decarboxylations of a number of suitable

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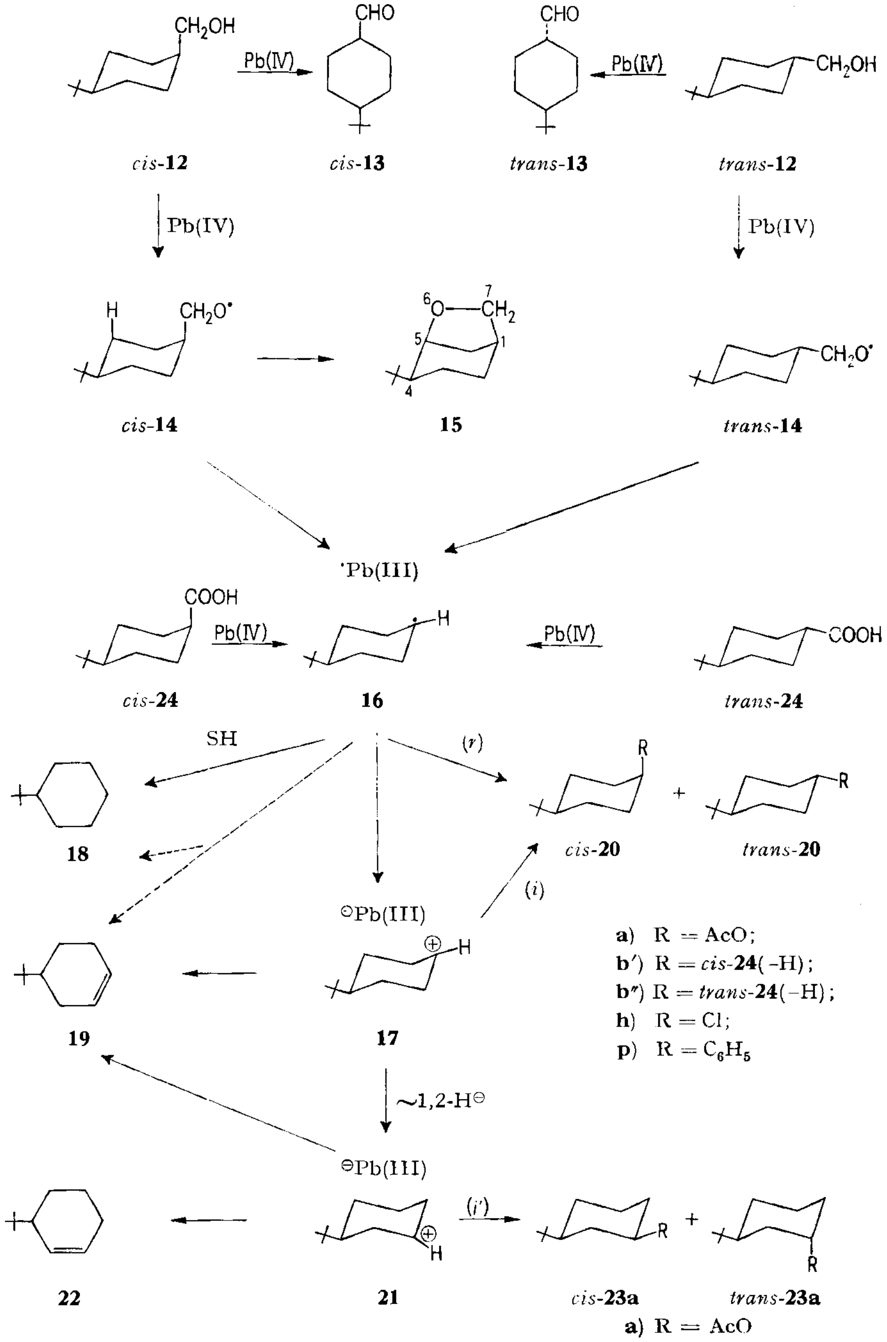
[3]) In contrast to these results, C(5)—C(10) bond cleavage (by means of LTA) of normal 5-hydroxy-steroids affords 'elimination' fragmentation products (of type **11**), *i.e.* 5,10-seco-steroids in which the 1(10)-cyclodecen-5-one ring is a mixture of *cis*- and *trans*-isomeric forms [32].

[4]) However, it has been found that photolysis (*Barton* reaction) of 17β-yl nitrites (of the androstane series) affords predominantly (in a purely homolytic reaction) compounds derived from the initially produced fragmentation 13α-nitroso-13,17-seco-products [36].

[5]) In contrast, the configuration and epimeric composition of fragmentation iodo-products formed in the 'hypoiodite reaction' (LTA + iodine) of similar pregnan-20β-ol substrates have been studied and established [8] [37]. (For another example of the hypoiodite fragmentation reaction of alcohols see [31]).

[6]) Earlier examples and possible mechanisms of these decarboxylation reactions are mentioned in [4] and [48].

Scheme 2



Pb(IV) = R'_4Pb, R'_4PbCl^-, etc.; Pb(III) = R'_3Pb, R'_3PbCl^-, etc.; R′ = AcO, **12**(–H), **24**(–H)

Table 1. *Products* (Scheme 2) *obtained in the lead tetraacetate oxidation of* cis- *and* trans-*4*-t-*butylcyclohexanemethanol* (cis- *and* trans-**12**)

			Reaction products[a]), yields (in %)[b]) and *cis/trans* ratios					
			β-Fragmentation				Cyclization	Oxidation
Run	Alcohol **12**	Reaction conditions (molar ratio ROH/LTA)	Total yield	*Hydrocarbons* **18** + **19** + **22**[c]) (**18**/**19**)	*Acetates*[d]) **20a** + **23a**[e]) (*cis-/trans*-**20a**)	*Phenyl-alkane* **20p** (*cis/trans*)	*Ether* **15**	*Aldehyde* **13**
		Thermal						
1	*cis*	in benzene, 80° (1:1)[f])	33	9 (12:88)	16 (52:48)	8 (19:81)	46	2 (*cis*)
2	*trans*	in benzene, 80° (1:1)[f])	59	16 (13:87)	36 (51:49)	7 (18:22)	–	3 (*tr.*)
3	*cis*	in benzene, 80° (1:1)						
		+ pyridine (4 mol-equiv.)	24	8 (12:88)	16 (38:62)	–	38	9.5 (*cis*)
4	*cis*	in pyridine, 20° (1:1)	11.5	2 (10:90)	9.5 (25:75)	–	16	38 (*cis*)
5	*trans*	in pyridine, 20° (1:1)	20	3 (10:90)	17 (23:77)	–	–	42 (*tr.*)
6	*cis*	in pyridine, 50° (1:1)	15	3.5 (11:89)	11.5 (24:76)	–	19	30[g]) (*cis*)
7	*trans*	in pyridine, 50° (1:1)	26	5.5 (11:89)	20.5 (22:78)	–	–	35[g]) (*tr.*)
		UV.-Photolytic (*20°*)						
8	*cis*	in benzene (1:1)	29	2.5[h])	20 (26:74)	6.5 (18:82)	41	–
9	*trans*	in benzene (1:1)	51.5	4.5[h])	41 (27:73)	6 (16:84)	–	–
10	*cis*	in benzene (1:4)	36	4 (23:77)	27.5 (28:72)	4.5 (17:83)	51	–
11	*trans*	in benzene (1:4)	61.5	7 (20:80)	51 (26:74)	3.5 (18:82)	–	–
12	*cis*	in benzene (1:4)						
		+ pyridine (5 mol-equiv.)	37	4 (20:80)	27.5 (28:72)	5.5 (18:82)	52	2 (*cis*)
13	*trans*	in benzene (1:4)						
		+ pyridine (5 mol-equiv.)	63.5	8 (21:79)	52 (27:73)	3.5 (17:83)	–	3 (*tr.*)

[a]) Other products isolated were starting alcohol (5–10%) and the corresponding acetate (5–15%) and formate (5–10%).

