

CONCLUSIONS.

The trans conformation of the NO group is most stable in 5-nitrosofuran, while C⁵ is the site for nucleophilic substitution.

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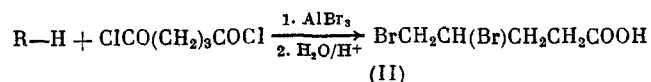
TRANSFORMATION OF GLUTARYL CHLORIDE TO 4,5-DIBROMOPENTANOIC ACID IN THE PRESENCE OF A SATURATED HYDROCARBON AS A REDUCING AGENT AND AlBr₃ AS THE BROMINATING AGENT

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RCOX·2AlBr₃ complexes (I) vigorously react with alkanes and cycloalkanes at 20°C, efficiently causing various transformations of the latter [1-3]. The saturated hydrocarbons in these reactions apparently act as hydride ion donors, reducing acid halides in the complexes initially to aldehydes, RCHO. However, attempts to establish the formation of RCHO (R = Me, Pr) proved unsuccessful. Only the formation of PhCHO was observed in the reaction of PhCOC1·2AlBr₃ with adamantane along with 1-bromoadamantane.*

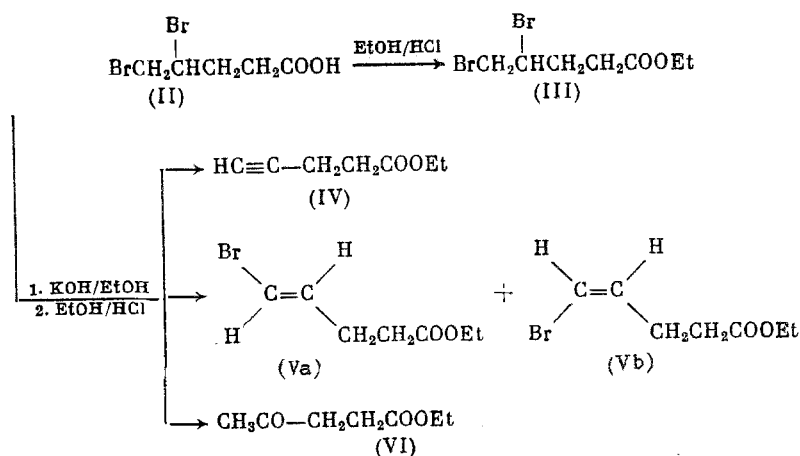
In the present work, we studied a reaction, in which the acid chloride of a dicarboxylic acid in a type-(I) complex is reduced by saturated hydrocarbon and brominated by AlBr₃. Thus, ClCO(CH₂)₃COCl reacts in the presence of a four-fold molar excess of AlBr₃ with hexane, cyclopentane, and adamantane at 20°C in CH₂Br₂ to form 4,5-dibromopentanoic acid (II) in 40% yield. In contrast to 2AlBr₃·ClCO(CH₂)₃COCl·2AlBr₃, AlBr₃·ClCO(CH₂)₃COCl·AlBr₃ does not react under analogous conditions.



The structure of (II) was demonstrated by elemental analysis, PMR, ¹³C NMR, and IR spectroscopy, and mass spectrometry as well as by transformation to (III)-(VI), which were identified by chromato-mass spectrometry.

The vicinal arrangement of the bromine atoms in (II) is unequivocally indicated by PMR and ¹³C NMR spectroscopy using the Imodecho and Gate modes. The ¹³C NMR spectrum indicates the presence of one carboxyl group, two methylene groups with similar ¹J_{C-H} direct coupling constants (130 Hz (triplets)), and two bromine-bearing carbon atoms with ¹J_{C-H} = 152 (CH₂Br) and

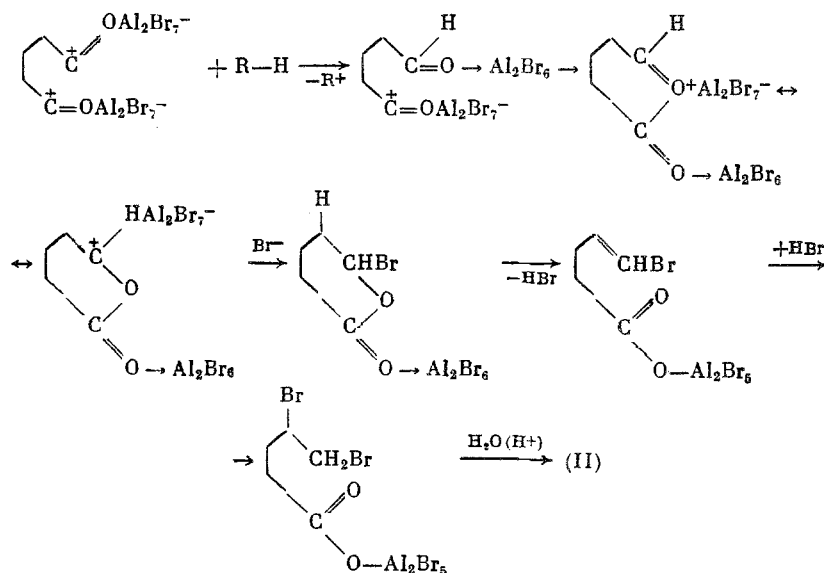
*The formation of only 1-bromoadamantane was observed with the reaction of adamantane with AcX·2AlBr₃.



