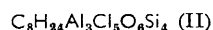
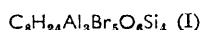


Aluminosiloxane Compounds. Part II.* Compounds of Formula $C_8H_{24}Al_3X_5O_6Si_4$ ($X = Cl$ or Br): Structure, and Reaction with Sodium Acetylacetonate

By C. Ercolani, A. Camilli, and G. Sartori

The synthesis of the compound of formula $C_8H_{24}Al_3Br_5O_6Si_4$ (I) from the reaction of octamethylcyclotetrasiloxane with aluminium bromide or with $Me_3Si \cdot O \cdot AlBr_2$ has been studied. With the latter, polyaluminium-organosiloxanes of formula $[C_2H_6AlBrO_2Si]_n$ are also formed. Information has been obtained about the structure of compound (I) and its chloro-analogue, $C_8H_{24}Al_3Cl_5O_6Si_4$, and about their reactions with sodium acetylacetonate.

FOLLOWING on the work described in Part I (preceding Paper), a study was undertaken of the synthesis, structure, and chemical properties of two crystalline compounds of formulae (I) and (II). The purpose of



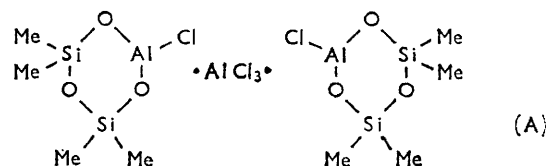
this study was, as before, to aid in the interpretation of the experimental results of the reaction between sodium acetylacetonate and certain polyaluminium-organosiloxanes, as described in Part III (following Paper).

Compound (II) was first characterised by Zhdanov *et al.*¹ † We subsequently found³ that it is produced, together with the polyaluminium-organosiloxanes, when dichlorotrimethylsiloxaluminium and octamethylcyclotetrasiloxane react together. Compound (II) is probably an intermediate in the formation of the polyaluminium-organosiloxanes. Compound (I) was prepared from aluminium bromide and octamethylcyclotetrasiloxane according to the description of Zhdanov *et al.* for the synthesis of compound (II).

We have also studied the reaction between dibromotrimethylsiloxaluminium and octamethylcyclotetrasiloxane (in molar ratio 4 : 1). If the reaction is carried out at 160–170° for 25 hr., the products are bromotrimethylsilane and about equal amounts of compound (I) and amorphous polyaluminium-organosiloxanes. The polymers are glassy substances, infusible below 300°, containing Al, Br, and Si in the ratio 1 : 1 : 1. They are very soluble in cold benzene, which enabled a cryoscopic determination of mean molecular weight to be carried out in benzene solution, despite difficulties encountered through their ease of hydrolysis. The value obtained was 2540. Analysis gives the formula $[C_2H_6AlBrO_2Si]_n$, where n , the mean degree of polymerisation, is about 13.

The structural formula which Zhdanov *et al.* proposed for compound (II) was based on its reaction with sodium acetylacetonate (and on analytical data). One aluminium atom in three in the compound was thereby liberated, in the form of aluminium acetylacetonate, which led the authors to suppose that 1 molecule of aluminium chloride was co-ordinated to 2 chloroaluminosiloxane rings as shown in (A). The following

observations led us to doubt the validity of this structure. (1) Compound (II) can be repeatedly sublimed under a vacuum without any appreciable alteration, which would be most strange for a compound containing $AlCl_3$ co-ordinated as in structure (A) (*i.e.*, five-co-ordinated). As far as we are aware, only one other aluminium compound has been reported to have five-co-ordinated aluminium, namely, $AlH_3 \cdot 2NMe_3$, but this becomes unstable at slightly above room temperature.⁴ In fact, an X-ray structural investigation in