[b]) Yields (mole %) were calculated from analytical GLC. and are based on the non-excess starting component. They represent mean values of at least two repeated runs.

[c]) 3-*t*-Butylcyclohexene (**22**) was present in trace amounts in runs 1, 2 and 3 (ratio **19**/**22** = 97:3). In other runs olefin **22** was not detected.

[d]) In runs 4–7 and 8–13, because of the presence of formate esters, the yield and relative *cis/trans* ratio of acetate **20a** was checked by reduction of part of the reaction product mixture with $LiAlH_4$ followed by GLC. analysis and separation of the resulting *cis-* and *trans*-4-*t*-butylcyclohexanols (corresponding to acetates *cis-* and *trans*-**20a**).

[e]) The rearranged 3-*t*-butylcyclohexyl acetate (**23a**) was present in small amounts in the thermal benzene runs 1, 2 and 3 (relative proportion **20a**/**23a** = 91–93:9–7) in a *cis/trans* ratio of 58–60:42–40, and in the UV.-photolytic runs 8–13 (relative proportion **20a**/**23a** = 96:4) in a *cis/trans* ratio of 69–70:31–30. In pyridine runs (4–7) **23a** could not be detected.

[f]) Oxidations of *cis-* and *trans*-**12** in benzene at 40–55°, in benzene at 80° in the presence of anhydrous $CaCO_3$ (1 mol-equiv.) or AcOH (2–4 mol-equiv.), or with excess LTA (2 mol-equiv.) gave similar results and the same *cis/trans* ratios of products **20a**, **23a** and **20p**.

[g]) Mixture of aldehyde **13** and corresponding acid **24** (7–9%), formed by further oxidation of **13**.

[h]) Relative proportion **18**/**19** not determined.

Table 2. *Products* (Scheme 2) *obtained in the lead tetraacetate oxidative decarboxylation of* cis- *and* trans-*4*-t-*butylcyclohexanecarboxylic acid* (cis- *and* trans-**24**)

Run	Acid **24**	Reaction conditions in benzene, N_2 (molar ratio RCOOH/LTA)	Fragmentation (decarboxylation) products, yields (in %) [a] and *cis/trans* ratios			
			Hydrocarbons **18** + **19** + **22** [b] (**18**/**19**)	*Acetates* **20a** + **23a** [c] (*cis*-**20a**/*trans*-**20a**)	*Carboxylate* **20b** [d] (*cis/trans*)	*Phenyl-alkane* **20p** (*cis/trans*)
		Thermal (80°)				
1	*cis*	(1:1) [e]	39 (12:88)	34.5 (53:47)	5.5 (51:49)	10.5 (22:78)
2	*trans*	(1:1) [e]	35 (10:90)	43 (52:48)	4.5 (50:50)	7.5 (21:79)
3	*cis*	(2:1)	43 (11:89)	28 (54:46)	7.5 (52:48)	16.5 (20:80)
4	*trans*	(2:1)	40 (10:90)	31 (53:47)	7 (51:49)	13.5 (19:81)
5	*cis*	(4:1)	49 (10:90)	15.5 (52:48)	12 (53:47)	20.5 (18:82)
6	*trans*	(4:1)	44 (11:89)	18 (51:49)	11 (52:48)	17 (20:80)
7	*cis*	(4:1), + pyridine (32 mol-equiv.)	49 (10:90)	14 (28:72)	[f]	15.5 (19:81)
		UV.-Photolytic (20°)				
8	*cis*	(2:1)	33 (25:75)	30 (28:72)	3.5 (44:56)	9.5 (19:81)
9	*trans*	(2:1)	29 (23:77)	34 (29:71)	3 (43:57)	8.5 (20:80)

[a] See Table 1, footnote [b].

[b] 3-*t*-Butylcyclohexene (**22**) was present in trace amounts in all runs (ratio **19**/**22** = 95–97:5–3).

[c] The rearranged 3-*t*-butylcyclohexyl acetate (**23a**) was formed in thermal runs (**1**–**7**) and photolytic runs (8 and 9) in similar yields and in the same *cis/trans* ratios given in Table 1, footnote [e], for the respective thermal and photolytic LTA oxidations of alcohols **12**.

[d] **b** = **b′** from *cis*-**24**, and **b** = **b″** from *trans*-**24** (see *Scheme 2*).

[e] Reported [52] relative product distribution in the thermal (80°) LTA decarboxylation in benzene (RCOOH/LTA/pyridine = 1:1.3:1.2), of *cis*-**24**: 38% **19**, 57% **20a** (*cis/trans* = 53:47,) 5% other products; of *trans*-**24**: 30% **19**, 63% **20a** (*cis/trans* = 53:47), 6% other products (probably containing *cis*- and *trans*-**23a**).

[f] Not investigated.

substrate acids with LTA [38] [50–52], with LTA-halogen combinations, such as LTA-iodine [8] [38] [51a] [53], LTA-bromine and LTA-CCl_4 [47], and with LTA-metal chloride reagents [38] [52] [54–56].

2. Results. – In order to obtain additional information on the mechanistic and particularly stereochemical paths of the LTA and LTA-metal chloride β-fragmentation reactions of alcohols, we have studied the oxidative action of these reagents on *cis*- and *trans*-4-*t*-butylcyclohexanemethanol (*cis*- and *trans*-**12**), and compared the fragmentation products (structure, stereochemistry, distribution), obtained under various reaction conditions, with those produced, under similar conditions, in the LTA and LTA-metal chloride decarboxylations of the corresponding diastereomeric 4-*t*-butylcyclohexanecarboxylic acids (*cis*- and *trans*-**24**). The results of these reactions are summarized in Tables 1–4, and the products isolated are shown in *Scheme 2*.

2.1. Oxidations with Lead Tetraacetate. – 2.1.1. *Thermal reactions in benzene.* As can be seen from Table 1 (runs 1 and 2), under thermal conditions (in refluxing benzene), both alcohols *cis*-**12** and *trans*-**12** afforded the *same* β-fragmentation products (hydrocarbons **18**, **19**, **22**; acetates **20a**, **23a**; phenyl-alkane **20p**) and *identical cis/trans* ratios of unrearranged 4-acetate **20a** (*ca.* 1:1), rearranged 3-acetate **23a** (*ca.* 1.4:1), and 4-phenyl-alkane **20p** (*ca.* 1:4). Alcohol *cis*-**12** (Table 1, run 1), because of a favourable steric arrangement of the oxygen of the axial hydroxymethyl group at C(1) and the axial δ-hydrogen at C(3) (in *cis*-**14**), underwent intramolecular cyclization (according to the general sequence **4** → **7** → **8**, shown on *Scheme 1*) to the ether **15** (*Scheme 2*) more readily than β-fragmentation, the relative proportion of these two competitive processes being about 1.4:1. Alcohol *trans*-**12** (Table 1, run 2), which did not cyclize in detectable amount⁷), gave under these and all other reaction conditions (Tables 1 and 3) about twice as much β-fragmentation products as its diastereomer *cis*-**12**.

