LXIII.—*Dimethoxydiphenylmethane and some of its Homologues.*

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TWENTY-FOUR years ago, Kekulé and Franchimont published a paper "On Benzophenone Chloride and the Formation of Anthraquinone in the Preparation of Benzophenone," in which they state that "we have, among other things, tried the action of sodium ethoxide, silver acetate, and silver benzoate on benzophenone chloride, but have not yet arrived at any definite results" (*Ber.*, 1872, 5, 909). On repeating this experiment, the following reaction was found to take place.

and by replacing the sodium ethoxide by the sodium compounds of other alcohols, the corresponding derivatives were obtained.

Of similar compounds having two alkyloxy-groups attached to one carbon atom, there seem to be at present known only acetal and its homologues, a benzaldehyde derivative, diethoxyphenylmethane, and acetone derivatives, such as diethoxydimethylmethane. The latter substances have recently been obtained by Claisen by the action of ethylic orthoformate on the corresponding aldehyde or ketone, thus:

The latter reaction, however, does not seem to succeed in the case of all ketones, notably in that of benzophenone (*Ber.*, 1896, **29**, 1008).

I was led to the above reaction by the negative results obtained in the course of an investigation, the object of which was the synthesis of ethylic β -phenyl- α -carboxycinnamate. In my first experiment, benzophenone and ethylic malonate, in molecular proportion, were brought together in presence of a dehydrating agent, in the hope that they might react according to the equation

But in no case did they do so, at least, to any appreciable extent. When glacial acetic acid or acetic anhydride was used as the dehydrating agent, only a very slight change was apparent, and almost all the benzophenone and ethylic malonate was recovered. On zinc chloride or aluminium chloride being added along with either of the above, a certain amount of a dark brown, sticky substance was formed, which could not, however, be made to crystallise, as it always separated from solvents in a gummy form. Here, also, most of the benzophenone and ethylic malonate were unchanged, although the experiments were made under different conditions and at various temperatures.

As these methods did not afford the wished-for result, it occurred to me that it might be attained in accordance with the following equation.

Accordingly benzophenone chloride was added to a mixture of ethylic disodiummalonate and ethylic alcohol, and in this way a beautiful crystalline compound was obtained, which proved to be, however, not ethylic β -phenyl- α -carboxycinnamate, but diethoxydi-

phenylmethane. The ethylic disodiummalonate had apparently given up its sodium to the alcohol, and the sodium ethoxide reacted on the benzophenone chloride according to the first equation (p. 985).

As yet my experiments have been mainly confined to the derivatives of benzophenone, but I hope, shortly, to be able to say something as to the derivatives obtainable from other ketones and aldehydes.

Dimethoxydiphenylmethane, $(C_6H_5)_2C(OCH_3)_2$.

The benzophenone chloride required for the synthesis of this substance was prepared according to the directions of Kekulé and Franchimont, molecular proportions of benzophenone and phosphorus pentachloride being heated to a temperature of 140—150° for two hours, and the product distilled under reduced pressure. In this way, 35 grams of a colourless oil, distilling at 204°—206° under 50 mm. pressure, were obtained from 27 grams of benzophenone. On redistilling this oil, the temperature remained steadily at 201—202° under 35 mm. pressure. The fraction 201—202° weighed 33 grams, a yield corresponding to more than 90 per cent. of the theoretical. Benzophenone chloride thus prepared is a colourless oil, showing a bluish fluorescence and having only a very faint odour.

For the preparation of dimethoxydiphenylmethane, 4.6 grams of sodium were dissolved in 44 grams of absolute methylic alcohol, and 23.7 grams of benzophenone chloride were then added to the cold solution, the mixture being shaken well. After remaining in the cold for two hours, a vigorous action took place, which had to be moderated by cooling; a white powder separated from the solution, and when cold the whole became nearly solid. After adding 50 grams of methylic alcohol, and boiling for three hours, the solution showed a neutral reaction. On cooling, beautiful prismatic crystals, apparently rhombic, separated from the solution, some exceeding an inch in length. To separate the new substance from the sodium chloride, the mixture was again heated and filtered through a hot filter, the solid residue being repeatedly extracted with methylic alcohol until no more dissolved. After concentration, the alcoholic solution afforded an abundant crop of crystals, and by concentrating the mother liquor more crystals were obtained, a repetition of the process yielding almost all the substance in the form of colourless crystals. After drying between filter paper, the crystals melted at 106—107°. In this way, 18.5 grams were obtained, corresponding to 81 per cent. of the calculated quantity. The analysis of the substance gave the following results.

