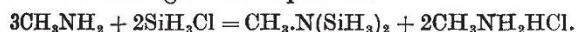observations. Thus we find that monochlorosilane reacts spontaneously and quantitatively with methyl-amine according to the equation :

$$3CH_3NH_2 + 2SiH_3Cl = CH_3.N(SiH_3)_2 + 2CH_3NH_2.HCl.$$

The product, methyldisilylamine, is a liquid, b.p. $+ 32 \cdot 3°$, which is stable in air, but is quantitatively hydrolysed by alkali : its formula has been established by analysis and by vapour density determinations. It differs from aliphatic amines in being quantitatively decomposed by hydrogen chloride :

$$CH_3N(SiH_3)_2 + 3HCl = 2SiH_3Cl + CH_3NH_2.HCl.$$
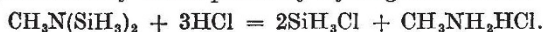
Ethyldisilylamine, prepared by identical methods, is a liquid of very similar properties, boiling at $+ 65 \cdot 9°$.

Trimethylamine and monochlorosilane have been found to combine in the cold in strictly equal volumes, giving a stable solid quaternary compound $N(CH_3)_3SiH_3Cl$. This differs from the organic quaternary compounds in being instantaneously decomposed by water to form trimethylamine hydrochloride and disiloxane, $(SiH_3)_2O$. It is also decomposed on standing in moist air. The ultimate products in this case are silicic acid and trimethylamine hydrochloride ; but the intermediate products are soluble in water, giving solutions with strong reducing properties. It is hydrolysed by alkali according to the equation :

$$N(CH_3)_3SiH_3Cl + 3NaOH = Na_2SiO_3 + NaCl + N(CH_3)_3 + 3H_2.$$
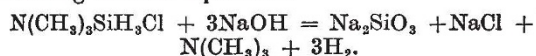
The dissociation pressure of the salt is 9 mm. at $20°$, and this increases to one atmosphere at $91°$. The dissociation, however, is not reversible, due to the disproportionation of the SiH_3Cl formed, thus :

$$N(CH_3)_3SiH_3Cl \rightleftharpoons N(CH_3)_3 + SiH_3Cl$$
$$2SiH_3Cl \rightleftharpoons SiH_4 + SiH_2Cl_2$$
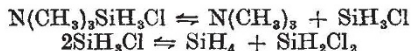
Trimethylsilylammonium chloride is a convenient silylating agent, as the trimethylamine present will fix quantitatively any hydrogen chloride formed in a reaction. Thus we have shown that it will react with alcohols to form volatile silyl alkyl ethers, which may be isolated with ease ; for example :

$$C_2H_5OH + N(SiH_3)(CH_3)_3Cl = SiH_3.O.C_2H_5 + N(CH_3)_3.HCl.$$
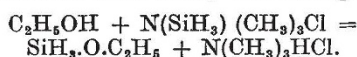
Monochlorosilane and dimethylamine react at room temperature with the production of the compound $N(SiH_3)(CH_3)_2$. This amine appears to form an unstable quaternary salt with excess of monochlorosilane. There is thus a gradual decrease in the stability of these quaternary salts, and we may formulate the following series :

I.	$N(CH_3)_4Cl$	Stable.
II.	$N(SiH_3)(CH_3)_3Cl$	Moderately stable.
III.	$N(SiH_3)_2(CH_3)_2Cl$	Unstable.
IV.	$N(SiH_3)_3(CH_3)Cl$	Not formed.
V.	$N(SiH_3)_4Cl$	Not formed.

The members IV and V, had they been formed, would have been detected in the preparation of the amines $N(SiH_3)_2(CH_3)$ and $N(SiH_3)_3$, since both of these preparations were carried out in the presence of an excess of monochlorosilane.

We are at present extending these observations, and attempting to prepare compounds of the silyl radical with other elements, such as phosphorus, arsenic and lead.

H. J. Emeléus.
Nicholas Miller.
Imperial College of Science
and Technology,
London, S.W.7.

A Degradation Reaction in Organic Chemistry

THE method described below by means of examples enables the group -CO-CO-CO- or -CO-CH$_2$-CO- to be converted into the dicarbonyl group -CO-CO-, which is virtually the degradation of a propane derivative into an ethane derivative.

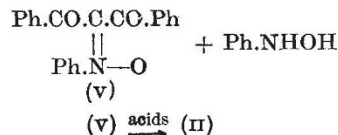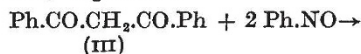For example, diphenyltriketone (I) is changed by warming with acids (for example, sulphuric acid-acetic acid) into benzil (II) :

$$Ph.CO.CO.C.OPh \xrightarrow{\text{acids}} Ph.CO.CO.Ph$$
$$\quad\quad\text{(I)} \quad\quad\quad\quad\quad\quad \text{(II)}$$
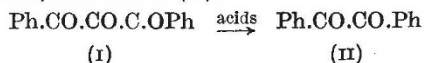
The conversion of dibenzoylmethane (III) into benzil involves first the change of the group -CO.CH$_2$.CO- into -CO-C-CO- (IV) and then warming with acids (for example, $\overset{||}{N}$

the resulting product with acids (for example, sulphuric acid-acetic acid). The nitrogen-containing intermediate compound with the group (IV) may be (V), which is readily obtained in half an hour by the action of (III) on nitrosobenzene in alcohol. Diphenyltriketone-2-anil oxide (V)[1] forms yellow crystals, m.p. $144°$.

$$Ph.CO.CH_2.CO.Ph + 2 Ph.NO \rightarrow$$
$$\text{(III)}$$

$$Ph.CO.C.CO.Ph$$
$$\quad\quad \overset{||}{Ph.N—O} \quad\quad + Ph.NHOH$$
$$\text{(V)}$$

$$\text{(V)} \xrightarrow{\text{acids}} \text{(II)}$$

Robert Michaelis and Cezar Azzam participated in this investigation.

A. Schönberg.
Faculty of Science,
Egyptian University,
Abbassia,
Cairo.

[1] Compare Schönberg, A., and Michaelis., R., J. Chem. Soc., 627 (1937).

Kinetics of Exchange Reactions

THE shape of the curve obtained by plotting the concentration of a reactant or product against the time can in general be used to yield information about the way the rate of the reaction depends on concentration, in particular about its order. In the case of isotopic exchange reactions this is not possible even in principle, supposing the isotopes to have identical chemical properties. This rather amusing result does not appear to have been placed on record hitherto.

Suppose the reaction is

$$AX^* + BX = AX + BX^*,$$

where X^* represents a labelled (for example, radioactive) X atom. Let the concentrations be : AX, a ; BX, b ; AX^*, x ; and BX^*, y ; if the compounds contain several similarly situated X atoms, these concentrations must be expressed in equivalents of X. We will assume that $a \gg x$ and $b \gg y$. Let the exchange proceed at a rate

$$R = k.f(a).\varphi(b),$$

where f and φ are any functions, and k is a constant. Then

$$\frac{dx}{dt} = - \frac{dy}{dt} = - \frac{x}{a} R + \frac{y}{b} R,$$

where t is the time. If $x = 0$ when $t = 0$, and $x = x\infty$