Following the usual method,[8] the reaction of I with leucine, and with phenylalanine, was attempted. In each case there was obtained a yellow oil which could not be crystallized from ethanol, dioxane, acetone or acetic acid. Further attempts at purification were abandoned.

Of all the amides formed, that with *n*-octylamine was most easily produced, while 2-aminothiazole reacted least readily. The pyridine-catalyzed alcoholysis proceeded more slowly than did the reactions of the propylamines. In every case where a reaction occurred, a quantitative yield was obtained.

The ultraviolet absorption spectra of a series of thiophene azlactones[3c] and rhodanines[7] having been previously determined, it was of interest to study the effect of various substituent groups on the ultraviolet absorption spectra of the amides and esters of α-benzamido-β-2-thienylacrylic acid. From the absorption curves shown on Fig. 1 and the data presented in Table I, it can be seen that the opening of the oxazole ring of the azlactone results in a shifting of the peaks to lower wave lengths and a diminution in the absorption intensity. Esterification or amidation of the acrylic acid, however, leads to a bathochromic shift in both peaks. Furthermore, it is of interest to note that the introduction of a thiazole ring produces a rise in the molecular extinction coefficients, the absorption maxima remaining, however, in the lower region.

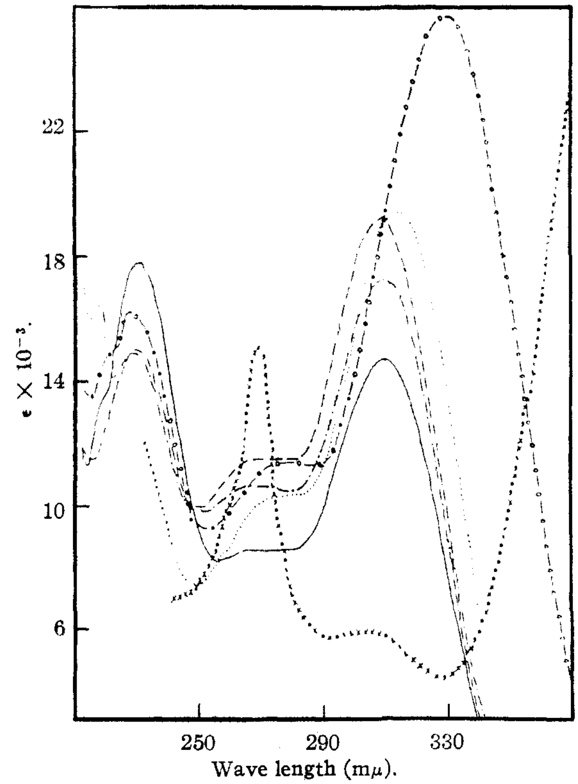


Fig. 1.—Ultraviolet absorption spectra of thiophene azlactone and derivatives: xxxxxx, thiophene azlactone; ......, acrylic acid ethyl ester; ----, *n*-octyl amide (R = C_3H_{17}); -O-O-, thiazolyl amide (R = C_3H_2NS); -·-··-·, phenylisopropyl amide (R = $C_6H_5CH_2CH(CH_3)$); —, thienylisopropyl amide (R = $C_4H_3SCH_2CH(CH_3)$).

Experimental

Preparation of Acrylic Acid Amides.—To 1 g. of the amine was added a stoichiometric amount of azlactone, and the mixture was refluxed in 30 ml. of ethanol for three hours. On cooling, the addition of water caused the precipitation of the amide, which was recrystallized three times from ethanol. The propyl amides were further recrystalized from benzene. 1-Phenyl-2-aminopropane yielded white crystalline 1-phenylisopropyl-α-benzamido-β-2-thienylacrylamide, m.p. 86.5–87° (uncor.).

Anal. Calcd. for $C_{23}H_{22}O_2N_2S$: C, 70.74; H, 5.68; N, 7.17. Found: C, 70.50; H, 5.75; N, 7.06.

1-(2-Thienyl)-2-aminopropane yielded white crystalline 1-(2-thienyl)-isopropyl-α-benzamido-β-2-thienylacrylamide, m.p. 163.5–164°.

Anal. Calcd. for $C_{21}H_{20}O_2N_2S_2$: C, 63.61; H, 5.08; N, 7.07. Found: C, 63.61; H, 4.96; N, 7.08.

2-Aminothiazole yielded white crystalline 2-thiazolyl α-benzamido-β-2-thienylacrylamide, m.p. 220–220.5°.

Anal. Calcd. for $C_{17}H_{13}O_2N_3S_2$: C, 57.44; H, 3.69; N, 11.82. Found: C, 57.56; H, 3.53; N, 11.80.

Cytosine and aniline gave no amide by the above method, nor did the latter when excess aniline was used as solvent. The *n*-octylamide was prepared as before.[2]

Alcoholysis of Thiophene Azlactone.—2.5 g. (0.01 mole) of I was refluxed for one hour in ethanol, in the presence of 1 g. of 2-aminopyridine (or its 3- or 6-methyl analog). On cooling, the addition of water precipitated the ester, which was recrystallized three times from ethanol. A quantitative yield was obtained of white needles of ethyl α-benzamido-β-2-thienylacrylate, m.p. 177.5–178°.