	Theory for $C_{17}H_{20}O_2$.	Found.	
		I.	II.
C.....	78.95	78.58	78.45 per cent.
H.....	7.01	7.08	7.01 „

The number 214.5 was obtained by the cryoscopic method, using benzene as the solvent, the calculated molecular weight being 228.

Under ordinary pressure, the substance distilled without decomposition at $288-290^\circ$, the distillate crystallising at once and melting sharply at $106.5-107^\circ$. From an ethereal solution, brilliant crystals were obtained, for the crystallographic examination of which, I am indebted to Dr. Hugh Marshall, of Edinburgh University.

Dimethoxydiphenylmethane.

Crystallised from methylic alcohol.

System and Class :—Rhombic bipyramidal.

$$a : b : c = 0.4662 : 1 : 2.6210.$$

Forms observed :— $c\{001\}$, $q\{011\}$, $o\{111\}$.

On some large crystals from ether, faces of a fourth form, $o'\{113\}$, truncating the edge $c : o$, were also observed.

FIG. 1.

Table of Angles.

Angle.	<i>n</i> .	Measured.	Mean.	Calculated.
111 : 011	14	63° 27'—63° 31'	63° 29'	—
001 : 011	12	69 2 —69 12	69 7*	—
111 : 001	7	80 50 —80 55	80 53	80° 50½'
111 : 111	3	49 17 —49 20	49 18½	49 18½
111 : 011	9	70 32 —70 37	70 34	70 33
001 : 113	1	—	64 5	64 11½

The faces are bright and give good reflections, but become dull on exposure to air. The habit is generally tabular on the basal pinacoid, or somewhat prismatic along the *a*-axis.

The crystals are brittle, and show no well-marked cleavage.

The optical axes lie in the plane (100). On examining through *c* in sodium light, the axes themselves cannot be observed owing to the large axial angle. A determination of the latter in bromonaphthalene

gave $87^{\circ} 15'$, so that c is probably the obtuse bisectrix. Double refraction is strong.

The crystals from the ethereal solution were comparatively stable in air, but in an exsiccator over sulphuric acid they steadily lost weight until benzophenone was formed. In a comparative experiment, A was in an exsiccator with sulphuric acid, while B was in an exsiccator not containing sulphuric acid or any dehydrating agent.

	A.	B.
Weight of powdered crystals . . .	0.4401 gram.	0.2763 gram.
Decrease in weight after 6 days..	0.0212 "	0.0007 "
" " 12 " "	0.0503 "	0.0016 "
" " 18 " "	0.0713 "	0.0025 "
" " 25 " "	0.0920 "	0.0043 "

In A, a slight vacuum formed each day, and after six days the powder had deliquesced all over. In B, no change was observable. After 25 days, the daily loss of weight in A scarcely exceeded half a milligram, and in three days after, the weight became constant. Thus, A was found to suffer a decrease of 0.0920 gram, or 20.90 per cent., whilst B only lost 0.0043 gram, or 1.5 per cent. in weight. The decrease in the case of A corresponded closely with that calculated for the change from $(C_6H_5)_2C(OCH_3)_2$ to $(C_6H_5)_2CO$, namely, 20.18 per cent. On the addition of a minute particle of benzophenone crystal to A, the oil at once crystallised in a fan-like form. The crystals melted at $48-48.5^{\circ}$, and on analysis gave the following figures.

	Theory for $C_{13}H_{10}O$.	Found.
C.	85.71	85.46 per cent.
H.	5.49	5.56 "

Evidently, the substance in presence of sulphuric acid lost methylic ether, and became benzophenone. To find out whether this separation occurs in the absence of absorbing agents, a small quantity of the substance was placed in a thick walled tube of about 35 c.c. capacity, one end of which was drawn out and exhausted to a pressure of 40 mm., and then sealed up; after standing a couple of days, the substance showed no apparent change. The tube was then connected by rubber tubing to a glass tube filled with mercury; on the point of the drawn-out tube being broken within the rubber tube, the mercury rushed up and nearly filled it. That the volume of gas left was air, and not ether vapour, was shown by subjecting it to pressure and cold, when it behaved as a permanent gas.

