CC.—*Investigations on the Bivalency of Carbon. Part II. The Displacement of Chlorine from Desyl Chloride. Benzoin Diethylacetal.*

By Allan Miles Ward.

The mechanism of the displacement of chlorine from diphenylchloromethane was considered in Part I (Ward, J., 1927, 2285), where it was shown that the results were in accordance with the conception of Nef that the halogen displacement proceeds through a phase $Ph_2C<$, involving bivalent carbon. The evidence was based on the observations that sodium hydroxide or ethoxide was without effect on the order of the reactions in alcoholic and aqueous-alcoholic solutions, the reactions in all cases being unimolecular. Further, *s*-tetraphenyldimethyl ether was readily formed from benzhydrol and also from diphenylchloromethane, and this may be easily accounted for on Nef's hypothesis. It was not claimed that the experiments provided a crucial test for Nef's views, and a possible alternative mechanism * was considered.

The above method, which was also used for α-chloroethylbenzene in connexion with the problem of the Walden inversion (Ward, J.,

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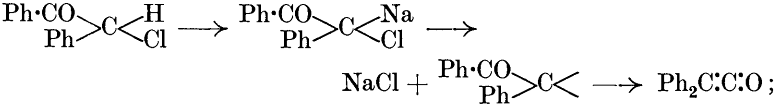
* In the British Chemical Abstracts (1927, **A**, 1061) this alternative was wrongly included as Nef's hypothesis.

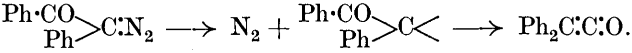
1927, 445) would serve to show if a number of reactions which have been assumed to proceed through a phase $R_1R_2C<$, do in fact all conform to the same reaction mechanism. With this end in view desyl chloride has been studied.

Schroeter (*Ber.*, 1909, **42**, 2336, 3356) sought to correlate the Hofmann–Curtius, Beckmann, and benzilic acid transformations on the basis that they proceed through a phase involving univalent nitrogen or bivalent carbon. He found that hydrogen is evolved when sodium is added to a benzene solution of desyl chloride, and that if the products be heated, sodium benzilate is formed; he assumed the mechanism of the reaction to be



$$\begin{matrix}Ph\cdot CO\\ Ph\end{matrix}\!>\!C\!<\!\begin{matrix}H\\ Cl\end{matrix} \longrightarrow \begin{matrix}Ph\cdot CO\\ Ph\end{matrix}\!>\!C\!<\!\begin{matrix}Na\\ Cl\end{matrix} \longrightarrow NaCl + \begin{matrix}Ph\cdot CO\\ Ph\end{matrix}\!>\!C\!< \longrightarrow Ph_2C{:}C{:}O;$$

diphenylketen was then assumed to combine with hydrogen peroxide (as its sodium salt) to give sodium benzilate. More recently, Nicolet and Pelc (*J. Amer. Chem. Soc.*, 1921, **43**, 935) have shown that hydrogen peroxide and diphenylketen, both alone and also in the presence of alkalis, do not react appreciably. Their results would not preclude diphenylketen as an intermediate phase, but the mechanism of the oxidation as suggested by Schroeter would appear highly improbable. Schroeter's main support for his view that desyl chloride reacts *via* benzoylphenylmethylene rests on his observation that azibenzil on being heated in benzene solution gives diphenylketen in good yield :



$$\begin{matrix}Ph\cdot CO\\ Ph\end{matrix}\!>\!C{:}N_2 \longrightarrow N_2 + \begin{matrix}Ph\cdot CO\\ Ph\end{matrix}\!>\!C\!< \longrightarrow Ph_2C{:}C{:}O.$$

In view of the results now to be described, it is superfluous at this stage to discuss these rearrangements in the light of more recent work.