The products resulting from β-fragmentation of alcohols *cis*-and *trans*-**12** were also obtained (although in somewhat different yields) in *identical cis/trans* ratios in the thermal decarboxylations (in refluxing benzene) of *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acid (*cis*- and *trans*-**24**) (Table 2, runs 1–6)⁸). In addition, both acids gave, as expected [38–39] [43], the fragmentation *cis*- and *trans*-4-*t*-butylcyclohexyl 4-*t*-butylcyclohexanecarboxylate esters (*cis*- and *trans*-**20b**; **b** = **b′** from *cis*-**24**, **b** = **b″** from *trans*-**24**), in a *cis/trans* ratio of approximately 1:1.

It should be noted that in the thermal LTA oxidations of alcohols *cis*- and *trans*-**12**, and decarboxylations of acids *cis*- and *trans*-**24** in benzene, the relative proportions of saturated and unsaturated hydrocarbons (**18**/**19** = *ca.* 1:8) and of unrearranged and rearranged acetates (**20a**/**23a** = *ca.* 10:1) (which were independent of substrate

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⁷) The non-formation of cyclic ether from alcohol *trans*-**12** is due to the fact that in order to undergo intramolecular 1,5-hydrogen abstraction (such as **4** → **7**, *Scheme 1*) the corresponding alkoxy radical *trans*-**14** (*Scheme 2*) would have to attain an unfavourable flexible (boat) conformation of the cyclohexane ring. (However, it appears that in some cases such a conformational change does take place to a small extent [31].)

⁸) While this work was in progress, partial results concerning mainly the *cis/trans* ratio fo the fragmentation 4-acetate **20a** and 4-chloride **20h**, were reported for the thermal decarboxylations of the acids *cis*- and *trans*-**24** with LTA [52] and LTA-LiCl [52] [55], which are in good agreement with our data (presented above).

used), and the *cis/trans* composition of the 4-acetate **20a**, 3-acetate **23a**, 4-phenylalkane **20p** and 4-carboxylate **20b** (the latter only from acids **24**) were not noticeably affected by changes of reactant concentrations, reaction temperature (40–80°), substrate/LTA ratio (from 1:1 to 1:2 and 1:4 for the alcohols **12**, and, as shown in Table 2, runs 1–6, from 1:1 to 2:1 and 4:1 for the acids **24**), and by addition of acetic acid (up to 4 mol-equiv. per mol of LTA) or pyridine (up to about one mol-equiv. per mol of LTA [52]), although some of these variations of conditions, particularly those concerning the relative amount of LTA, did alter to a certain extent, as expected, the relative distribution of hydrocarbons (**18** + **19**), acetate **20a**, carboxylate **20b** and phenyl derivative **20p** in the LTA decarboxylations of acids *cis*- and *trans*-**24** (Table 2, runs 1–6).

2.1.2. *Thermal reactions in pyridine.* When pyridine was used as solvent, the LTA oxidation of alcohols *cis*- and *trans*-**12** at 20° and 50° afforded predominantly (Table 1, runs 4–7) the corresponding aldehydes *cis*- and *trans*-**13**, respectively (which, in benzene as solvent, were formed in only very low yield). On the other hand, β-fragmentation of both alcohols (*cis*- and *trans*-**12**) and cyclization of *cis*-**12** (to **15**) were partly suppressed[9]), in comparison to thermal oxidations in benzene (Section 2.1.1.), although the proportion of these two processes in the case of *cis*-**12** remained unchanged (*i.e.* cyclization/fragmentation = *ca.* 1.4:1)[9]). However, the *cis/trans* composition of the fragmentation 4-acetate **20a** obtained from both alcohols (*cis*- and *trans*-**12**) was now different and amounted approximately to 1:3 in favour of the more stable diequatorial epimer *trans*-**20a**[10]),[11]).

A similar stereochemical situation concerning the *cis/trans* ratio of 4-acetate **20a** (*cis/trans* = 1:2.6) was encountered in the thermal decarboxylation of the acid *cis*-**24** in refluxing benzene in the presence of 32 mol-equiv. of pyridine (Table 2, run 7)[10]).

Under these conditions, the *cis/trans* composition of the phenyl-alkane **20p** (*cis/trans* = 1:4), and the relative proportion of saturated and unsaturated hydrocarbons (**18**/**19** = 1:8–9) formed from both alcohols *cis*- and *trans*-**12** and from acid *cis*-**24**, were practically the same as those observed in the thermal oxidations of these substrates in benzene alone (see Section 2.1.1.).

2.1.3. *UV.-Photolytic reactions in benzene at 20°.* By irradiation of the LTA-substrate mixtures with UV.-light (above 300 nm, in benzene at room temp.), both alcohols *cis*- and *trans*-**12** (Table 1, runs 8–13) and the corresponding acids *cis*- and *trans*-**24** (Table 2, runs 8 and 9) gave again indistinguishable results concerning the configuration of the fragmentation products **20a**, **23a**, **20p** and **20b** (the latter only from acids **24**), but the *cis/trans* ratios of the unrearranged 4-acetate **20a**, rearranged 3-acetate **23a** and 4-carboxylate **20b** (the latter only from acids **24**) were different

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[9]) These results in pyridine (as compared to those in benzene) are not unexpected [5–6] [12] [21] and provide further evidence that the LTA β-fragmentation and cyclization of alcohols are competitive, in their first stages (up to the respective carbon radicals **5** and **7** (*Scheme 1*)) homolytic processes involving a common alkoxy radical-type transition state **3** and/or intermediate **4** (*Scheme 1*).

[10]) The presence of the rearranged 3-acetate **23a** could not be detected in these runs.

[11]) An intermediate *cis/trans* ratio (*ca.* 1:1.6) of 4-acetate **20a** was observed in the thermal reaction of alcohol *cis*-**12** with LTA in refluxing benzene, in the presence of 4 mol-equiv. of pyridine (Table 1, run 3).

from those observed in the thermal reactions in benzene (Section 2.1.1.) and more in favour of the respective diequatorial (energetically preferred) diastereomers, *i.e.* the *cis/trans* ratio was approximately 1:2.7 for **20a**, 2.3:1 for **23a**, and 1:1.3 for **20b**, while the relative *cis/trans* distibution for the 4-phenyl derivative **20p** remained unchanged (*cis/trans* = *ca.* 1:4). It should also be noted that in the photolytic reactions of alcohols **12** and acids **24** the yields of the rearranged 3-acetate **23a**, 4-phenylalkane **20p** and 4-carboxylate **20b** (the latter only from acids **24**) were slightly lower and the amount of alkane **18** (relative to that of alkene **19**) somewhat larger (**18**/**19** = 1:3–4) than in the thermal reactions in benzene (see Section 2.1.1.)[12]. Alcohol *cis*-**12**, under optimal photolytic conditions (Table 1, runs 10 and 12), gave ether **15** in particularly good yield [5] [7] [12] [57], but here again the ratio of cyclization to β-fragmentation was 1.4:1 (*i.e.* as in the thermal reactions in benzene and pyridine; see Sections 2.1.1. and 2.1.2.).

2.2. Reactions with Lead Tetraacetate-Metal Chloride Combinations. – As may be seen from Table 3 (runs 1–4), the thermal LTA oxidation of alcohols *cis*- and *trans*-**12** in refluxing benzene in the presence of lithium chloride or cupric chloride gave in each case as major fragmentation product a mixture of the epimeric 4-*t*-butylcyclohexyl chlorides (*cis*- and *trans*-**20h**), in a *cis-trans* ratio of about 2:1, whereas the formation of the other fragmentation compounds (**18**, **19**, **20a**, **20p**) was largely suppressed[13]. The UV.-photochemical reaction of *trans*-**12** in the presence of cupric chloride (Table 3, run 6) furnished the 4-chloro derivative **20h** in considerably lower yield, but unchanged *cis/trans* composition (*ca.* 2:1).