160 Hz (CHBr). Evaluation by an incremental scheme developed for polybromides [4] of the ^{13}C chemical shift for the CH_2Br group in the $\text{CH}_2\text{Br}-\text{CHBr}-\text{CH}_2$ chain leads to a value $\delta = 34.2$ ppm, which is similar to the observed value (34.9 ppm). On the other hand, the calculated value for the CH_2Br group in the $\text{CH}_2\text{Br}-\text{CH}_2-\text{CHBr}$ chain is 29.4 ppm. This argues in favor of structure (II).

Analysis of the PMR spectrum leads to the same conclusion. Thus, the signal for the CH_2Br group unequivocally corresponds to the AB part of the ABX spin system: $\delta_A = 3.87$, $\delta_B = 3.53$ ppm, $J_{AB} = 10.5$, $J_{AX} = 4$, $J_{BX} = 11$ Hz. The absolute value of the $^2J_{\text{H}-\text{H}}$ geminal coupling constant is 10.5 Hz, which indicates the presence of a bromine atom in this methylene group. An alternative possibility is the presence of the bromine atom at C^3 , i.e., existence of a $\text{CHBr}-\text{CH}_2\text{CO}_2\text{H}$ segment is excluded since the methine hydrogen atom would give an ABX system with the methylene group of the $\text{CH}_2\text{CO}_2\text{H}$ fragment. In this case, J_{AB} should be about 15 Hz since the replacement of one halogen atom on a carbon atom raises the geminal constant by about 4 Hz [5]. Furthermore, the CH_2Br group in this case would be in an ABXY spin system with characteristic multiplicity, differing from an ABX system and not observed in the PMR spectrum.

On the basis of our previous data [1] on the structure of type-(I) complexes, we present a mechanism for this reaction, which involves the reduction of one of the two CO^+ groups to an aldehyde group and attack of the acylium cation at the oxygen atom of the aldehyde group, leading to closure of the ring, stabilized as an α -bromolactone. Decomposition of the α -bromolactone leads to a salt of 5-bromo-4-pentenoic acid, which adds HBr and then undergoes hydrolysis to give (II).



EXPERIMENTAL

A sample of $\text{ClCO}(\text{CH}_2)_3\text{COCl}$ was obtained according to Cason and Reist [6], purified by standard procedures, and distilled over P_2O_5 and CaH_2 . Ampoules containing AlBr_3 were opened in an argon atmosphere. Benzoyl chloride was distilled over PCl_5 and stored in an argon at-

mosphere. Methylene bromide was purified with H_2SO_4 , washed with aqueous Na_2CO_3 and water, dried over MgSO_4 , and distilled over CaH_2 .

The chromato-mass spectral analysis was carried out on an MSDB-1073 instrument with direct attachment of a $25 \text{ m} \times 0.32 \text{ mm}$ Oribond SE-54 quartz capillary column. The ionizing potential was 28.5 eV and the temperature of the ion source was 220°C . The temperature program was $30^\circ(4)-250^\circ\text{C}$. The heating rate was $2^\circ\text{C}/\text{min}$.

The PMR and ^{13}C NMR spectra were taken on a Bruker WP-200SY spectrometer at 200 MHz (PMR) and 50.3 MHz (^{13}C NMR).

Reaction of Adamantane with $\text{PhCOCl} \cdot 2\text{AlBr}_3$. A sample of 0.5 g (3.7 mmoles) PhCOCl in 2 ml CH_2Br_2 was added to 2.0 g (7.4 mmoles) AlBr_3 and then 0.5 g (3.7 mmoles) adamantane was added. The mixture was stirred for 2 h at 20°C , hydrolyzed with water, and extracted with ether. The washed and dried ethereal extracts were analyzed by gas-liquid chromatography and chromato-mass spectrometry. The conversion of adamantane was 82%. The yield of 1-bromodantane was 70%, while the yield of benzaldehyde was 82%. 2-Bromoadamantane is also formed in 3% yield. The mass spectra of the reaction products were identical to the spectra of authentic samples.