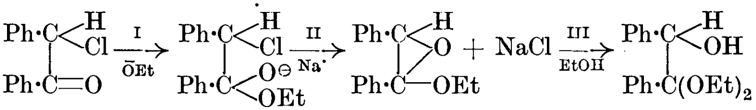
Experiments on the displacement of chlorine from desyl chloride in alcoholic and in 10% aqueous alcoholic solutions in the presence and in the absence of sodium hydroxide or of sodium ethoxide at 15·0° and at 25·0° are described in the present paper, but the mechanism of the chlorine elimination is quite different from that observed for diphenylchloromethane (*loc. cit.*). Thus, in alcoholic or in aqueous-alcoholic solution at 25·0°, desyl chloride is stable, but the addition of sodium hydroxide or ethoxide to the solution brings about a very rapid displacement of chlorine, the reaction being complete for $N/10$-alkali in less than an hour. The velocity coefficients (k) calculated on the basis of a bimolecular reaction are in good agreement when the concentrations of the reactants are approximately $M/10$, but for $N/5$-sodium hydroxide or ethoxide they are less regular and often show a considerable drift (see p. 1548). These variations may be due to side reactions or to inaccuracy in measurement owing to the rapidity of the reaction. The magnitude of k also diminishes with increasing concentrations of alkali. A more detailed examination of the kinetic measurements is projected but is beyond the scope of the present work, which was undertaken to establish the identity or otherwise of Schroeter's mechanism with those of the reactions previously studied by the author.

The difference in the mechanism of the reaction in this case from those previously studied (as shown by the kinetic results), finds further support on the basis of the products obtained from desyl chloride in alcoholic and aqueous-alcoholic solution with sodium hydroxide and sodium ethoxide. When the final reaction mixture was added to dilute hydrochloric acid the product was benzoin. No evidence was obtained for the formation of benzoin ethyl ether (Fischer, *Ber.*, 1893, **26**, 2415; Irvine and McNicholl, J., 1908, **93**, 1604), which, moreover, was found not to be decomposed by dilute hydrochloric acid at room temperature.

The formation of benzoin only would appear to indicate that the chlorine of desyl chloride was displaced entirely by the hydroxyl group in ethyl-alcoholic solution (lime-dried) by the agency of sodium ethoxide. Intermediate compounds were therefore sought, and *benzoin diethylacetal* was isolated from the material obtained by evaporating the solvent from the solution remaining after the reaction of desyl chloride with sodium ethoxide in alcoholic solution, and also with sodium hydroxide in alcoholic and in aqueous-alcoholic solutions. Further, this compound was found to be decomposed rapidly to benzoin in the presence of dilute hydrochloric acid.

A number of experiments were carried out in an attempt to identify all the products of reaction and to separate them quantitatively. The acetal and benzoin were isolated in all cases, but their quantitative separation was not accomplished (small amounts of higher-melting products were occasionally formed, presumably during the attempted separations). Since weighed amounts of the products, when treated with aqueous hydrochloric acid, yielded benzoin quantitatively, the proportions of the acetal and benzoin were deduced from a Zeisel determination of the ethoxyl group in the product. The determinations given in the experimental portion of the paper correspond with the production of 78% of the acetal at 15° in ethyl-alcoholic sodium ethoxide solution, of 74% in ethyl-alcoholic sodium hydroxide solution, and of 54% in 10% aqueous ethyl-alcoholic sodium hydroxide solution.

It is suggested that the mechanism of the formation of the acetal is as follows,



the primary reaction consisting of an addition at the carbonyl group. Such addition is feasible in view of the results of a number of workers, *e.g.*, Lachman (*J. Amer. Chem. Soc.*, 1923, **45**, 1513, 1534) found that both benzil and benzoin form equimolecular additive compounds with sodium ethoxide. The kinetic results would find a general explanation if it is assumed that stage I is slow compared with stage II. No explanation of the dependence of the magnitude of the velocity coefficients on the concentrations of the reactants would, of course, be obtained on this scheme.

EXPERIMENTAL.