The crystals of dimethoxydiphenylmethane were quite insoluble in water, but very easily soluble in ether, hot methylic and ethylic

alcohols, much less so in cold. They were not affected by boiling water and were volatile with steam. In one experiment, 2 grams of the substance were distilled with steam, and from the distillate 1.9 gram was recovered, corresponding to 95 per cent. of the original quantity. A trace of gummy substance remained in the distilling flask. The substance was not affected by aqueous or alcoholic solutions of caustic alkalis; acids, on the other hand, completely decomposed it. In some molecular weight determinations by the cryoscopic method, acetic acid was used as the solvent, and results were obtained which pointed to dissociation. In the case of diethoxydiphenylmethane (see below), this was confirmed by the recovery of benzophenone from the acetic acid solution.

Diethoxydiphenylmethane, (C₆H₅)₂C(OC₂H₅)₂.

As previously stated, this was first prepared by the action of benzophenone chloride on ethylic disodiummalonate mixed with ethylic alcohol, the quantities taken being those required by the equation already given (p. 985). After the action was finished, the alcohol was distilled off and the residue poured into water. The oil, which separated from the water, was dried and then fractionally distilled under reduced pressure. When placed in a freezing mixture, the fractions which came over between 180° and 220° under a pressure of 40 mm. crystallised, and, by recrystallisation from hot ethylic alcohol, brilliant crystals were obtained, which agreed in all their properties with those prepared in the manner described below, and, on analysis, afforded the following figures.

	Theory for C ₁₇ H ₂₀ O ₂ .	Found.
C.....	79.69	79.16 per cent.
H.....	7.81	7.79 „

In preparing diethoxydiphenylmethane from benzophenone chloride and sodium ethoxide, the process used was exactly similar to that described under dimethoxydiphenylmethane, the quantities taken being 4.6 grams of sodium, 72 grams of ethylic alcohol, and 23.9 grams of benzophenone chloride. After two hours' heating in a water bath, the solution, which was neutral, was filtered through a hot filter and the residue extracted several times with hot ethylic alcohol. On adding hot water to the hot alcoholic solution, from which the excess of alcohol had been distilled, until the turbidity at first produced just disappeared, almost all the substance separated on cooling in long prismatic crystals. In this way, 22.5 grams were obtained, or 88 per cent. of the theoretical yield. On analysis, the following results were obtained.

	Theory for $C_{17}H_{20}O_2$.	Found.
C.....	79.69	79.40 per cent.
H.....	7.81	7.87 „

The molecular weight, as determined by the cryoscopic method, using benzene as the solvent, was found to be 236.2 instead of 256.

The crystals melted at 51.5–52°, forming a colourless oil, which distilled unaltered at 294–295°. The colourless distillate crystallised on the introduction of a fragment of crystal, the crystals again melting at 52°. They were comparatively stable in air, but in an exsiccator over sulphuric acid they behaved like the dimethoxy-compound. 0.2555 gram lost 0.0732 gram in weight after 16 days in an exsiccator over sulphuric acid, thereafter remaining constant. This corresponds to a decrease of 29.65 per cent., the calculated decrease for $(C_6H_5)_2C(OC_2H_5)_2$ when it loses $(C_2H_5)_2O$ being 29.81 per cent. The analysis of the residue gave numbers which agree well with those required for benzophenone.

	Theory for $C_{13}H_{10}O$.	Found.
C.....	85.71	85.35 per cent.
H.....	5.49	5.62 „

Diethoxydiphenylmethane is quite insoluble in water, but is very easily soluble in ether, light petroleum, hot methylic and ethylic alcohols, less so in cold. It is volatile with steam. It is not affected by boiling aqueous or alcoholic solutions of caustic alkalis, but it is decomposed by acids. Thus, by the action of acetic acid, benzophenone was formed, the melting point (48–49°) and the numbers obtained on analysis agreeing well with those required by that compound. Acetic anhydride also split it up, the same product being produced.

