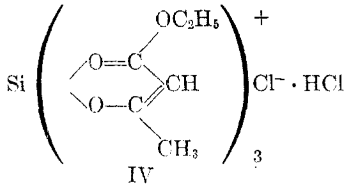
No pure compounds could be isolated from the reaction between methyltrichlorosilane and ethylacetoacetate or its sodium derivative. The undistillable oily residues which were formed had infrared absorption similar to that of the compounds described above. The reaction between silicon tetrachloride and ethyl acetoacetate, on the other hand, gives a crystalline solid with the empirical formula $C_{18}H_{28}O_9SiCl_2$. This compound was first prepared by Rosenheim and his co-workers[7] and assigned a structure (IV) in which three ethylacetoacetate groups are chelated to a positively charged siliconium ion. The infrared spectrum of the compound shows a single very strong, broad band in the 1500–1800 cm.$^{-1}$ region, centered at 1520 cm.$^{-1}$, with shoulders at 1568 and 1604.$^{-1}$ This strong, very low frequency carbonyl absorption is typical of metal chelates[8] generally and occurs in those 2,4-pentanedione derivatives of silicon which are chelated.[5] The infrared evidence therefore confirms the siliconium structure IV for the compound. As with the analogous siliconium chelate with 2,4-pentanedione,[5] the extra mole of HCl is probably present as the hydrogen dichloride anion.[9]



IV

EXPERIMENTAL

Ethyl 3-trimethylsiloxy-2-butenoate. Sodium sand was prepared from 3.4 g. (0.15 g.-atom) of sodium in 250 ml. of toluene. A solution of 20 g. (0.15 mole) of freshly distilled ethyl acetoacetate in 100 ml. of toluene was added and the mixture was warmed to 45° and stirred for 30 min. To the resulting clear solution was added 16.3 g. (0.15 mole) of trimethylchlorosilane in 60 ml. of toluene. The mixture was then refluxed with stirring for 2 hr., then cooled, and filtered with suction to remove sodium chloride. Fractional distillation at reduced pressure gave 18 g. (61%) of product boiling at 76–78° (7 mm.). The compound is a colorless oil with n_D^{25} 1.4393, d_4^{25} 0.941. It has a strong camphor-like odor. Water hydrolyzes the liquid rapidly to give hexamethyldisiloxane and ethyl acetoacetate. The absence of hydroxylic hydrogen is indicated by the fact that the substance reacts only very slowly with sodium, as well as by the lack of appropriate absorption bands in the infrared and N.M.R. spectra.

Anal. Calcd. for $C_9H_{18}O_3Si$: C, 53.4; H, 8.97; mol. ref.,[10] 55.4. Found: C, 53.4; H, 8.70; Mol. ref., 56.6.[11]

Dimethylsilylbis(ethyl 3-oxy-2-butenoate). This compound was prepared from 5.2 g. (0.23 g.-atom) of sodium, 30 g. (0.225 mole) of ethyl acetoacetate, and 14 g. (0.11 mole) of dimethyldichlorosilane, using the procedure described above for the trimethylsilyl derivative. After two distillations *in vacuo* 7 g. (20%) of pure product was obtained, boiling at 119–121° (0.1 mm.), with n_D^{25} 1.4602, d_4^{25} 1.049. The compound is a colorless liquid resembling the trimethylsilyl derivative in its properties.

Anal. Calcd. for $C_{14}H_{21}O_6Si$: C, 53.1; H, 7.65; Mol. ref., 80.4. Found: C, 52.7; H, 7.64; Mol. ref., 82.6.[11]

Reaction of ethyl acetoacetate with methyltrichlorosilane. The sodium derivative of ethyl acetoacetate (0.22 mole) in toluene was treated with methyltrichlorosilane (16.5 g., 0.11 mole) as described above. The solution was filtered and distilled under reduced pressure. The only product obtained was 4 g. of strongly acidic material boiling at 70–80° (1 mm.) which did not contain silicon. The residue (ca. 40 g.) carbonized to give a black resin.

