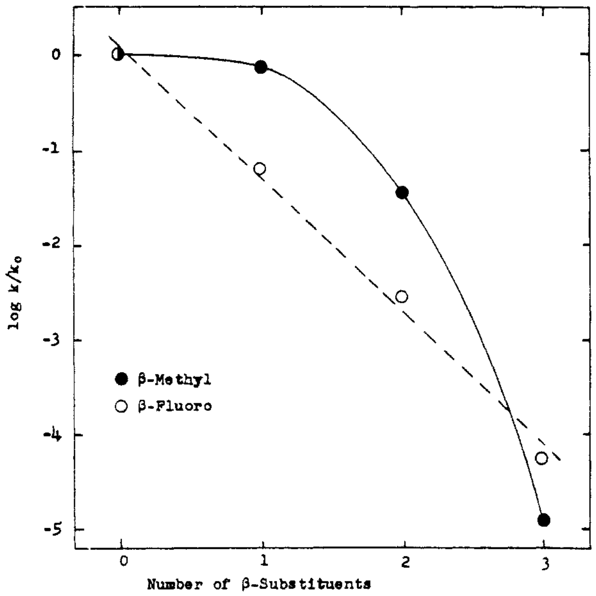

Fig. 1. Plot of log (k/k_0) for S_N2 reactions of ethyl iodides *vs.* the number of β-fluorine or β-methyl substituents

phenylethyl chlorides toward iodide in acetone is increased by both *p*-methoxy and *p*-nitro groups.[19] Both α- and β-halogen substituents decrease S_N2 reactivity to an extent that is proportional to neither their polar nor steric factors alone.[19] α-Haloketones (and also γ-chlorobutyrophenone[20]) are quite reactive.[19] In the β-position alkoxy groups deactivate and in the α-position they activate.[19,21] Benzyl and allyl halides are often more reactive than the corresponding methyl halides.[19]

School of Chemistry
Georgia Institute of Technology
Atlanta, Ga.

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[21] P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

Structures of Silyl Derivatives of Ethyl Acetoacetate

Robert West

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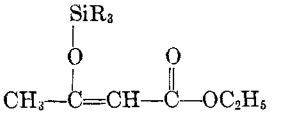
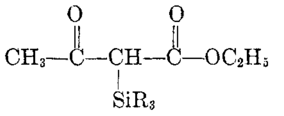
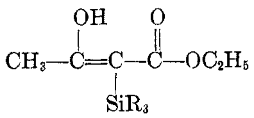
The triethylsilyl derivative of ethylacetoacetate was first prepared in 1946 by Gilman and Clark.[1] On the basis of chemical reactions these workers proposed a structure of the type I below with the triethylsilyl group attached to the oxygen of the carbonyl group. However, others have pointed out that the chemical reactions shown by the substance might also be observed if the compound had the C-silylated structure of type II[2]; and recently Hurwitz, de Benneville, and Yoncoskie have obtained the trimethylsilyl derivative of ethylacetoacetate and implied that it has the type II structure.[3]


$CH_3-C(OSiR_3)=CH-C(=O)-OC_2H_5$

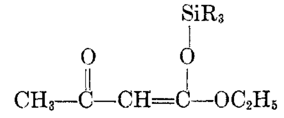
I


$CH_3-C(=O)-CH(SiR_3)-C(=O)-OC_2H_5$

II


$CH_3-C(OH)=C(SiR_3)-C(=O)-OC_2H_5$

IIa


$CH_3-C(=O)-CH=C(OSiR_3)-OC_2H_5$

III

We have prepared the trimethylsilyl and dimethylsilyl derivatives of ethylacetoacetate, and determined their infrared spectra in the sodium chloride region. These spectra are very similar. In the 1500–1800 cm.$^{-1}$ region, the trimethylsilyl compound has strong bands at 1714 and 1630 cm.$^{-1}$, while in the dimethylsilyl derivative these bands appear at 1712 and 1630 cm.$^{-1}$. The higher frequency band is in the right range either for a *conjugated* ester or for a *nonconjugated* ketone carbonyl absorption.[4] The 1630 cm.$^{-1}$ band, as in our earlier work with silyl acetylacetonates,[5] is attributed to carbon-carbon double bond absorption, with its position shifted and intensified by conjugation and by substitution with an electronegative (siloxy) group.[6] The *C*-silylated structure II for these compounds should show only nonconjugated ketone and ester carbonyl absorption, and hence can be eliminated from consideration. It is true that the enol form of the *C*-silylated structure, IIa, would have absorption in the 1500–1800 cm.$^{-1}$ region similar to that observed; but this structure can be eliminated since the compounds in question do not contain a hydroxylic hydrogen atom. The alternate *O*-silylated structure III contains a conjugated ketonic carbonyl group, and therefore should absorb near 1670 cm.$^{-1}$ as enol ethers of acetylacetone do.[5] Thus, the only structure compatible both with physical and chemical properties and with the observed infrared spectra is the β-siloxycrotonate structure I originally proposed by Gilman. An *O*-silylated structure is further substantiated by the fact that the compounds have strong bands near 1000 cm.$^{-1}$, attributable to Si—O vibrations.

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[1] H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **69**, 967 (1947).

[2] F. C. Whitmore, L. M. Sommer, J. Gold, and R. E. van Strien, *J. Am. Chem. Soc.*, **69**, 1551 (1947); C. R. Hance and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 994 (1953).

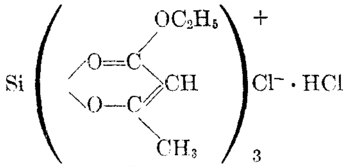
[3] M. J. Hurwitz, P. L. de Benneville, and R. A. Yoncoskie, Abstracts of Papers, 131st National Meeting, American Chemical Society, 1957, pp. 52–0.

[4] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., London, 1954.

[5] R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

[6] R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949); see also ref. 4, p. 117 ff.

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.

Department of Chemistry
University of Wisconsin
Madison 6, Wis.

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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

Received April 1, 1958

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).

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(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).