Ultraviolet Absorption Spectra.—These measurements were made with a Beckman quartz spectrophotometer, model DU, using ethanol as the solvent.

Acknowledgments.—All analyses were done by Mr. A. A. Sirotenko of this Department. This investigation was carried out under the aegis of the Atomic Energy Commission.

Communication No. 235 from the
Department of Organic Chemistry and Enzymology
Fordham University
New York 58, N. Y. Received July 20, 1951

(8) M. Bergmann and A. Miekeley, *Ann.*, **458**, 40 (1927).

The Reaction of Some Tetrasubstituted Silanes with *n*-Butyllithium

By Henry Gilman and Howard Hartzfeld

It has been shown[1] that when triphenylsilanol, tri-*p*-tolylsilanol, diphenyl-*p*-tolylsilanol or hexaphenyldisiloxane is refluxed with *n*-butyllithium in ether, there is cleavage of a carbon-to-silicon bond, whereas in the case of tri-1-naphthylsilanol, there is no cleavage. In that publication it was shown that under the same conditions there is no cleavage of a carbon-to-silicon bond in any of a number of tetraaryl- and mixed arylalkylsilanes of the type R_4Si. However, it has been found[2] that certain tetrasubstituted silanes are readily cleaved by potassium hydroxide. The present studies were made in order to determine whether some of the tetrasubstituted silanes which were most readily cleaved by potassium hydroxide might also be cleaved by *n*-butyllithium.

Accordingly, triphenyl-(phenylethynyl)-silane

---

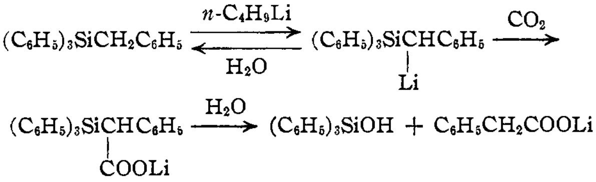
(1) H. Gilman, R. A. Benkeser and G. E. Dunn, This Journal, **72**, 1689 (1950).

(2) Unpublished studies by Dr. L. S. Miller. See, also, L. H. Sommer, L. J. Tyler and F. C. Whitmore, This Journal, **70**, 2872 (1948); J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **70**, 1117 (1948); E. Larsson and L. O. Knopp, *Acta Chem. Scand.*, **1**, 268 (1947) [*C. A.*, **42**, 5416 (1948)]; A. Bygden, *J. prakt. Chem.*, **96**, 86 (1917); F. S. Kipping, *J. Chem. Soc.*, **125**, 2291 (1924).

was treated with an excess of *n*-butyllithium by the method used for triphenylsilanol.[1] Upon carbonation of the reaction mixture, phenylpropiolic acid and *n*-butyltriphenylsilane were isolated, indicating that there had been cleavage of a carbon-to-silicon bond in this R_4Si compound in accordance with the equation

$$(C_6H_5)_3SiC{\equiv}CC_6H_5 + n\text{-}C_4H_9Li \longrightarrow n\text{-}C_4H_9Si(C_6H_5)_3 + C_6H_5C{\equiv}CLi$$

When, in a similar manner, triphenylbenzylsilane was treated with an excess of *n*-butyllithium, and the reaction mixture was again carbonated, triphenylsilanol and phenylacetic acid were isolated. In view of the results[1] obtained in the reaction of *n*-butyllithium with trimethyl-9-fluorenylsilane, it seemed reasonable to suppose that the initial reaction was metalation rather than cleavage of a carbon-to-silicon bond. Therefore, a second trial was made in the same manner, except that this time a portion of the reaction mixture of *n*-butyllithium with triphenylbenzylsilane was hydrolyzed instead of carbonated. The starting material was recovered in good yield from this hydrolyzed portion of the reaction mixture, indicating that the initial reaction is a metalation, and that the acid formed on carbonation is quite unstable, resulting in cleavage of a carbon-to-silicon bond, as had been postulated for the case of trimethyl-9-fluorenylsilane.



$$(C_6H_5)_3SiCH_2C_6H_5 \underset{H_2O}{\overset{n\text{-}C_4H_9Li}{\rightleftarrows}} (C_6H_5)_3\underset{\displaystyle Li}{SiCHC_6H_5} \xrightarrow{CO_2}$$

$$(C_6H_5)_3\underset{\displaystyle COOLi}{SiCHC_6H_5} \xrightarrow{H_2O} (C_6H_5)_3SiOH + C_6H_5CH_2COOLi$$

The other portion of the reaction mixture of triphenylbenzylsilane with *n*-butyllithium was carbonated, and from this carbonated mixture triphenylsilanol and phenylacetic acid were isolated as in the first trial.