In another trial 14.5 g. (0.11 mole) of ethyl acetoacetate was mixed with 8 g. (0.054 mole) of methyltrichlorosilane in 30 ml. of benzene and the solution was refluxed for 12 hr. The benzene was evaporated giving a brown oily residue which, like the product described above, decomposed upon distillation. The crude oily product had strong infrared absorption bands at about 1640 and 1700 cm.$^{-1}$

Tris(ethyl acetoacetato)siliconium chloride 1-hydrogen chloride. To 19.5 g. (0.15 mole) of ethyl acetoacetate dissolved in 75 ml. of ether was added 8.5 g. (0.05 mole) of silicon tetrachloride. The solution became warm and a lower liquid phase soon separated. The mixture was refluxed for 1 hr. and then cooled in ice. After several hours the lower layer crystallized. It was filtered with suction, washed with anhydrous ether, and dried *in vacuo.*

The white crystalline product is soluble in water. The chlorine can be titrated immediately. The hydrolysis of chelate groups is not immediately complete, but is more rapid than with the analogous acetylacetone siliconium ion. The material can be stored for several months if kept out of contact with moisture.

Anal. Calcd. for $C_{18}H_{28}O_9SiCl_2$: C, 44.4; H, 5.79; Cl, 14.5. Found: C, 44.1;[12] H, 5.80; Cl, 14.6.

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[7] A. Rosenheim, W. Loewenstamm, and L. Singer, *Ber.*, **36,** 1833 (1903); W. Dilthey, *Ann.*, **344,** 305 (1906).

[8] L. J. Bellamy, Ref. 4 , p. 126.

[9] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **76,** 4046 (1954); R. West, *J. Am. Chem. Soc.*, **79,** 4568 (1957).

[10] E. L. Warrick, *J. Am. Chem. Soc.*, **68,** 2445 (1946).

[11] The refractive exalations shown by these two substances are typical for conjugated carbonyl compounds. *Cf.* reference 5.

[12] Including 1.2% retained as silicon carbide residue.

Note on the Preparation of Cyclohexen-1-aldehyde

ERNST D. BERGMANN AND ABRAHAM BECKER

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Of the various methods described for the preparation of cyclohexene-1-aldehyde (I)[1–4] only the last one[4] has preparative interest: it consists in the reduction of 2-isobutoxymethylenecyclohexanone by lithium aluminium hydride. However, even this method gives a yield of not more than 30% (calculated on cyclohexanone) and is somewhat cum-

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[1] O. Wallach, *Ann.*, **359,** 292 (1908).

[2] P. A. Plattner and L. M. Jampolsky, *Helv. Chim. Acta,* **26,** 687 (1943).

[3] E. A. Braude and E. A. Evans, *J. Chem. Soc.,* 3334 (1955).

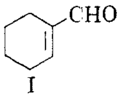
[4] P. Seifert and H. Schinz, *Helv. Chim. Acta,* **34,** 728 (1951).

bersome. It has recently been reported that cyclohexenyltrichloromethylcarbinol (II) decomposes under the influence of alkali to (I) and cyclohexenylglycolic acid (III) in yields of 35 and 30%, respectively.[5,6] Since (II) is easily accessible from chloral and cyclohexene in the presence of aluminum chloride[6] (yield 82%), this sequence of reaction appeared to provide an easy, even if not very lucrative, method for the preparation of I.

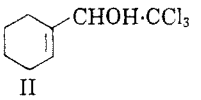
We have found that II, when heated with 4 moles of 20% sodium hydroxide solution, gives reproducibly a 25% yield of III, but that the yield of I is variable, much polymeric material being formed. Equally, all experiments failed to pyrolyze II in the presence of potassium hydroxide, potassium carbonate or copper powder, or to split it by means of concentrated sulfuric acid or lead tetraacetate.

An indirect method, however, led to the desired result. In accordance with the data of Weizmann, Bergmann, and Sulzbacher,[7] treatment of II with 5 moles of sodium hydroxide, dissolved in methanol or propanol, gave cyclohexenyl-α-methoxy- and -α-propoxy-acetic acid (IV) in 54% and 73% yield, respectively. Pyrolysis of these acids in the presence of copper powder[8] led to I in 34% and 82% yield, so that the over-all yield, calculated on cyclohexene, was 15 and 49%, respectively.

Treatment of II with 2 moles of methanolic sodium methoxide gave in 90% yield a neutral liquid which, according to its analysis and properties, was the glycolide (V). Sodium hydroxide (1 mole) converted V into III, sodium methoxide (1 mole) into IV (R = CH_3); in both cases the yields were nearly quantitative.



I



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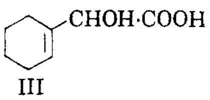
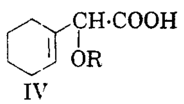
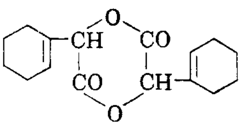


III



IV



V

EXPERIMENTAL

Cyclohexenyltrichloromethylcarbinol (II) was prepared in 82% yield from 1 mole of chloral, 2 moles of cyclohexene, and 14 g. of aluminum chloride. B.p. 150° (15 mm.).