Analogous results and an identical (2:1) *cis/trans* relationship of chloride **20h** were also obtained in the LTA-metal chloride (LiCl or $CuCl_2$) decarboxylation of the acids *cis*- and *trans*-**24** under corresponding thermal[8]) and UV.-photolytic conditions (Table 4, runs 1–4 and 7–8, respectively). It should be noted that in the thermal LTA reaction cuprous chloride is somewhat less efficient in converting alcohol *cis*-**12** to the chloride **20h** (Table 3, run 5), and unsuitable for chlorodecarboxylation of the acids **24** (Table 4, runs 5 and 6), which in this case gave mainly 4-*t*-butylcyclohexene **19**. (The chloride **20h** obtained here had again a 2:1 *cis/trans* composition).

Other products formed under these conditions (LTA + metal chloride) from alcohols **12** (Table 3) and acids **24** (Table 4) were obtained in proportions (*e.g.* **18**/**19**) and *cis/trans* ratios (for **20a**, **23a**, **20p** and **20b**) characteristic of thermal and photolytic LTA oxidations in benzene (see Sections 2.1.1. and 2.1.3.).

Numerous separate control experiments performed in the presence or absence of LTA with authentic samples of alkenes **19** and **22**, and with *cis*- and *trans*-diastereomers of **20a**, **23a**, **20p**, **20b** (**b** = **b′** or **b″**) and **20h**, showed that under various reaction conditions used in the present study (and given in Tables 1–4 and in Experimental Part), these fragmentation products remained unchanged. Also, no *cis-trans* isomerization of the starting alcohols **12** and acids **24** was observed in control experiments. Moreover, the unreacted substrate recovered from LTA oxidations listed in

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[12]) These findings are in general agreement with results reported [43] for the thermal and photo chemical LTA decarboxylations of cyclohexanecarboxylic acid.

[13]) However, in the case of *cis*-**12**, the relative proportion of cyclization to β-fragmentation was the same (*ca.* 1.4:1) as that observed in all other LTA oxidations of *cis*-**12** (see Section 2.1.).

Table 3. *Products* (Scheme 2) *obtained in the oxidation of* cis- *and* trans-*4-t-butylcyclohexanemethanol* (cis- *and* trans-**12**) *with lead tetraacetate in the presence of metal chlorides*

Run	Alcohol **12**	Metal chloride	Reaction conditions in benzene (molar ratio ROH/LTA/MCl_m)	Reaction products[a]), yields (in %)[b]) and *cis/trans* ratios					
				β-Fragmentation					Cyclization
				Total yield	*Hydrocarbons*[c]) **18** + **19** (**18**/**19**)	*Acetate*[c]) **20a** (*cis/trans*)	*Phenyl-alkane* **20p** (*cis/trans*)	*Chloride* **20h** (*cis/trans*)	*Ether* **15**
			Thermal (*80°*)						
1	*cis*	LiCl	(1:1:1.2)	31.5	3.5 (8:92)	2.5 (51:49)	2.5 (22:78)	23 (67:33)	45
2	*trans*	LiCl	(1:1:1.2)	70	4 (9:91)	2 (52:48)	2 (21:79)	62 (67:33)	–
3	*cis*	$CuCl_2$	(1:1:1)	31.5	1.5 (12:88)	1.5 (52:48)	1.5 (20:80)	27 (66:34)	41.5
4	*trans*	$CuCl_2$	(1:1:1)	73	3 (12:88)	0.5 (~50:50)	1.5 (21:79)	68 (67:33)	–
5	*cis*	CuCl	(1:1:1.2)	32	6.5 (10:90)	4.5 (53:47)	1 (22:78)	20 (66:34)	45
			UV.-Photolytic (*20°*)						
6	*trans*	$CuCl_2$	(1:4:4)	54	7.5 (20:80)	28.5[d]) (26:74)	6 (21:79)	12 (67:33)	–

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[a]), [b]) See Table 1, footnotes [a]) and [b]). Small amounts of aldehyde **13** (2–3%) were also formed.

[c]) No attempts were made to detect the rearranged olefin **22** and 3-acetate **23a** in runs 1–5.

[d]) The presence of a small amount of the rearranged 3-acetate **23a** was detected in this run (**20a**/**23a** = 96:4), the *cis/trans* ratio of **23a** being 70:30 (see Table 1, footnote [e])).

Table 4. *Products* (Scheme 2) *obtained in the oxidative decarboxylation of* cis- *and* trans-*4-*t-*butylcyclohexanecarboxylic acid* (cis- *and* trans-**24**) *with lead tetraacetate in the presence of metal chlorides*

Run	Acid **24**	Metal chloride	Reaction conditions in benzene, N_2 (molar ratio $RCOOH/LTA/MCl_m$)	Fragmentation (decarboxylation) products, yields (in %)[a] and *cis/trans* ratios				
				Hydrocarbons[b] **18** + **19** (**18**/**19**)	*Acetate*[b] **20a** (*cis/trans*)	*Carboxylate*[b] **20b**[c] (*cis/trans*)	*Phenyl-alkane* **20p** (*cis/trans*)	*Chloride* **20h** (*cis/trans*)
			***Thermal** (80°)*					
1	*cis*	LiCl	(4:1:1.2)	10 (13:87)	4 (52:48)	–	4 (18:82)	72 (67:33)[d]
2	*trans*	LiCl	(4:1:1.2)	9 (14:86)	2 (51:49)	–	3 (19:81)	76 (66:34)[d]
3	*cis*	$CuCl_2$	(4:1:1)	12 (11:89)	–	–	–	70 (68:32)
4	*trans*	$CuCl_2$	(4:1:1)	8 (12:88)	–	–	–	80 (67:33)
5	*cis*	CuCl	(4:1:1.2)	80 (11:89)	–	–	–	13 (66:34)
6	*trans*	CuCl	(4:1:1.2)	63 (10:90)	–	–	–	31 (67:33)
			UV.-Photolytic (20°)					
7	*cis*	LiCl	(4:1:1.2)	31 (24:72)	31[e] (28:72)	6 (43:57)	12 (21:79)	6 (67:33)
8	*trans*	LiCl	(4:1:1.2)	24 (23:77)	25[e] (27:73)	4 (43:57)	10 (20:80)	11 (67:33)

[a] See Table 1, footnote [b].

[b] No attempts were made to detect the 3-olefin **22**, 3-acetate **23a** and 4-carboxylate **20b** in runs 1–6, since these products, if formed at all, were present only in trace amounts.

[c] **b** = **b'** from *cis*-**24**, and **b** = **b''** from *trans*-**24** (see *Scheme 2*).

[d] The same *cis/trans* ratio of **20a** in this reaction was also recently observed by other authors [52] [55].

[e] See Table 3, footnote [d]).

Tables 1–4 had the starting stereochemistry. Finally, prolonged treatment (46 h) of *cis*- or *trans*-4-*t*-butylcyclohexyl- *p*-toluenesulphonate with LTA or with two equivalents of AcOH + $CaCO_3$ in refluxing benzene, resulted in almost quantitative formation of alkene **19**.

3. Discussion. – On the basis of these findings, it can be concluded that under comparable reaction conditions the LTA *β*-fragmentation of both alcohols *cis*- and *trans*-**12** and the LTA decarboxylation of the corresponding acids *cis*- and *trans*-**24** produce 4-*t*-butylcyclohexyl fragments with the same stereochemistry at the electron-deficient reaction center and similar environmental characteristics around this center.