The Preparation of Desyl Chloride.—The preparation was first carried out essentially as indicated by Schroeter (*Ber.*, 1909, **42**, 2348) and adopted by McKenzie and Wren (J., 1910, **97**, 481), with *l*-benzoin. The yields of pure desyl chloride obtained were poor, and considerable amounts of benzil were formed. Various modifications were tried, and the preparation was finally accomplished satisfactorily by applying the method of Darzens (*Compt. rend.*, 1911, **152**, 1314). Benzoin (20 g.), and pyridine (10 g.) were heated together until a homogeneous solution was obtained. The melt was rapidly cooled, and the solid was roughly powdered and treated with thionyl chloride (15 g.), added slowly with vigorous stirring and water cooling. Considerable heat evolution accompanied each addition, and the material became pasty. The product soon set to a hard light brown solid, and after about an hour, water was added, the product filtered off, twice finely triturated with water, and then dried over sulphuric acid; yield, 21 g. The whole of this was refluxed (charcoal) for 20 minutes with about 500 c.c. of light petroleum (b. p. 40—60°), and filtered from a considerable amount of solid. Clusters of short colourless needles soon began to separate from the yellow solution; after about ½ hour the crop was filtered off, washed with light petroleum, and air-dried; yield, 7·5 g. The mother-liquors were used for a second extraction of the undissolved solid, yielding 5·0 g. of colourless crystals. A third extraction gave 3·5 g. of colourless needles, and only a few crystals separated after a fourth extraction. The combined crops (16 g.) melted at 67—67·5°. The solvent was distilled off on a water-bath from the mother-liquors, until the volume of solution remaining was about

75 c.c.; on cooling, a crop of crystals (1·85 g.) was deposited; and when recrystallised from light petroleum, had m. p. 67° (yield 1·6 g.). The yellow liquors, when allowed to evaporate spontaneously, left a brownish pasty solid (0·5 g.) and some long yellowish-green needles. About a dozen of these were picked out, and had m. p. 92—93°; mixed m. p. with benzil 93—94°. Benzil is, therefore, formed in this reaction in small amount. (The specimen of benzoin used was free from benzil.)

Desyl chloride crystallises from light petroleum (b. p. 40—60°) in clusters of fine colourless needles, m. p. 67° (very slow heating) [Found : Cl (Stepanow's method), 15·4. Calc. : 15·4%]; it decomposes and becomes brown when exposed to sunlight.

Kinetic Experiments.

Experiments failed to detect any reaction of desyl chloride in alcoholic or in aqueous-alcoholic solution during 5 days at 25°, but the presence of sodium hydroxide or ethoxide caused the displacement of the halogen to take place very rapidly. For instance, desyl chloride (1·5205 g.) was dissolved in 90 c.c. of ethyl alcohol at 25·0° and 10 c.c. of aqueous 1·22*N*-sodium hydroxide were added; 10 c.c. of the solution, when withdrawn at times *t* and titrated at once against alcoholic benzoic acid (0·946*N*/10) with phenolphthalein as indicator, gave the following results :

t (mins.)	3	8	13	18	28	48	108	1140	3960
Titre (c.c.)	8·20	6·30	5·69	5·50	5·38	5·13	4·61	2·25	2·00

The theoretical initial titre is 12·90 c.c., and the theoretical final titre, corresponding to the formation of 1 mol. of hydrogen chloride per mol. of desyl chloride, is 5·91 c.c. The above figures therefore indicate that a rapid reaction takes place corresponding to the halogen displacement, followed and possibly accompanied by a much slower reaction. Further experiments with desyl chloride in ethyl-alcoholic solution with sodium hydroxide or ethoxide gave similar results, but the extent of the assumed slow reaction was variable.

It appeared probable that the slow reaction depends upon the presence of oxygen, for vigorous shaking of the solution in contact with air caused a much more rapid change in titre than in the absence of shaking. Benzoin may possibly be formed as a result of the displacement of the chlorine from desyl chloride, and it is known that, in alcoholic sodium hydroxide solution in contact with air, this undergoes transformation to benzilic acid (see Klinger, *Ber.*, 1886, **19**, 1868; Knoevenagel and Arndts, *ibid.*, 1902, **35**, 1982; Lachman, *J. Amer. Chem. Soc.*, 1923, **45**, 1529), and this would account for the slow disappearance of alkali.