this laboratory has shown that compound (II) contains five-co-ordinated aluminium (see below) but the structure is quite different from that proposed by Zhdanov *et al.* (2) Compound (II) can be obtained from the reaction of dichlorotrimethylsiloxaluminium with octamethylcyclotetrasiloxane, a reaction in which $AlCl_3$ is, at least initially, not present.³ (3) The formation of $Al(acac)_3$ from the reaction of compound (II) with sodium acetylacetonate does not necessarily mean that $AlCl_3$ is present in the molecule, for a group such as $-Si \cdot O \cdot AlCl_2$ could equally well behave in the same way (see Part I). Polyaluminium-organosiloxanes also release a certain amount of the aluminium present in them in the form of $Al(acac)_3$ on treatment with sodium acetylacetonate (see Part III), even though they are synthesised, like compound (II), from dichlorotrimethylsiloxaluminium and octamethylcyclotetrasiloxane. In the light of these observations, which are equally applicable to compound (I), it was decided to examine the problem by two lines of approach. On the one hand, a complete X-ray crystallographic investigation of compound (I) was undertaken, so as to determine definitively its structure and that of compound (II). On the other hand, the behaviour of compounds (I) and (II) towards sodium acetylacetonate was examined in detail,

¹ A. A. Zhdanov, K. A. Andrianov, and A. A. Bogdanova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1261.

² J. F. Hyde, U.S.P. 2,645,183/1952; *idem*, B.P. 685,183/1952.

³ C. Ercolani, A. Camilli, and L. De Luca, *J. Chem. Soc.*, 1964, 5278.

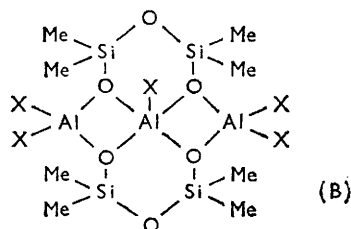
⁴ G. W. Frazer, N. N. Greenwood, and B. P. Strangham, *J. Chem. Soc.*, 1963, 3742.

* Part I, C. Ercolani, A. Camilli, and G. Sartori, preceding Paper.

† Previously, Hyde² described the same reaction as later employed by Zhdanov *et al.* to prepare this compound, but reported different results. Our results confirmed those of the Russian workers.

especially with regard to the quantity of $\text{Al}(\text{acac})_3$ formed.

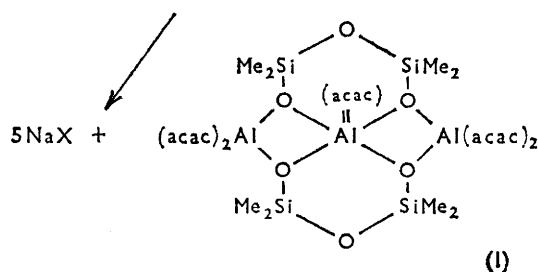
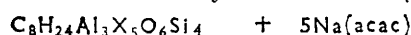
The X-ray investigation showed⁵ that the compounds of formula $\text{C}_8\text{H}_{24}\text{Al}_3\text{X}_5\text{O}_6\text{Si}_4$ ($\text{X} = \text{Cl}$ or Br) are isomorphous, and have the structure (B). (An idea of the spatial arrangement is given if one imagines the central aluminium atom at the peak of a pyramid, with a halogen atom above it, and the four rings lying approximately in the planes of the four sloping sides.) There is the same type of co-ordination between aluminium and oxygen atoms as in the dimers of the dihalogenotrimethylsiloxyaluminiums; however, it extends here over all three aluminium atoms. It is worth



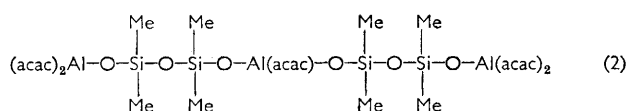
noting that, whilst the external aluminium atoms are four-co-ordinated, the central one is five-co-ordinated; this is quite a rare occurrence.

The reaction of sodium acetylacetonate with compounds (I) and (II) was carried out in anhydrous ethanol in a similar way to that described by Zhdanov *et al.* for compound (II). In both cases the quantity of $\text{Al}(\text{acac})_3$ formed corresponds to 41–44% of the total aluminium present in the reactant. In addition to the $\text{Al}(\text{acac})_3$, a mixture of solid and liquid polymeric products was separated from the reaction mixture by extraction with ligroin. Their mean molecular weight varied between 500 and 2000.