The presence of the saturated hydrocarbon **18** (in all reactions) and the formation (without rearrangement) of chloride **20h** (in all LTA-metal chloride reactions), in a diastereomeric ratio favouring the less stable [58–59] axial isomer *cis*-**20h** (by *ca.* 2:1) and similar to that observed in some other, purely free-radical processes[14]), confirm that the initial fragment from either alcohols **12** or acids **24** (in the LTA oxidations) is the *same* 4-*t*-butylcyclohexyl radical **16**, which is largely free from the steric influence of surrounding lead-containing (and other) species.

On the other hand, the formation of considerably more 4-alkene **19** than alkane **18** (in all thermal reactions and, to a smaller degree, in all photolytic reactions of **12** and **24**), and particularly the formation of some rearranged 3-alkene **22** and 3-acetate **23a** (in all thermal and photolytic reactions of **12** and **24** in benzene), imply that the carbon radical fragment **16** is converted by one-electron oxidation to the 4-*t*-butylcyclohexyl cation **17**, which undergoes characteristic reactions of carbonium ions (*Scheme 2*), to give **19**, **20a**, **20b** (the latter only with acids **24**) and the rearranged products **22** and **23a**, *via* the 3-cation **21**. Whereas in most reactions involving 4-*t*-butylcyclohexyl cations as intermediates [52] [64–66], the distribution and configuration of products are strongly influenced by the stereochemistry of the substrate and the nature of the leaving group, the LTA oxidations of **12** and **24** lead, under comparable conditions, to similar relative proportions of unrearranged and rearranged products (**19**/**22**, **20a**/**23a**) and the same *cis/trans* ratios of products **20a**, **20b**, and **23a** (all derived from the carbonium ion **17**). This would indicate that the cationic center of the intermediate **17** produced in the LTA reactions of **12** and **24** is, similarly to its carbon radical precursor **16**, relatively free, in its further *stereochemical* behaviour, from the influence of surrounding counterspecies[15]).

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[14]) Such as the photochemical and thermal decomposition of *cis*- or *trans*-α,α-dimethyl-4-*t*-butylcyclohexanemethyl hypochlorite in carbon tetrachloride at 0–78° [60] and the sulfuryl chloride cleavage of either *cis*- or *trans*-4-*t*-butylcyclohexylmercuric chloride at 46° [61][14a]).

[14a]) For some other stereochemical results concerning reactions of 4-*t*-butylcyclohexyl radicals see [62–63].

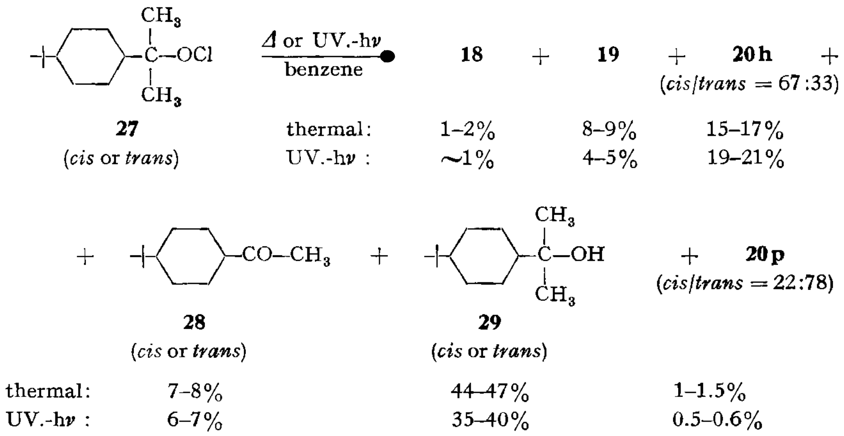
[15]) However, as regards their *reactivity*, it appears that both intermediate electron-deficient species **16** and **17**, particularly the latter, are somewhat dependent upon their provenience and, therefore, also upon environmental conditions, such as the polarity of the reaction medium (resulting from the presence, in the reaction mixture, of substrate, carbonyl fragment moieties (HCHO, CO_2), etc.), the kind of lead-containing species and other effects, since, for instance, the relative proportion of 'elimination' and 'substitution' fragmentation products **19** and **20** is not the same in analogously performed LTA oxidations of alcohols **12** (Tables 1 and 3) and acids **24** (Tables 2 and 4), and is even slightly influenced by the configuration

The stereochemical results obtained in the present study can be rationalized in terms of torsional strain factors and amount of bonding character involved in product development control [61] and /or ligand transfer control [63] [68][16]), combined with steric interactions in the transition states [61] [68].

The reaction of benzene (as solvent) with alkyl fragments to give alkyl-substituted benzenes has been observed in a number of LTA oxidations of alcohols [10] [18a–18b] [31] [67a] [71] and LTA decarboxylations of acids [38–40] [42b–45] [51] [72], but only a few stereochemical studies of such phenyl-containing fragmentation products have been reported [31] [51]. Since in the majority of cases the alkyl-moieties of the phenyl-alkanes obtained have not undergone structural changes which are frequently observed in electrophilic aromatic substitutions, it was postulated [38] [39b] [72] that in the LTA reactions (of acids) the fragmentation phenyl derivatives are formed by homolytic substitution involving attack of carbon radicals of type **5** (*Scheme 1*) on benzene (as solvent)[17]).

As shown on Tables 1 and 2 (and also 3 and 4), all LTA reactions of alcohols *cis*- and *trans*-**12** and acids *cis*- and *trans*-**24** gave rise to the formation of 4-*t*-butyl-1-phenylcyclohexane **20p**, in a constant *cis*/*trans* ratio of *ca.* 1:4, irrespective of substrate (**12** or **24**), substrate configuration (*cis* or *trans*) and reaction conditions

Scheme 3

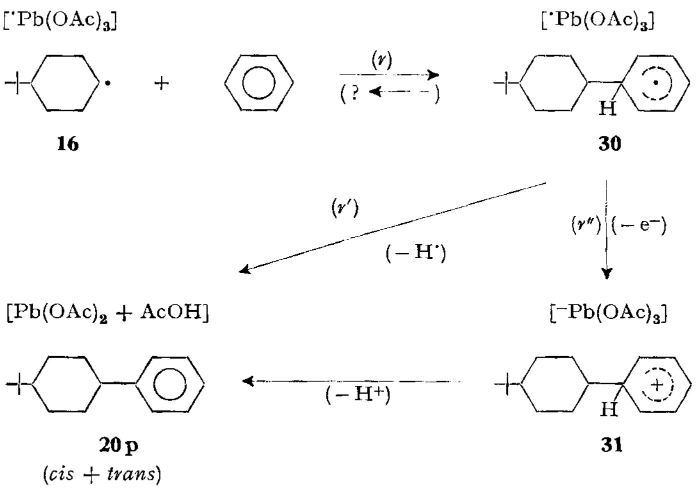


(*cis* or *trans*) of the substrate. One should also bear in mind that whereas the LTA decarboxylations of acids are free-radical chain reactions [38–46], the LTA oxidations (*i.e.* fragmentation and cyclization) of simple alcohols appear to be, in the majority of cases, non-chain homolytic processes or reactions with very short kinetic chain length [6] [19]. (However, a normal radical chain mechanism has been proposed for the LTA oxidative rearrangement of triarylmethanols in benzene [67]).

[16]) Reported explanations [61] [63] [68] and our own considerations regarding the orientation of attack at the planar site of the electron-deficient carbon center in intermediates **16**, **17** and **21**, are based on chair-like conformations of the cyclohexane ring in the transition states. (ESR. evidence [61] [69] indicates that 4-substituted cyclohexyl radicals exist predominantly in a chair-like form with a coplanar arrangement of bonds at the radical carbon). However, one could also invoke non-chair flexible (twist-boat) conformations [60] [65a–65b] and unsymmetrical charge distribution (*e.g.* [69a]) in the transition state, in order to account for some of the stereochemical data observed in our studies.