Experimental

Triphenyl-(phenylethynyl)-silane and *n*-Butyllithium.—To 10.0 g. (0.0278 mole) of triphenyl-(phenylethynyl)-silane (m.p. 100–101°)[3] dissolved in 50 ml. of dry ether was added 144 ml. of an ethereal solution of 0.0875 mole of *n*-butyllithium.[4] The resulting yellow-orange solution was refluxed, with stirring, in an atmosphere of dry nitrogen for 24 hours. The reaction mixture was poured jetwise on a slurry of crushed Dry Ice in ether, and the carbonated mixture was acidified with dilute hydrochloric acid. The aqueous layer was separated and washed with ether. The combined ether extracts were extracted with aqueous sodium bicarbonate. The aqueous bicarbonate solution was acidified with hydrochloric acid, and the acidic solution was extracted with ether. The ether extract was dried, and the solvent was distilled. The partially crystalline residue was recrystallized from hot water with the aid of Norit to give 0.77 g. (19%) of phenylpropiolic acid melting at 135–136°. The identity of the acid was confirmed by a mixed melting point.

The ethereal solution remaining after the bicarbonate extraction was dried, and the solvent was distilled. The crystalline residue was recrystallized first from petroleum ether (b.p. 28–38°), then from a methanol–ethyl acetate solution, to give 5.97 g. of material melting at 83–84°. Another recrystallization from a methanol–ethyl acetate solution gave 5.12 g. (58%) of *n*-butyltriphenylsilane melting at 85–86°. The identity of the material was confirmed by a mixed melting point.

Triphenylbenzylsilane and *n*-Butyllithium.—To 15.0 g. (0.0429 mole) of triphenylbenzylsilane (m.p. 97–98°)[3] dissolved in 100 ml. of dry ether was added 194 ml. of an ethereal solution of 0.151 mole of *n*-butyllithium.[4] The solution was refluxed, with stirring, in an atmosphere of dry nitrogen for 24 hours. The reaction mixture was then divided into two equal portions of 130 ml. each.

One portion of the reaction mixture was poured jetwise on a slurry of crushed Dry Ice in ether; water was then added to the carbonated mixture. More ether was added, and the aqueous layer was separated. The aqueous solution was heated to boiling to remove dissolved ether. The alkaline solution was then extracted[5] with petroleum ether (b.p. 60–70°) in a continuous extractor for 18 hours to remove non-acidic organic impurities. The aqueous solution was acidified, and the acidic solution was extracted with petroleum ether (b.p. 60–70°) in a continuous extractor for 24 hours. Upon evaporation of the petroleum ether, together with the valeric acid which it contained, there remained 1.25 g. (43%) of phenylacetic acid melting at 71–74°. The identity of the acid was confirmed by a mixed melting point.

The ether layer of the aqueous carbonated reaction mixture was dried, and the solvent was distilled. The partially crystalline residue was recrystallized from petroleum ether (b.p. 77–115°) to give 3.8 g. of material melting at 144–152°. A second recrystallization from petroleum ether (b.p. 77–115°) gave 3.1 g. (52%) of triphenylsilanol melting at 151–153°. The identity of the material was confirmed by a mixed melting point.

The other 130-ml. portion of the reaction mixture was hydrolyzed without carbonating. The ether layer was separated and dried, and the solvent was distilled. The crystalline residue was recrystallized from a methanol–ethyl acetate solution to give 6.0 g. of triphenylbenzylsilane melting at 96–98°, representing a recovery of 80% of the silane used in the reaction. The identity of the material was confirmed by a mixed melting point.

Acknowledgment.—The authors are grateful to G. E. Dunn for assistance.

---

[3] Kindly provided by Dr. L. S. Miller.

[4] The *n*-butyllithium was prepared by the method of H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949). The normality of the *n*-butyllithium was determined by the analytical procedure of H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

[5] H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED MARCH 19, 1951

Cyclization of Aryl-Aliphatic Esters with Phosphorus Pentoxide in Phosphoric Acid

BY RICHARD C. GILMORE, JR.

The general usefulness of phosphorus pentoxide in 85% orthophosphoric acid for the cyclization of aryl-aliphatic acids in high yield without a great expenditure of time and labor has been reported.[1,2] On further investigating the usefulness of this polyphosphoric acid mixture for cyclizations, it was most surprising to find that esters could be used to give products identical to those obtained from the corresponding acids.

Methyl β-phenylpropionate was cyclized to α-hydrindone in 93% yield. β-Phenylpropionic acid produced the desired ketone in an amount comparable to that obtained when the ester was used. This is in direct opposition to the result achieved when the acid was treated with phosphorus pentoxide in which reaction 40% truxene and no α-hydrindone was isolated.[3] The amount of com-

---

[1] W. E. Bachmann and W. J. Horton, THIS JOURNAL, **69**, 58 (1947).

[2] R. C. Gilmore, Jr., and W. J. Horton, *ibid.*, **73**, 1411 (1951).

[3] F. S. Kipping, *J. Chem. Soc.*, **65**, 269 (1894).