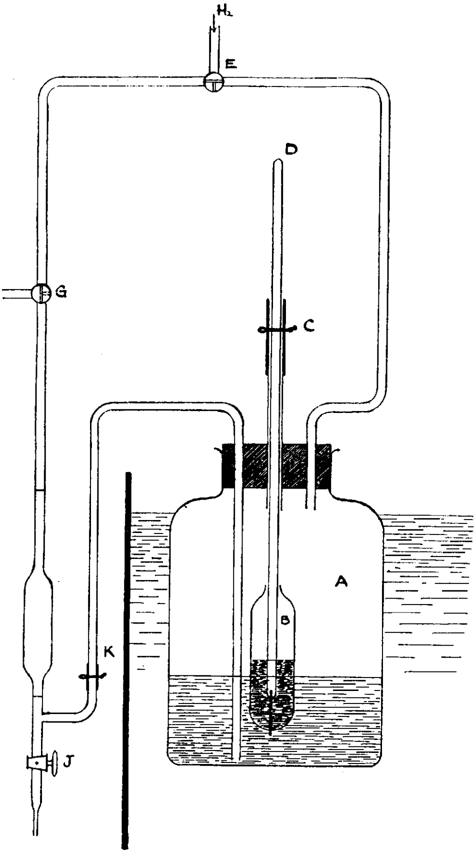
The following observations on benzoin illustrate this point :

Ethyl alcohol (about 70 c.c.) was added to benzoin (2·088 g.), followed by 20 c.c. of aqueous sodium hydroxide, and the total volume was made up to 100 c.c. with ethyl alcohol, the temperature being 25·0°. The solution became cherry-red and some solid remained undissolved. Samples (10 c.c.) withdrawn at the times shown gave the following titres against alcoholic benzoic acid (0·946*N*/10) with phenolphthalein as indicator.

Time (hrs.)	0·1	0·58	6·55	18	42·5	114
Titre (c.c.)	24·40	23·59	21·90	21·41	14·25	10·44

The reaction mixture was shaken from time to time; the abnormally small change in titre between $t = 6·55$ and $t = 18$ corresponds to the solution being kept over-night without shaking. At the time of the final titre, all solid had dissolved, forming a yellow solution.

FIG. 1.



The progressive change in titre beyond an amount corresponding to the formation of 1 mol. of hydrogen chloride per mol. of desyl chloride was avoided by carrying out all experiments in an atmosphere of hydrogen, as follows : A measured volume of ethyl alcohol was added to a known weight of desyl chloride in A (Fig. 1). The mixture was well shaken, and the desyl chloride dissolved completely to a colourless solution. (All ethyl alcohol used was dried by refluxing and distilling ordinary absolute alcohol over quick-lime.) Measured volumes of standardised sodium hydroxide or ethoxide solutions (10 c.c., or 20 c.c. in some experiments) were contained in B. The relative volumes in A and B were so adjusted that the total volume of solution was 100 c.c. B consisted of a boiling tube, modified as shown, of about 25 c.c. capacity. A short length of platinum wire was sealed through the bottom of B, and fused into a glass rod D. B was then held in position as indicated by means of the pinch-clip and rubber tubing at C. The reaction vessel was immersed in the thermostat and the apparatus well swept out with dry hydrogen, which had first passed through a flask immersed in the thermostat and containing solvent of the same composition as in A (after mixing). The clip C was then released, the glass rod pushed through the bottom of B, the apparatus well shaken, and the rod withdrawn, C being at once closed. Zero time was taken by means of a stop-watch, started immediately after breaking B. Samples (10 c.c.) were transferred to the pipette by suitable adjustment of taps E, G, J, K, and C, and added to 25 c.c. of standard hydrochloric acid ($N/10$ approx.) at times t. The reaction was thus at once stopped, and titrations of excess acid in the solution were made against standard sodium hydroxide with phenolphthalein as indicator.

Below are given two typical results at 25° showing the rapidity of the displacement in the presence of sodium hydroxide or sodium ethoxide, together with the method of calculation. The concentrations of desyl chloride and of sodium hydroxide and ethoxide are expressed in g.-mols./l.; and the amount of water added (if any) is given as % by vol.