(thermal or photolytic decomposition, relative amounts of reactant and oxidant, presence of metal chloride[18]). This fact indicates again that the intermediate fragment responsible for the formation of **20p** is not influenced by the structure and configuration of its precursor. Since no rearranged 3-phenyl-alkane (such as **23p**) could be detected in these reactions, and since we found, as shown on *Scheme 3*, that the thermal and photolytic decompostion in benzene of either *cis*- or *trans*-α,α-dimethyl-4-*t*-butylcyclohexanemethyl hypochlorite (*cis*- and *trans*-**27**), which are well-authenticated free-radical reactions [2] [60], afford, among other products[19]), a small amount (0.5–1.5%) of 4-phenyl-alkane **20p** in the same *cis/trans* ratio (*ca.* 1:4) as that obtained in the LTA reactions, it can be concluded that the formation of **20p** in the LTA oxidations of **12** and **24** proceeds mainly by the (initially homolytic) pathway *r* (*Scheme 2*). This would involve (*Scheme 4*) the alkyl radical **16** and an intermediate radical addition complex **30** (of the σ- or possibly π-type [39b]), followed by the ionic oxidative route *r''* via the cationic complex **31** [39b] [73] (in contrast to the

Scheme 4



[ ] in LTA reactions

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[17]) The small amount of rearranged 2-phenylbutane (about 3–5% relative to the unrearranged 1-phenylbutane) obtained in the LTA oxidations of 2-methyl-2-hexanol [18a] and valeric acid [39b], would indicate that alkylbenzenes can also be produced (to a minor extent and depending on reaction conditions) by electrophilic aromatic substitution (on benzene as solvent), involving carbonium ion fragments (of type **9** and **9a**, *Scheme 1*) [45]. Such an ionic mechanism was preferred to the homolytic process for explaining the formation of allylbenzene obtained in the LTA oxidation (*i.e.* β-fragmentation) of 3-butenol [10].

[18]) It should be noted, however, that the yield of **20p** was in general somewhat higher: (i) in thermal runs[12]), (ii) in reactions of *cis*-substrates, (iii) in oxidations of acids **24**, and (iv) when the substrate (*i.e.* acid **24**) was used as the excess component. In the presence of metal chlorides (LiCl or $CuCl_2$) the formation of **20p** was suppressed (Tables 3 and 4).

[19]) Product distribution using benzene as solvent (*Scheme 3*) was different from that reported for the same decompositions (of *cis*- and *trans*-**27**) but with carbon tetrachloride as solvent [60] (when the chloride **20h** was obtained in 49% yield under thermal conditions, and in 85–93% yield under photolytic conditions).

energetically less favourable direct homolytic elimination step *r'* which is operative in the decomposition of the hypochlorites **27**)[20]).

4. Conclusions. – This study has shown: (a) that the LTA β-fragmentation of alcohols **12** (*cis* and *trans*) and the LTA decarboxylation of the corresponding acids **24** (*cis* and *trans*) are remarkably similar in their mechanistic and stereochemical course; (b) that the intermediate alkyl radical and alkyl cation fragments **16** and **17** are not influenced in their further stereochemical behaviour by the nature (alcohol **12** or acid **24**) and configuration (*cis* or *trans*) of the substrate; (c) that the fragmentation phenyl-alkane **20p** and chloride **20h** (the latter when metal chlorides are used as additives) are derived from the carbon radical **16**, while the fragmentation acetate **20a** and carboxylate **20b** (the latter only from acids **24**) are formed predominantly from the carbon cation **17**, which partly undergoes a 1,2-hydride shift to the carbonium ion **21**; (d) that the 4-*t*-butylcyclohexyl cation **17** generated in the LTA oxidations appears to be more 'free' than in most other of its known reactions.

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Experimental Part[21])

B.p. and m.p. are uncorrected. *Gas chromatography* (GLC.): *Varian* Aerograph instrument, Series 1400 (flame-ionization detector) for analytical purposes; *Varian* Aerograph instrument, Model 90-P (thermistor detector) for preparative separations; the columns (2 m × 2 mm, 4 m × 4 mm and 6 m × 8 mm) consisted of Carbowax 20M, TCEP [1,2,3-tris(2-cyanoethoxy)propane] or Apiezon L, as stationary phases, adsorbed on Chromosorb P or Celite (5–30%); carrier gas – H_2 and Ar; temp. programmed from 40°. *IR. spectra*: *Perkin-Elmer* Infracord instruments, Models 137 B and 337 (as film or in CCl_4 solution). *NMR. spectra*: *Varian* Spectrometer A-60 A (60 MHz); CCl_4 or $CDCl_3$ solutions and TMS as internal standard were used (chemical shifts are given in δ ppm values). *Mass spectra*: Massenspektrometer *Varian* MAT, Model CH-5, at 70 eV. *Fractional distillations* were performed on well isolated, modified semi-micro *Vigreux* columns. All compounds synthesized for use as reactants or for comparison purposes, and which were previously described in the literature, gave satisfactory elemental analyses and had correct spectral data.

A. Starting Materials. – Lead tetraacetate was prepared and dried as previously described [5] [20]. Solvents (benzene, pyridine) and additives ($CaCO_3$, LiCl, $CuCl_2$, CuCl) were commercial *p.a.* reagents, dried (if necessary) by conventional techniques and used in their anhydrous form.

a) *Preparation of* cis- *and* trans-*4-*t*-butylcyclohexanecarboxylic acids* (cis- *and* trans-**24**). Catalytic hydrogenation (PtO_2 in AcOH) of 4-*t*-butylbenzoic acid and separation of the resulting *cis-trans* acid mixture according to reported procedures [74–75][22]) afforded *cis*-**24**, m.p. 116–117°, and *trans*-**24**, m.p. 174–175°.

b) *Preparation of* cis- *and* trans-*4-*t*-butylcyclohexanemethanols* (cis- *and* trans-**12**). Reduction of *cis*- and *trans*-**24** with $LiAlH_4$ in the usual way gave (in 85–95% yield) the corresponding alcohols *cis*-**12**, m.p. 57–57.5°, and *trans*-**12**, m.p. 25–26° [77–78].

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[20]) The 1:4 *cis/trans* ratio of the phenyl-alkane **20p** reflects the rather large steric interactions (in the transition state) encountered in the axial attack of the voluminous benzene molecules on the carbon radicals **16**. (It is not known whether the first step in this process, *i.e.* **16** → **30**, shown on *Scheme 4*, is reversible or not.)

[21]) Spectral measurements were performed in the Laboratories for Instrumental Analysis (directed by Dr. *D. Jeremić*), and elemental microanalyses in the Microanalytical Laboratory (Dr. *R. Tasovac*) of our Department.

[22]) Modifications of the synthesis of acids *cis*- and *trans*-**24** have been recently described [61] [76].

c) *Preparation of* cis- *and* trans-*α,α-dimethyl-4-*t*-butylcyclohexanemethyl hypochlorites* (cis- *and* trans-**27**) *in benzene solution.* Conversion of acids *cis*- and *trans*-**24** to the corresponding methyl esters followed by the action of methylmagnesium iodide gave the diastereomeric α,α-dimethyl-4-*t*-butylcyclohexanemethanols (**29**); *cis*, m.p. 49–50°; *trans*, m.p. 101–101.5° [60b] [79]. To 100 ml of a stirred, ice-cold 4.5% aqueous sodium hypochlorite solution, containing about 4.5 g (0.06 mol) of NaOCl, was added (under N_2) dropwise in the dark first alcohol *cis*- or *trans*-**29** (3 g, 0.015 mol) followed by 5.8 ml (0.1 mol) of glacial AcOH. After 2 h stirring at 0–5° in the dark (under N_2), the mixture was extracted with benzene (2 × 20 ml), the benzene solution washed with 3% aqueous $NaHCO_3$ solution (until neutral) and with water, and dried ($CaSO_4$), affording an approximately 0.35–0.37 M benzene solution of *cis*-**27** (from *cis*-**29**) and *trans*-**27** (from *trans*-**29**). Both solutions thus prepared [60] [80] were kept under N_2 in the dark at 0–5°.