Assuming that the structure found in the solid for compounds (I) and (II) is present also in anhydrous ethanol solution, one can suppose that the initial reaction with sodium acetylacetonate is (1). The molecule

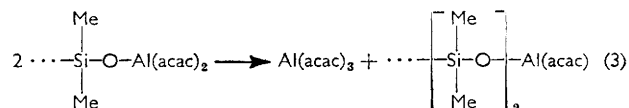


formed in this way is unstable. The co-ordination between aluminium and oxygen atoms breaks down, and the molecule opens out [reaction (2)]. The terminal



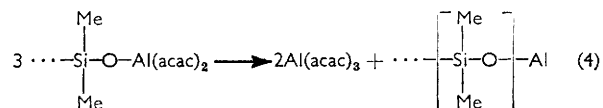
groups react together, giving rise to $\text{Al}(\text{acac})_3$ [reaction (3)]. The fact that the polyorgano-aluminosiloxanes

are obtained in a range of molecular weights shows that reaction (3) could be either intra- or inter-molecular.



The central aluminium atom cannot behave in the same way as the two external aluminium atoms [see (2)], not only because it is stably co-ordinated, but also because it is bound to the molecule by not one, but two, oxygen atoms.

According to this reaction path, only one aluminium atom in three ought to form $\text{Al}(\text{acac})_3$. The experimentally higher value is probably due to some secondary reaction, for example (4). It may be noted that this



mechanism is analogous to that proposed for the formation of $\text{Al}(\text{acac})_3$ in the case of dihalogenotrimethylsiloxyaluminium compounds. Seeing that the latter compounds have structures similar to that of compounds (I) and (II), this fact will be of particular importance, both in deducing the constitution of the polyaluminium-organosiloxanes and in explaining their behaviour towards sodium acetylacetonate (see Part III).

EXPERIMENTAL

The molecular weights were determined cryoscopically in benzene solution in the case of polyaluminium-organosiloxanes, and with a Mechrolab 301A osmometer in ethanol solution in the case of the secondary products obtained from the reactions of compounds (I) and (II) with sodium acetylacetonate.

Reaction A (Aluminium Tribromide and Octamethylcyclotetrasiloxane).—Aluminium tribromide (8.01 g., 0.030 mole), purified by vacuum-sublimation, was added to octamethylcyclotetrasiloxane (6.85 g., 0.023 mole) in a flask fitted with a reflux condenser and CaCl_2 tube. The mixture was heated under reflux at 150° for 28 hr. At the end of the reaction, the $\omega\omega'$ -dibromosiloxanes were distilled from the mixture, and collected in two fractions: (i) b. p. $65\text{--}85^\circ/15\text{ mm.}$, (ii) b. p. up to $95^\circ/1\text{ mm.}$ On continuing the distillation under a vacuum, a white crystalline product (11.18 g.) sublimed at $150\text{--}155^\circ/0.16\text{ mm.}$; it was resublimed, and could be recrystallised from benzene and from hexane [Found: C, 11.7; H, 3.1; Al, 9.9; Br, 48.7; Si, 13.7. Formula (I) requires C, 11.9; H, 3.0; Al, 10.0; Br, 49.4; Si, 13.9%], m. p. (sealed tube) $154\text{--}155^\circ$. Fractions (i) and (ii) had a bromine content of 46.5 and 39.3%, respectively, from which one can deduce that the two fractions consist of a mixture of largely short-chain $\omega\omega'$ -dibromosiloxanes. In fact, the general formula $\text{BrSiMe}_2[\text{O-SiMe}_2]_n\text{O-SiMe}_2\text{Br}$ requires: for $n = 0$, Br 55%; for $n = 1$, Br 44%; for $n = 2$, Br 36.4%.

Reaction B (Dibromotrimethylsiloxyaluminium and Octamethylcyclotetrasiloxane at $160\text{--}170^\circ$).—Dibromotrimethylsiloxyaluminium was prepared according to Orlov's method⁶

⁵ M. Bonamico, unpublished results.