(1) Desyl chloride, 0·0828 mol./l.; sodium hydroxide, 0·1193 mol./l.; 10 c.c. of reaction mixture added to 25 c.c. of $0{\cdot}988N/10$-HCl and titrated by $0{\cdot}999N/10$-NaOH. The values at $t = 0$ are calculated from the amounts of sodium hydroxide (b) and desyl chloride (a) used. The amount of sodium hydroxide at time t (*i.e.*, $b - x$) is given by $25 \times 0{\cdot}988 - 0{\cdot}999 \times$ (titre at time t). The amount of desyl chloride present at time t (*i.e.*, $a - x$) is calculated on the assumption that desyl chloride and sodium hydroxide react molecule for molecule. On this basis the theoretical final titration is 21·07 c.c. The velocity coefficients are calculated for a bimolecular reaction, $k = 2{\cdot}3/t(a - b).\ \log_{10}b(a - x)/a(b - x)$, where t is expressed in minutes, and a, b, and x are measured in c.c. of $N/10$ strength per 10 c.c. of solution. The values of k in all experiments are thus calculated.

t.	Titre.	x.	$k \times 10^4$.	t.	Titre.	x.	$k \times 10^4$.
0	12·78	—	—	8	19·80	7·01	338
1·25	15·93	3·14	375	11	20·33	7·54	352
2	16·90	4·11	361	14	20·52	7·73	326
3·75	18·21	5·42	334	60	21·03	8·24	—
5	18·91	6·12	342	360	21·18	—	—
						Mean	347

(2) Desyl chloride, 0·0860 mol./l.; sodium ethoxide, 0·1205 mol./l.; 10 c.c. of reaction mixture added to 25 c.c. of 0·994*N*/10-HCl and titrated by 1·040*N*/10-NaOH.

t.	Titre.	*x*.	$k \times 10^4$.	*t*.	Titre.	*x*.	$k \times 10^4$.
0	12·31	—	—	7	18·72	6·67	285
0·75	14·29	2·06	(334)	10	19·37	7·35	286
1·5	15·32	3·13	293	13	19·85	7·84	306
2·5	16·54	4·40	304	317	20·51	—	—
4	17·49	5·39	284	∞ (calc.)	20·58	—	—
						Mean	293

The complete results obtained at 25·0° are summarised in the following table.

Desyl chloride.	Water, %.	NaOH.	NaOEt.	$k \times 10^4$ (limits).	$k \times 10^4$ (mean).
0·0713	10	0·1079	—	400—419	409
0·1259	10	0·1079	—	389—479	430
0·0839	10	0·1016	—	429—473	455
0·0795	10	0·1016	—	428—476	449
0·0780	10	0·1016	—	413—480	445
0·0828	—	0·1193	—	326—375	347
0·1039	—	0·0869	—	317—383	354
0·0802	—	—	0·1168	279—305	292
0·0860	—	—	0·1205	284—306	293
0·0739	—	—	0·2104	240—262	237
0·0854	—	0·2288	—	140—188	168

The last two sets of values in the above table were the only observations made at 25·0° for sodium hydroxide or ethoxide of concentration approximately *N*/5; more extended experiments were made at 15·0°, and a typical set of results at this temperature is set out to exhibit the greater variation amongst the individual values of the velocity coefficients in a given set of measurements, and the considerable drift often shown, together with the wider deviation of the final observed from the final calculated titration, as compared with experiments for *N*/10-solutions :

Desyl chloride, 0·0845 mol./l.; sodium hydroxide, 0·2086 mol./l.; water, 10%; 10 c.c. of reaction mixture added to 25c.c. of 0·998*N*/10-HCl and titrated by 1·040*N*/10-NaOH.

t.	Titre.	$k \times 10^4$.	*t*.	Titre.	$k \times 10^4$.
0	3·76	—	11	10·54	119
1·3	6·06	138	15	10·97	115
3	7·82	134	20	11·10	97
5	8·93	126	384	11·88	—
8	10·07	127	∞ (calc.)	11·53	—

The solution became yellow as soon as the alcoholic solutions of desyl chloride and of sodium hydroxide were mixed. The colour changed to cherry-red, which was quite definite at about 8 minutes after mixing and persisted during the remainder of the experiment. The colour change from yellow to cherry-red, which was not observed in any experiments with *N*/10-alkali, took place in all experiments in which *N*/5-alkali was used.