B. Reactions with Lead Tetraacetate. – The molar proportions of reactants[23]), general reaction conditions [solvent, additive, mode of decomposition (thermal or UV.-photolytic)] and distribution of products are given in Tables 1–4. After completion of the reaction (*i.e.* disappearance of Pb(IV)) and working up, the resulting product mixture was subjected to GLC. In runs with 0.02–0.05 mol of substrate **12** or **24**, most of the products were separated and isolated by preparative GLC., and identified and characterized by comparison of their IR. and NMR. spectral data (and, if necessary, other physical constants) with those of authentic compounds. In small-scale runs (with 0.003–0.01 mol of **12** or **24**), products were identified by comparison of their GLC. retention times (usually on two different columns) with those of synthetic products[24]). Yields were calculated planimetrically from analytical GLC.

1. *Oxidations of Alcohols* cis- *and* trans-**12**. – a) *Thermal reactions in benzene* (Table 1, runs 1 and 2) were carried out as described previously [5] [17] [20], with 8.5 g (0.05 mol) of alcohol **12** and 22.2 g (0.05 mol) of LTA in 150 ml of dry benzene (reaction time: 45 h for *cis*-**12**, 49 h for *trans*-**12**). (Addition of 5 g (0.05 mol) of anhydrous $CaCO_3$ had no influence on the reaction course or on product distribution.) The major product obtained from *cis*-**12** was 4-*t*-butyl-6-oxa-bicyclo[3.2.1]octane (**15**). – IR. (film): ν_{max} = 1093, 1010, 875 cm^{-1}. – NMR. (CCl_4): 4.30 (1 H, broad *t*, H_e—C(5)—O), 3.65 (2 H, *m*, $H_2C(7)$—O), 0.88 (9 H, split *s*, Me_3) ppm.

$C_{11}H_{20}O$ (168.27) Calc. C 78.51 H 11.98% Found C 78.23 H 11.93%

Other thermal LTA oxidations of *cis*- and *trans*-**12** in benzene at 40–50°, in benzene at 80° with addition of 2–4 mol-equiv. of AcOH, or in benzene at 80° with 2–4 mol-equiv. of LTA (not listed in Table 1) gave similar results and the same *cis/trans* ratios of products **20a**, **23a** and **20p**.

b) *Thermal reactions in pyridine* (Table 1, runs 4–7 and run 3). Runs 4 and 5 were performed with 0.02 mol (3.4 g) of *cis*- and *trans*-**12** in 60 ml of dry pyridine (reaction time 8–9 h), runs 6 and 7 with 0.01 mol (1.70 g) of *cis*- and *trans*-**12** in 30 ml of pyridine (reaction time 0.6 h), and run 3 with 0.003 mol (0.51 g) of *cis*-**12** in 15 ml of benzene in the presence of 0.012 mol (0.95 g) of pyridine (reaction time about 1.5 h). After completion of the oxidation, pyridine was largely removed by fractional distillation and the residue treated with 50 ml of ether. The ethereal solution was washed with water, dilute HCl, aqueous $NaHCO_3$ and water. After drying ($CaSO_4$) and evaporation of solvent, the product mixture was subjected to GLC. Part of the mixture was also reduced with $LiAlH_4$ and the *cis/trans* ratio of the epimeric 4-*t*-butylcyclohexanols determined by GLC., in order to check the *cis/trans* composition of the originally produced acetates *cis*- and *trans*-**20a**.

c) *UV.-Photolytic reactions* (Table 1, runs 8–13). These oxidations were performed in a Pyrex photochemical vessel as described previously [5] [7] [57], by irradiation with a high-pressure mercury lamp *Hanau* Q 81 (wavelegths above 300 nm) at room temp., and with 0.51 g (0.003 mol) of **12** in 200 ml of benzene (reaction times: 0.5–3 h). In order to check the *cis/trans* ratio of acetate **20a**, part of the reaction mixture was reduced with $LiAlH_4$ (in ether) and the relative distribution of the resulting *cis*- and *trans*-4-*t*-butylcyclohexanols was determined by GLC.

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[23]) The mol-equiv. and gram-amounts of LTA given in the Tables and in the text below are based on a 100% pure compound. Since, actually, LTA was of 93–97% purity, the quantity of the reagent used in each run was accordingly corrected.

[24]) Conditions for a satisfactory separation and analysis by GLC. of mixtures containing products **19**, **22**, *cis*- and *trans*-**20a**, *cis*- and *trans*-**23a** have been discussed previously [81].

d) *Reactions in the presence of metal chlorides* (Table 3). The thermal reactions (runs **1–5**) were carried out with 0.85 g (0.005 mol) of **12** in 50 ml of refluxing benzene, in the same way as in benzene alone (see B.1.a.); reaction times: 6–7 h with LiCl, 3–3.5 h with $CuCl_2$, 2 h with CuCl. The UV.-photochemical reaction (run 6) was performed with 0.25 g (0.0015 mol) of *trans*-**12** in 150 ml of benzene, as described above (B.1.c.).

2. *Decarboxylations of Acids* cis- *and* trans-**24** (Tables 2 and 4). – These oxidative reactions were performed (a) in preparative-scale experiments (Table 2, runs 1 and 5; Table 4, run 1) with 9.2 g (0.05 mol) of acid **24** in 150 ml of benzene, and (b) in analytical experiments with 0.92 g (0.005 mol) of acid **24** in 20–40 ml of benzene (thermal conditions) or in 100–200 ml of benzene (photolytic conditions), and with the given amounts of LTA and additive (see Tables 2 and 4). Before starting the oxidative decomposition, a slow stream of prepurified nitrogen was introduced for 0.5 h at room temp. and in the absence of light, into the stirred mixture of acid **24** and LTA in benzene [38] [39b].

a) *Thermal reactions in benzene* (Table 2, runs 1–6). The oxygen-free mixture resulting from the above described degassing procedure was heated (with stirring) to reflux (without light protection) until completion, *i.e.* until disappearance of Pb(IV), and then worked up as usual [5] [20] [38] [39b] (reaction times: **14–18** h).

b) *Thermal reactions in the presence of pyridine* (Table 2, run 7); c) *Thermal reactions in the presence of metal chlorides* (Table 4, runs 1–6). The degassed acid-LTA mixture was treated with the additive (pyridine or metal chloride) and again flushed with nitrogen (with stirring, in the dark at room temp.) for another 15–30 min. The mixture was then refluxed and stirred (without light protection) until disappearance of Pb(IV) (reaction times: 3.5 h with pyridine, 6–7 h with LiCl, 3–4 h with $CuCl_2$, 0.5–1 h with CuCl), and worked up as usual [5] [20] [38] [39b] [41b].

d) *UV.-Photolytic reactions in benzene alone* (Table 2, runs 8 and 9); e) *UV.-Photolytic reactions in the presence of lithium chloride* (Table 4, runs 7 and 8). Degassing of the reactant mixture was conducted (as described above) in a photochemical vessel [5] [7] [43] [57], followed by UV.-irradiation with a mercury lamp *Hanau* Q 81 at 20° (without interrupting the slow stream of N_2) until LTA was completely consumed (reaction times: about 0.5 h).