On recrystallisation from hot absolute ethylic alcohol, very perfect crystals were obtained. I have also to express my thanks to Dr. Hugh Marshall, of Edinburgh University, for the following crystallographic examination.

Diethoxydiphenylmethane.

Crystallised from ethylic alcohol.

System and Class :—Monoclinic prismatic.

$$a : b : c = 1.5016 : 1 : 1.2740.$$

$$\beta = 106^\circ 26\frac{1}{2}'.$$

Forms observed :— $a\{100\}$, $c\{001\}$, $r\{10\bar{1}\}$, $p\{110\}$, $w\{11\bar{1}\}$. A few crystals also showed minute faces of the form $o\{111\}$ (determined by zones).

FIG. 2.

Table of Angles.

Angle.	<i>n</i> .	Measured.	Mean.	Calculated.
100 : 110	15	55° 7' — 55° 25'	55° 13½'*	—
100 : 001	8	73 24 — 73 36	73 33½*	—
111 : 110	12	36 24 — 36 49	36 39*	—
001 : 101	5	46 36 — 47 5	46 49	46° 57½'
001 : 110	11	80 26 — 80 54	80 40	80 42½
100 : 111	7	109 50 — 110 3	109 56	110 0
110 : 111	6	65 33 — 65 44	65 36	65 40
101 : 111	8	47 32 — 47 45	47 42	47 40
101 : 110	—	—	—	73 10

The crystals are often tabular on the basal pinacoid, or prismatic along the axis of symmetry. The best reflections are given by the faces of the forms *p* and *w*. The faces soon become dull if left exposed to air.

There is no well-marked cleavage.

When examined through the basal pinacoid in convergent polarised sodium light, one bisectrix is seen to be almost normal to that form. The axes themselves lie in the plane (010), but are not observable.

Attempts to prepare diisopropoxydiphenylmethane,

have not yet been successful. When benzophenone chloride was treated with sodium propoxide under conditions similar to those employed in the previous cases, benzophenone was the chief product, 85 per cent. of the benzophenone chloride being converted into it. Further experiments to obtain this compound are in progress.

Dibenzoxydiphenylmethane, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OC}_6\text{H}_5)_2$.

The method of preparing this substance differed slightly from the above-mentioned. 2.3 grams of sodium were dissolved in 53 grams of benzylic alcohol, and to the cold solution, which resembled glycerin in consistency, 12.8 grams of benzophenone chloride were added. After being heated for nine hours in a water bath, the mixture had become a solid jelly, but still gave a strongly alkaline reaction with litmus; to complete the change, the mixture was heated in an oil

bath at 205—210° for five hours, but even at the end of that time the reaction was still faintly alkaline. On adding ether to the white, jelly-like product, a white, powdery solid separated. The ethereal solution, which was neutral, was filtered off, and the residue extracted with ether several times; on distilling off the ether, a yellow oil remained, which, on standing, yielded a crop of fine, prismatic, needle-like crystals. The oil was separated from the crystals by filtration with a filter pump, and the crystals dried between filter paper. On fractional distillation, the oil was found to be benzylic alcohol, distilling under a pressure of 60 mm. at 142°. The crystals were recrystallised from methylic alcohol, in which they are only sparingly soluble when cold, but more readily when hot. They melted between 104° and 105°. In this manner, a yield corresponding to more than 60 per cent. of the theoretical was obtained, although it may probably be increased by modifying the conditions of the experiment.

An analysis gave the following results.

	Calculated for $C_{27}H_{24}O_2$.	Found.
C.....	85.26	84.83 per cent.
H.....	6.32	6.36 „

This substance was easily soluble in hot ethylic alcohol and light petroleum, but much less so in cold. On exposure to the air, the crystals lost their brilliancy and deliquesced. When distilled under the ordinary pressure, decomposition appeared to take place, the temperature rising steadily from 260° to above 360°, and the distillate forming a colourless, fragrant smelling liquid, which crystallised only very partially, even after the introduction of a crystal of the original substance. Under a pressure of 40 mm., it distilled without decomposition at about 305°, the distillate being colourless and solidifying at once to crystals, melting at 103—105°.

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