The complete results at 15·0° are as follows :

Desyl chloride.	Water, %.	NaOH.	NaOEt.	$k \times 10^4$ (limits).	$k \times 10^4$ (mean).
0·0827	10	0·1027	—	177—204	189
0·0832	10	0·1025	—	182—195	189
0·0845	10	0·2086	—	97—138	122
0·0805	—	0·0897	—	138—168	152
0·0818	—	0·1159	—	122—148	136
0·0873	—	0·1738	—	113—122	117
0·0791	—	0·1794	—	118—144	124
0·0852	—	0·2318	—	66— 95	84
0·0814	—	—	0·1011	152—201	159
0·0852	—	—	0·1223	136—157	140
0·0815	—	—	0·1787	101—118	108
0·0896	—	—	0·2092	102—111	103
0·0831	—	—	0·2100	79— 94	87

Products formed from Desyl Chloride.

(*a*) Desyl chloride (2 g.) was dissolved in 100 c.c. of ethyl alcohol (lime-dried ethyl alcohol was used in all experiments) and maintained at 25·0° for 3 days. The solution was poured into 100 c.c. of *N*/10-hydrochloric acid. The product was filtered off (1·85 g. after washing and drying) and identified as unchanged desyl chloride, m. p. 66—67°, mixed m. p. 66—67°.

(*b*) The same result was obtained when the absolute alcohol was replaced by 90% alcohol.

(*c*) Desyl chloride (2 g.) was added to 100 c.c. of ethyl-alcoholic sodium ethoxide solution (0·2254*N*) at 25·0°, hydrogen having been bubbled through the solution to displace air, and the flask was then stoppered. This procedure was followed in experiments (*d*), (*e*), (*g*), (*h*), and (*i*). The yellow solution remained clear for a few minutes, and precipitation of sodium chloride then began. After an hour the solution was poured into some 200 c.c. of *N*/20-hydrochloric acid at room temperature, and well stirred. The white precipitate which immediately separated was at once filtered, well washed with water, and dried in a vacuum desiccator over concentrated sulphuric acid; yield, 1·65 g. (calc. for benzoin, 1·84 g.), m. p. 132—134°; mixed m. p. with benzoin (m. p. 133—134°) 133—134°.

(*d*) An experiment, carried out similarly to (*c*), with desyl chloride (2 g.) dissolved in 90 c.c. of ethyl alcohol and 10 c.c. of aqueous sodium hydroxide (1·079*N*) yielded 1·65 g. of benzoin, m. p. 129° (shrinkage at 115°), mixed m. p. 132° (softening at 120°). The m. p.'s found in these experiments were often lower than 134°, the value recorded for pure *r*-benzoin (Hopper and Wilson, J., 1928, 2489), but considerable difficulty is experienced in raising the m. p. to this value. Various temperatures are given in the literature for the m. p. of benzoin, *e.g.*, 129° (" Organic Syntheses," I, 33), 129—130° (Delacre, *Bull. Acad. roy. Belg.*, 1893, **26**, 270), 132·5—133·5° (McKenzie and Wren, J., 1908, **93**, 311), 137° (Jena and Limpricht, *Annalen*, 1870, **155**, 89).