C. Other Reactions. – 1. *Decomposition of Hypochlorites* cis- *and* trans-**27** (*Scheme 3*). – a) *Thermal conditions.* The benzene solutions of *cis*- and *trans*-**27** (see A.c.) were each divided into two parts. One part was first swept with prepurified nitrogen at 0–5° in the dark (see B.2.) for 0.5 h, and then stirred and heated to reflux (with an incandescent 250 watt tungsten lamp serving as heat source) until disappearance of hypochlorite (3–4 h). The solvent was removed by fractional distillation and the resulting product mixture analysed by GLC.

b) *UV.-Photolytic conditions.* The other part of the benzene solutions of *cis*- and *trans*-**27** was diluted with dry benzene to about 150–200 ml, purged of oxygen as above, and subjected to UV.-irradiation at 20° (see B.1.c.) until completion (about 0.5 h). GLC. analysis of the reaction mixture (after evaporation of solvent) gave results shown in *Scheme 3*.

2. *Decomposition of* cis- *and* trans-*4*-t-*butylcyclohexyl* p-*toluenesulphonates.* – a) *In benzene solution.* A mixture of 0.5 g (0.0016 mol) of *cis*- or *trans*-4-*t*-butylcyclohexyl *p*-toluenesulphonate [64] [65e] [82], 0.19 g (0.0032 mol) of glacial AcOH and 0.16 g (0.0016 mol) of dry $CaCO_3$ in 20 ml of dry benzene was heated under reflux for 46 h. According to GLC. analysis, 4-*t*-butylcyclohexene (**19**) was formed in over 98% yield.

b) *In benzene in the presence of LTA.* A mixture containing 1.0 g (0.0032 mol) of *cis*- or *trans*-tosylate, 1.4 g (0.0032 mol) of LTA and 0.32 g (0.0032 mol) of dry $CaCO_3$ in 20 ml of dry benzene was refluxed until disappearance of Pb(IV) (about 46 h). The product obtained in over 98% yield from the reaction mixture (after the usual work-up) was 4-*t*-butylcyclohexene (**19**).

In these two reactions no attempts were made to detect the eventual presence (in olefin **19**) of the isomeric 3-*t*-butylcyclohexene (**22**).

D. Reaction Products. – Acetates of the starting alcohols *cis*- and *trans*-**12** [83], and the fragmentation acetates, *i.e. cis*- and *trans*-4-*t*-butylcyclohexyl acetate (*cis*- and *trans*-**20a**) [84], and *cis*- and *trans*-3-*t*-butylcyclohexyl acetate (*cis*- and *trans*-**23a**) [85] were prepared from the corresponding alcohols[25] by the usual Ac_2O-pyridine or Ac_2O—KOAc procedures [81] [89–90].

4-*t*-Butylcyclohexene (**19**), b.p. 170–172° [64] [82] [91], was obtained by pyrolysis of acetate **20a** [89] [91], or by refluxing for 0.5 h a *cis/trans* mixture of 4-*t*-butylcyclohexanol (3.1 g, 0.02 mol) and conc. H_3PO_4 (0.3 ml), distilling the products up to 172°, and subjecting the distillate, after the usual work-up, to preparative GLC. 3-*t*-Butylcyclohexene (**22**), b.p. 169–171° [65e] [90] [92], was prepared from 3-bromocyclohexene and *t*-butylmagnesium chloride [65e] [92]. *t*-Butylcyclohexane (**18**), b.p. 168–170° [93], was obtained by catalytic hydrogenation (PtO_2, ethyl acetate) of either **19** or **22**.

The isomeric *cis*- and *trans*-4-*t*-butylcyclohexanecarboxaldehydes (*cis*- and *trans*-**13**) were prepared by oxidation of alcohols *cis*- and *trans*-**12** with CrO_3 in 90% AcOH [94]. *Raney* nickel hydrogenolysis [95] of the hydroxyl group of the diastereomeric 4-*t*-butyl-1-phenylcyclohexanols [95–96] was used to obtain *cis*-4-*t*-butyl-1-phenylcyclohexane (*cis*-**20p**), m.p. 23–24°, and its epimer *trans*-**20p**, m.p. 41–42° [95]. The isomeric *cis*- and *trans*-4-*t*-butylcyclohexyl chlorides (*cis*- and *trans*-**20h**) [60b] [97] were synthesized from the corresponding *trans*- and *cis*-4-*t*-butylcyclohexanols and thionyl chloride in the presence of tri-*n*-amylamine [60b]. All four diastereomeric 4-*t*-butylcyclohexyl 4-*t*-butylcyclohexanecarboxylates **20b** (*cis-cis*, *trans-cis*, *cis-trans* and *trans-trans*) [74] were prepared by conversion of the acids *cis*- and *trans*-**24** to the acid chlorides (with thionyl chloride) followed by esterification with *cis*- or *trans*-4-*t*-butylcyclohexanol [74]. 4-*t*-Butylcyclohexyl methyl ketone (**28**) was obtained [76] from *t*-butylbenzene, *via* 4-*t*-butylacetophenone and α-methyl-4-*t*-butylcyclohexanemethanol, and the resulting *cis-trans* mixture separated into the pure diastereomers *cis*- and *trans*-**28** by preparative GLC. [76].

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112. Metal Complexes with Macrocyclic Ligands, IV[1]). Synthesis, Properties and Kinetics of Complexation with Three N-methyl Substituted 1,4,8,11-tetraazacyclotetradecanes

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(20. II. 74)

Summary. The synthesis, properties and complexation of 1-methyl-1,4,8,11-tetraazacyclotetradecane (1-MeCyclam-14), 1,5-dimethyl-1,5,8,12-tetraazacyclotetradecane (2-MeCyclam-14) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (4-MeCyclam-14) are described.

While the Ni^{2+} and Cu^{2+} complexes of 1-MeCyclam-14 and 2-MeCyclam-14 exhibit square planar geometries, 4-MeCyclam-14 forms Ni^{2+} and Cu^{2+} complexes, whose absorption spectra are best explained by assuming pentaco-ordination of the metal ions.

The complexation rate of the three N-methyl substituted macrocycles with Cu^{2+} and Ni^{2+} is slower than can be accounted for by water exchange and little affected by introducing methyl groups at the nitrogens. Both results are in contrast to what is known for open chain amine ligands. A mechanism for the complexation is proposed, which also explains why the products of the reaction of 4-MeCyclam-14 with Cu^{2+} and Ni^{2+} are pentaco-ordinated.

The complexation rate of transition metal ions with macrocyclic ligands is much slower than with analogous open chain compounds [2–4]. Based on such comparisons it has been concluded that the rate determining step of the complex formation with tetraazacyclotetradecanes is not the dissociation of the first co-ordinated water molecule [2–4]. In the meantime *Rorabacher et al.* [5] have shown that N-substitution strongly affects the complexation rate of open chain amines with Ni^{2+} raising the question whether the observed slow reaction with macrocyclic ligands could similarly be explained.

The present investigation was undertaken with a twofold aim. For one we wanted to study systematically the effects of N-methyl substitution on the complexation rate of tetraazacyclotetradecanes, secondly we hoped to prove the hypothesis, that the conjugate base of the pentaco-ordinated [6] blue intermediate plays an important role in the complexation of *meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a or 1,7-CTH) with Cu^{2+} [3]. Replacement of all the hydrogen atoms of the four amino groups of the ligand by methyl groups should prevent the forma-

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[1]) Part III, see [1].