Dicyclohexenylglycolide (V). A solution of 1 mole of II and 2 moles of sodium methoxide in 500 ml. of methanol was refluxed for 3 hr. The methanol was distilled off and the remaining solid filtered and washed with 100 ml. of ether. To the filtrate and washings, water and 200 ml. of ether were added, and the ethereal liquid was dried over magnesium sulfate and distilled. B.p. 140° (20 mm.). Yield, 124 g. (90%).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 70.6; H, 7.2. Found: C, 70.3; H, 6.9.

Cyclohexenylglycolic acid (III). (*a*) A mixture of 57 g. (0.25 mole) of II and 50 g. (1.25 moles) of sodium hydroxide in 100 ml. of water was refluxed for 1 hr. and the solution cooled, extracted with ether, and acidified with 10% hydrochloric acid. Renewed extraction with ether gave 10 g. (25%) of III. B.p. 155° (30 mm.), m.p. 125°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.5; H, 7.8. Found: C, 61.2; H, 8.1.

(*b*) When 27.6 g. of (V) was refluxed for 3 hr. with 8 g. of sodium hydroxide in 100 ml. of water, 30 g. (96%) of III was obtained, which solidified spontaneously and melted at 125° without further purification.

Cyclohexenylmethoxyacetic acid (IV, R = CH_3). (*a*) To a solution of 50 g. of sodium hydroxide in 200 ml. of methanol and a little water, 57 g. of II was added slowly. When the exothermic reaction had subsided, the mixture was refluxed for 1 hr. and the alcohol removed *in vacuo*. Addition of water, extraction with ether, and acidification of the aqueous layer gave the desired acid, which was extracted with ether and distilled. B.p. 124° (0.1 mm). Yield, 23 g. (54%).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.5; H, 8.4. Found: C, 63.7; H, 8.5.

(*b*) The same result was obtained when instead of sodium hydroxide sodium methoxide was used.

(*c*) A mixture of 27.6 g. of the glycolide (V), 18 g. of sodium methoxide, and 100 ml. of alcohol was refluxed for 2 hr. Water was added and the mixture acidified and extracted with ether. Thus, 31 g. (97%) of IV (R = CH_3) was obtained; b.p. 124° (0.1 mm.).

Cyclohexenylpropoxyacetic acid (IV, R = C_3H_7). To a solution of 50 g. of sodium hydroxide in 300 ml. of propanol, 57 g. of II was added slowly. When the reaction had subsided, the mixture was refluxed for 1 hr. and worked up as above; b.p. 156° (25 mm.). Yield, 36 g. (73%).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.7, H, 9.1. Found: C, 66.9; H, 9.4.

Cyclohexen-1-aldehyde (I). (*a*) A mixture of 17 g. of cyclohexenylmethoxyacetic acid (IV, R = CH_3) and 1 g. of copper powder was heated in a distillation flask at 200° for 2 hr. The distillate was fractionated; b.p. 61° (1 mm.). Yield, 3.7 g. (34%).

(*b*) A mixture of 10 g. of cyclohexenylpropoxyacetic acid (IV, R = C_3H_7) and 1 g. of copper powder was heated at 200° for 2 hr. and worked up as above. Yield, 4.5 g. (82%).

The *2,4-dinitrophenylhydrazone*, after recrystallization from butanol, melted at 212°.

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[5] J. Colonge and A. Perrot, *Compt. rend.*, **239**, 541 (1954).

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[7] Ch. Weizmann, E. D. Bergmann, and M. Sulzbacher, *J. Am. Chem. Soc.*, **70**, 1153 (1948). *Cf.* E. D. Bergmann, D. Ginsburg, and D. Lavie, *J. Am. Chem. Soc.*, **72**, 5012 (1950), and H. Gilman and G. R. Wilder, *J. Am. Chem. Soc.*, **77**, 6644, 6659 (1955).

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Isomerization of *N*-*p*-Ethoxybenzoylethylenimine

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Our earlier interest in ethylenimine and its derivatives[1] and oxazolines[2] has prompted the current

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[1] H. W. Heine and B. L. Kapur, *J. Am. Chem. Soc.*, **77**, 4892 (1955); H. W. Heine, B. L. Kapur, and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).