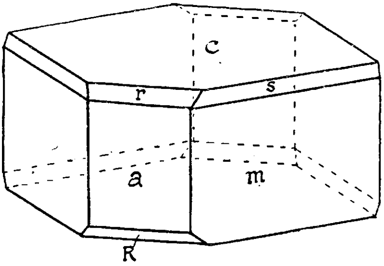
(*e*) *Isolation of Benzoin Diethylacetal.*—Desyl chloride (4·565 g.) was dissolved in 100 c.c. of ethyl alcohol, 100 c.c. of ethyl-alcoholic sodium ethoxide solution (1·98*N*/10) were added, and the solution was kept at 15° for 2 days. The precipitate which began to separate almost immediately after mixing was filtered off and washed with alcohol; yield, 1·05 g. (calc. for NaCl, 1·16 g.). When the yellow filtrate was concentrated to about 75 c.c. by distillation under diminished pressure on the water-bath at 25° a yellow gum began to separate; it dissolved on shaking, giving a turbid yellow solution, which was evaporated at room temperature. After 9 days a yellow oil remained together with a few crystals. Some 25 c.c. of light petroleum (b. p. 40—60°) were added; a clear solution was obtained, and a few crystals did not dissolve. The solution was inoculated with benzoin diethylacetal (from a previous preparation) and a crop of crystals separated from the solution. The solvent was allowed to evaporate completely, giving 5·3 g. of a well-crystallised, but slightly yellow product. This was warmed with about 15 c.c. of light petroleum (b. p. 40—60°). A part (A) which did not dissolve was filtered off, giving 0·71 g.; the clear solution on cooling deposited large colourless crystals (B), which were filtered; yield, 2·90 g. The liquors were allowed to evaporate and gave 1·53 g. of a yellow, oily solid (C). A, B, and C were examined separately: A was boiled with 25 c.c. of alcohol and left 0·08 g. of sodium chloride; the colourless solution remained homogeneous on standing, but addition of water gave a colourless crystalline precipitate (0·47 g.; m. p. 66—67°) which was doubtless benzoin diethylacetal. Excess of water precipitated a further 0·08 g. of solid from the solution. B was crystallised from some 10 c.c. of light petroleum (b. p. 40—60°), giving 2·07 g. of large colourless crystals of *benzoin diethylacetal* [Found: C, 75·1; H, 7·7; OEt, 30·4. $C_{14}H_{12}O(OEt)_2$ requires C, 75·5; H, 7·7; OEt, 31·5%]. Without special precautions, the ethoxyl determinations were somewhat lower (29·3, 29·8%), but if the mixture was kept at room temperature for 3 hours, and then slowly heated during a further 2 hours, in order to avoid loss of ethyl alcohol, the results were better. Crop C and the liquors from B yielded benzoin (0·64 g.) and benzoin diethylacetal (0·53 g.).

Benzoin diethylacetal was readily soluble in all the common organic solvents tried, but least soluble in light petroleum (b. p.

40—60°), from which it separated in large colourless crystals, m. p. 68°. Dr. G. M. Bennett, with the assistance of Mr. W. B. Waddington, kindly examined the crystals and reports as follows :

The substance is monoclinic with $a : b : c = 1{\cdot}099 : 1 : 1{\cdot}010$, and $\beta = 94° 7'$, the forms developed being $c(001)$, $a(100)$, $m(110)$, $r(101)$, $R(\bar{1}01)$ and $s(221)$, as illustrated by Fig. 2. This represents the full development of crystals obtained by slow crystallisation from light petroleum. The forms r, R, and s were frequently absent, while still simpler rhomb-shaped tabular crystals were often obtained having c large and bounded by m alone. The following are the mean angular values observed with six crystals :

FIG. 2.



	a (100).	m (110).	c (001).	r (101).	R ($\bar{1}$01).	s (221).
ϕ	0° 0′	*47° 37′	0° 0′	0° 0′	180° 0′	47° 3′
ρ	90° 0′	90° 0′	*4° 7′	*44° 48′	40° 19′	70° 5′

The face c tends to be replaced by a pair of vicinal faces. No marked cleavage could be detected.

A straight extinction was observed on a and on c with reference to the edge rc. Examination in convergent polarised light shows the substance to be biaxial with one optic axis emerging through a nearly perpendicular to that face, the optic axial plane being coincident with the plane of symmetry (010).