Reaction of $\text{ClCO}(\text{CH}_2)_3\text{COCl} \cdot 4\text{AlBr}_3$ with Hexane. The complex formed from 1.76 g (10.4 mmoles) $\text{ClCO}(\text{CH}_2)_3\text{COCl}$ and 11.1 g (41.6 mmoles) AlBr_3 in 15 ml CH_2Br_2 was stirred with 1.34 g (15.6 mmoles) hexane at about 20°C for 1 h. The mixture was poured onto ice and extracted with ether. The ethereal extracts were washed with water and dried over MgSO_4 . The residue after removal of the solvent and volatile products in vacuum was dissolved in hexane at 50°C . The saturated hexane solution was slowly cooled to -20°C to give 0.9 g (II) as colorless crystals. The mother liquor evaporated to 50% volume was treated with aqueous NaHCO_3 and the bicarbonate extracts were immediately acidified with 10% hydrochloric acid to give an additional 0.27 g (II). The total yield was 1.17 g (43%). Repeated recrystallization from hexane gave 1.04 g (II) (38%), mp 56°C [7]. Found: C 23.19; H 3.14; Br 60.97%. Calculated for $\text{C}_5\text{H}_8\text{Br}_2\text{O}_2$: C 23.10; H 3.10; Br 61.48%. IR spectrum in CH_2Cl_2 (NaCl , cm^{-1}): ν_{CO} 1717 s, $\nu_{\text{assoc CO}}$ 1750 m, ν_{OH} 2600-3300 v.br., $\nu_{\text{assoc OH}}$ 3500 m. Mass spectrum, m/z : 179, 181 ($\text{M} - \text{Br}$) $^+$, 178, 180 ($\text{M} - \text{HBr}$) $^+$, 148, 150 ($\text{M} - \text{CH}_2\text{Br} - \text{OH}$) $^+$, 121, 123 ($\text{M} - \text{HBr} - \text{CH}_2\text{CO}_2\text{H}$) $^+$, 106, 108 ($\text{M} - \text{Br} - \text{CH}_2\text{CH}_2\text{CO}_2\text{H}$) $^+$, 99 ($\text{M} - \text{HBr} - \text{Br}$) $^+$. PMR spectrum (ppm rel. to TMS): 11.85 s (OH), 4.24 m (CHBr), 3.74 m (CH_2Br), 2.61 m ($\text{CH}_2\text{CO}_2\text{H}$), 2.30 m (CH_2). ^{13}C NMR spectrum (δ rel. to TMS, $^1\text{J}_{\text{CH}}$, Hz): 178.5 (CO), 50.5 (CHBr), 160; 34.9 (CH_2Br) 152; 31.3 (CH_2) 130; 30.8 (CH_2), 130.

Reduction of $\text{ClCO}(\text{CH}_2)_3\text{COCl} \cdot 4\text{AlBr}_3$ by Cyclopentane. By analogy, 1.76 g (39%) (II) was obtained from 1.25 g (18 mmoles) cyclopentane, 2.29 g (17.6 mmoles) $\text{ClCO}(\text{CH}_2)_3\text{COCl}$ and 18.8 g (70.5 mmoles) AlBr_3 in 25 ml CH_2Br_2 .

Ethyl Ester of 4,5-Dibromopentanoic Acid (III). A sample of 0.3 g (II) was heated at reflux for 1 h with 30 ml 3% hydrochloric acid in ethanol. The mixture was treated with water, extracted with ether, and analyzed by chromato-mass spectrometry. Mass spectrum of (III), m/z : 387, 389, 391 ($\text{M} + 1$) $^+$, 241, 243, 245 ($\text{M} - \text{OEt}$) $^+$, 213, 215, 217 ($\text{M} - \text{CO}_2\text{Et}$) $^+$, 207, 209 ($\text{M} - \text{Br}$) $^+$, 179, 181 ($\text{M} - \text{Br} - \text{C}_2\text{H}_4$) $^+$, 161, 163 ($\text{M} - \text{Br} - \text{EtOH}$) $^+$, 133, 135 ($\text{M} - \text{Br} - \text{HCO}_2\text{Et}$) $^+$, 127 ($\text{M} - \text{Br} - \text{HBr}$) $^+$, 99 ($\text{M} - \text{Br} - \text{HBr} - \text{C}_2\text{H}_4$) $^+$.