⁶ N. F. Orlov, *Doklady Akad. Nauk S.S.S.R.*, 1957, **114**, 1033.

from hexamethyldisiloxane and anhydrous aluminium tribromide, and purified by distillation at 110°/1 mm. This substance (9.8 g., 0.036 mole) was heated under anhydrous conditions with octamethylcyclotetrasiloxane (2.7 g., 0.009 mole) at 160–170° for 25 hr. in a Claisen flask with a fractionation side-arm. The liquid distilled during reaction was collected (2.5 g.) in a trap cooled by acetone–solid CO₂. The reaction mixture, which started off as a liquid, was semi-solid at the end of the reaction. On heating under a vacuum (0.16 mm.), unreacted reagents were driven off. At 150–155° a crystalline white solid sublimed (4.95 g.). An amorphous solid residue (4.0 g.) remained in the flask. The liquid distilled during reaction (2.5 g.) was further distilled. It consisted entirely of Me₃SiBr (b. p. 79–80°) (Found: Br, 51.5. Calc. for Me₃SiBr: Br, 52.2%). The white crystalline solid was further sublimed at 150–155°/0.16 mm. [Found: C, 11.9; H, 3.2; Al, 10.5; Br, 48.4; Si, 13.5. Formula (I) requires C, 11.9; H, 3.0; Al, 10.0; Br, 49.4; Si, 13.9%]. The solid amorphous residue was completely soluble in benzene, and was infusible below 300°. Its molecular weight, measured cryoscopically in benzene, was 2540 [Found: C, 12.0; H, 3.1; Al, 12.4–12.8; Br, 40.6; Si, 13.8. (C₂H₆AlBrO₂Si)_x requires C, 12.2; H, 3.1; Al, 13.7; Br, 40.6; Si, 14.2%].

Reaction C [Compound (II) and Sodium Acetylacetonate].—Sodium acetylacetonate (6.20 g., 0.05 mole) and compound (II) (6.17 g., 0.01 mole) together with anhydrous ethanol (40 c.c.) were placed in a flask fitted with a reflux condenser and CaCl₂ tube. The mixture was stirred for 4 hr. at 60°, after which anhydrous benzene (10–15 c.c.) was added to ensure complete precipitation of sodium chloride. This was filtered off from the reaction mixture (3.16 g.; calc., 3.08 g.). Benzene and ethanol were removed from the filtrate by distillation, and light petroleum was added. The mixture was stirred, cold, for 1 hr. The undissolved solid was filtered off from the solution. This

solid (4.83 g.) was divided into two parts. From one part (2.63 g.), Al(acac)₃ (2.32 g.) was completely separated by recrystallisation from anhydrous ethanol. From the other part (2.20 g.), Al(acac)₃ (1.94 g.) was separated by sublimation at 160–170°/1 mm. The two quantities obtained agree quite well with each other. Thus, in 4.83 g. of solid there were 4.26 g. of Al(acac)₃, equivalent to 41.7% of the total aluminium originally present in compound (II). The solution in light petroleum was evaporated to dryness. The residue was a dense mixture of solid and liquid. Fractionating of this, carried out in part using solvent-extraction and in part by distillation at reduced pressure, gave various fractions having molecular weights between 500 and 2000.

Reaction D [Compound (I) and Sodium Acetylacetonate].—In the same way as described for reaction C, compound (I) (5.34 g., 0.0066 mole) and sodium acetylacetonate (4.03 g., 0.033 mole) in anhydrous ethanol (40 c.c.) were stirred for 4 hr. at 60° in a flask fitted with a reflux condenser and CaCl₂ tube. At the end of the reaction, after addition of benzene, sodium bromide (3.15 g.; calc., 3.39 g.) was filtered off. The filtrate was evaporated to dryness, and the residue shaken with ligroin for 1 hr. The Al(acac)₃ present in the solid remaining undissolved was determined by recrystallisation and sublimation. The Al(acac)₃ obtained contains 43.7% of the total aluminium originally present in compound (I). The ligroin solution was evaporated to dryness. A dense liquid was obtained containing suspended solid. This mixture also was fractionated, giving fractions having molecular weights between 500 and 2000.

CENTRO DEI COMPOSTI DI COORDINAZIONE ED
ELEMENTORGANICI DEL C.N.R.,
ISTITUTO DI CHIMICA GENERALE ED INORGANICA,
UNIVERSITA DI ROMA,
ITALY.

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