(*f*) *Reaction between Benzoin Diethylacetal and Hydrochloric Acid.*—Benzoin diethylacetal (1 g.), dissolved in 50 c.c. of ethyl alcohol at room temperature, was poured into about 200 c.c. of $N/5$-hydrochloric acid. The resulting benzoin was filtered off after 5 minutes, washed with water, and dried ; m. p. 129—132° ; yield, 0·8 g. (Calc., 0·75 g.).

(*g*) *Reaction between Desyl Chloride and Ethyl-alcoholic Sodium Hydroxide.*—Desyl chloride (2 g.), dissolved in 83 c.c. of ethyl-alcoholic sodium hydroxide solution ($1{\cdot}043N/10$) at 15°, was kept over-night. The precipitate (0·42 g. ; calc. for NaCl, 0·51 g.) was filtered off, washed with alcohol, and the washings were added to the filtrate, from which the solvent was evaporated at room temperature. After 10 days, the liquid had evaporated completely, and the product consisted of large colourless crystals, together with a small amount of yellow, pasty solid with an odour resembling that of ethyl benzoate. The finely powdered product (Found : OEt, 23·3%) softened at 51°, the main portion had melted by 65°, and a very small amount (? sodium chloride) remained unmelted at 140°. The ethoxyl determination was carried out as in (*e*), except that the silver halide was well washed with dilute ammonia to remove any silver chloride which might be present with the iodide. Not more than a trace of silver chloride should be present in (*g*) and (*i*). Adjustment was made in the calculation of results in (*h*) for the theoretical amount of sodium chloride which should be present in the products on which the Zeisel determination was made.

1 G. of the product was shaken with a few c.c. of alcohol (a very small amount did not dissolve), and 100 c.c. of 2*N*-hydrochloric acid were added. The oil which separated solidified on stirring to a hard, very pale yellow solid, which was filtered off, ground to a fine paste with water, and washed with dilute hydrochloric acid. The colourless solid obtained was washed with water, and dried in a desiccator over calcium chloride; yield, 0·69 g., m. p. 125—129° (shrinkage at 119°); mixed m. p. with benzoin 131—132° (shrinkage 127°).

(*h*) *Reaction between Desyl Chloride and Aqueous Ethyl-alcoholic Sodium Hydroxide.*—Desyl chloride (2·3 g.) was dissolved in 90 c.c. of ethyl alcohol at 15·0°, 10 c.c. of aqueous *N*-sodium hydroxide were added, and the solution was left over-night. Without separation of the considerable crop of small colourless cubes which slowly formed, the solution was evaporated at room temperature and after 9 days a mixture of colourless and pale yellow crystals resulted (Found : OEt, 17·0%) with a slight ethereal smell; yield, 3·08 g. (of which 0·58 g. should be sodium chloride). The substance softened at 53°, and the main bulk melted by 120°, although a considerable amount (? sodium chloride) remained unmelted at 140°.

1 G. of the product was treated with about 10 c.c. of alcohol; an appreciable amount did not dissolve. Hydrochloric acid (100 c.c.; 2*N*) was added, and crystals rapidly separated; yield 0·63 g., m. p. 124—129° (softening at 118°), mixed m. p. with benzoin 130—132° (softening at 130°).

(*i*) *Reaction between Desyl Chloride and Ethyl-alcoholic Sodium Ethoxide.*—To sodium ethoxide solution (100 c.c.; 1·067*N*/10) at 15°, desyl chloride (2·45 g.) was added, and the mixture kept overnight. The resulting solid was filtered off and washed with alcohol, the washings being added to the filtrate; yield, 0·55 g. (Calc. for sodium chloride, 0·62 g.). Evaporation of the solvent at room temperature yielded large colourless crystals of the acetal and a small amount of yellow pasty solid as described above. The powdered products (2·85 g.) showed no trace of oiliness. A sample softened at 53°, the main bulk melted by 65°, and a very small amount (? sodium chloride) remained unmelted at 140° (Found: OEt, 24·5%).

1 G. of the product was treated as in (*g*); yield 0·71 g., m. p. 128—131° (softening at 127°), mixed m. p. with benzoin, 131—133° (softening at 128°).

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