Transformations of (II) by the Action of Ethanolic KOH. A sample of 0.15 g (II) was heated at reflux in a solution of 0.3 g KOH in 3 ml ethanol for 3 h. The mixture was neutralized by dilute aqueous HCl and extracted with ether. The ethereal extracts were dried and evaporated. The residue was esterified by heating at reflux with 2 ml 3% HCl in ethanol for 1 h and analyzed by chromato-mass spectrometry. The reaction mixture contains four major products: (IV), (Va), (Vb), and (VI). (IV), m/z : 126 (M^+), 111 ($\text{M} - \text{Me}$) $^+$, 98 ($\text{M} - \text{C}_2\text{H}_4$) $^+$, 97 ($\text{M} - \text{Et}$) $^+$, 81 ($\text{M} - \text{OEt}$) $^+$. (Va) or (Vb), m/z : 206, 208 (M^+), 161, 163 ($\text{M} - \text{OEt}$) $^+$, 133, 135 ($\text{M} - \text{CO}_2\text{Et}$) $^+$, 127 ($\text{M} - \text{Br}$) $^+$, 119, 121 ($\text{M} - \text{CH}_2\text{CO}_2\text{Et}$) $^+$, 99 ($\text{M} - \text{C}_2\text{H}_4 - \text{Br}$) $^+$, (VI), m/z : 144 (M^+), 129 ($\text{M} - \text{Me}$) $^+$, 116 ($\text{M} - \text{C}_2\text{H}_4$) $^+$, 115 ($\text{M} - \text{Et}$) $^+$, 101 ($\text{M} - \text{Ac}$) $^+$, 99 ($\text{M} - \text{OEt}$) $^+$.

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CONCLUSIONS

Glutaryl chloride in the complex, $\text{ClCO}(\text{CH}_2)_3\text{COCl} \cdot 4\text{AlBr}_3$, reacts with normal alkanes and cycloalkanes with the formation of 4,5-dibromopentanoic acid after hydrolysis.

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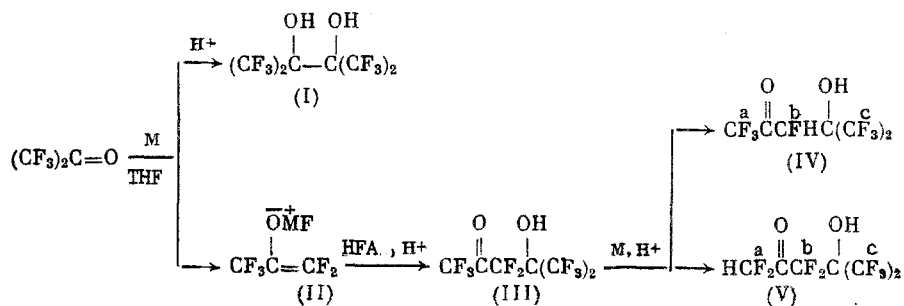
REDUCTIVE DEFLUORINATION OF HEXAFLUOROACETONE AND THE SYNTHESIS OF HALOPENTAFLUOROACETONES

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Carbonyl compounds containing halogen atoms other than fluorine in the α -position readily undergo reductive dehalogenation by the action of metals in aprotic media with the formation of enolates of the corresponding metals. Such dechlorination and debromination is characteristic for monohalo derivatives [1] and for aldehydes and ketones with CHCl_2 [2], CCl_3 , CBr_3 [3], or ClCF_2 groups [4]. The reductive defluorination (RDF) of α -fluoroacarbonyl compounds is usually achieved only with considerable difficulty and has been observed only under conditions leading to the replacement of fluorine by hydrogen [5, 6]. It has also been reported that hexafluoroacetone (HFA) [7-9], trifluoroacetophenone [10], and methyl trifluoropyruvate [11], in contrast to other α -halocarbonyl compounds, under pinacolization upon the action of metals.

We have discovered that the reaction of HFA with metals gives RDF with the formation of pentafluoropropenolates (II) and the products of their subsequent transformations in addition to reductive coupling to give perfluoropinacol (I).^{*} The results of the reaction depends on the nature of the metal and solvent.



Thus, the reaction of HFA with Mg in THF gives not only pinacol, as first reported by Middleton and Lindsey [7], but also hydroketones (III) and (IV) as major products. Chromatography also indicated the formation of (V) and C_9 dihydroxyketones. Magnesium enolate (II) upon formation apparently undergoes condensation with HFA[†] to give the magnesium

^{*}For previous communication, see [12].

[†]The pentafluoroenolate generated by the deprotonation of pentafluoroacetone or pentafluoro-2-propenol (VI) by bases enters an analogous reaction with fluoroketones [13, 14].