Summary

1. The action of sodium on ditolyltrichloro-ethane in boiling toluene results in the formation of *p,p'*-dimethylstilbene and *p,p'*-dimethyltolane.

2. A similar reaction takes place when sodium acts on diphenyltrichloroethane.

3. A possible interpretation of the reaction is given, involving the formation of monovalent carbon followed by the rearrangement of the phenyl groups within the molecule and the redistribution of the hydrogens between the molecules.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE POLYHYDRIC ALCOHOL-POLYBASIC ACID REACTION. II. ETHYLENE GLYCOL-PHTHALIC ANHYDRIDE

BY R. H. KIENLE AND A. G. HOVEY

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Introduction

In the first paper of this series[1] the reaction between glycerol and phthalic anhydride was described. The changes in properties were shown to be gradual and continuous. The conclusion was drawn that although the reaction proceeded by esterification, it did not necessarily take place with the formation of definite mono-, di- or triglycerides, but that a heterogeneous complexity of esters resulted.

It is interesting to compare the reaction of ethylene glycol and phthalic anhydride with the reaction of glycerol and the same acid, for ethylene glycol is a smaller and simpler molecule than glycerol. Any differences in properties of the resinous products of the reactions should therefore be due to the difference in size and structure of the alcohols.

Historical.—The reaction of ethylene glycol with phthalic anhydride was known to M. J. Callahan[2] in 1914, but the resin did not receive commercial application as soon as that formed from the glycerol-phthalic anhydride reaction, because ethylene glycol has not been available in considerable quantities until within the last five or six years. Much additional work was done by J. G. E. Wright and co-workers, the authors, and others, with the result that certain modifications of the reaction have been effected and several novel resins of commercial value have been produced. Recently, R. H. Kienle and C. S. Ferguson[3] described the product of the ethylene glycol-phthalic anhydride reaction as belonging to a "heat-

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[1] R. H. Kienle and A. G. Hovey, THIS JOURNAL, 51, 509 (1929).

[2] M. J. Callahan, unpublished data and such patents as U. S. Patents 1,091,627, 1,091,628 and 1,091,732.

[3] R. H. Kienle and C. S. Ferguson, *Ind. Eng. Chem.*, 21, 399 (1929).

non-convertible" type of film-forming resins. Carothers and Arvin[4] gave a description of methods of preparing glycol phthalate esters and obtained their molecular weights.

Materials.—C. P. phthalic anhydride (Monsanto Chemical Co.) having a melting point of 131.1°, and ethylene glycol of the best grade furnished by Carbide and Carbon Chemicals Corporation, having a specific gravity of 1.069 and boiling point of 194°, were used.

Experimental Part

I. A Study of the Products of the Reaction.—In the first paper of this series[1] the products of the glycerol–phthalic anhydride reaction were studied and found to be nothing more than water and resin. It was concluded that the only reaction involved was that of esterification. A similar result was obtained for the glycol–phthalic anhydride reaction.

Using an apparatus as described in our previous paper, the reaction mixture was heated in a tared Erlenmeyer flask on a sand-bath. To prevent oxidation, a stream of nitrogen carried the vapors evolved through Traps A, B and C where solid, liquid and gas were collected, respectively, and then finally through Trap D which contained a solution of rosaniline and sulfurous acid to detect any volatile aldehyde or reducing compounds which might not condense in the liquid-air trap if blown through too rapidly.

Stoichiometrical proportions (186 g. of ethylene glycol and 444 g. of phthalic anhydride) were gradually heated from room temperature to 230°. At this temperature the mix was maintained for three and one-quarter hours, when it seemed that a final equilibrium had been reached. Unlike the resinous product of the glycerol–phthalic anhydride reaction, no gelation takes place, so there is no way of knowing how far the reaction has gone except by taking out some of the reaction mixture and testing it. After cooling, the reaction mixture was found to consist of a clear, transparent, brittle resin (yield 568 g.) having the following characteristics: flow point, 69°; acid number, 22.8; saponification number, 582.8; (calcd.) percentage of esterification, 96.5%.

The traps A, B and C were disconnected and weighed. The total amount of material collected was 62.0 g., which agreed with the loss in weight of the reaction mixture. The amount of phthalic anhydride in each trap was found by titration with standard potassium hydroxide solution using phenolphthalein as an indicator. The samples were then made acid and tested for the presence of aldehydes using a standard rosaniline–sulfurous acid solution,[5] shaking and allowing to stand overnight.

Table I shows the results obtained upon examining the products collected in the various traps. As in the case of the glycerol reaction, the amount of phthalic anhydride evolved is far less than would be expected from watching the reaction take place. Most of the material in each trap was a clear transparent liquid with melting point approximately zero. Making due allowance for the effect of varying quantities of dissolved phthalic anhydride on the melting points of the liquids, nothing but phthalic anhydride, glycol and water were found. A determination of the amount of glycol distilled over was not made.

The tests for aldehyde were so weak that it is very doubtful whether any

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[4] W. H. Carothers and J. A. Arvin, This Journal, 51, 2568 (1929).

[5] Allen, "Commercial Organic Analysis," 5th ed., Vol. I, p. 324.

TABLE I

RESULTS OF EXPERIMENTS

Trap no.	A	B	C	D	Total
Material coll., g.	52.1	3.8	6.1	...	62.0
0.0874 N KOH, cc.	149.42	1.78	14.36	...	165.56
Equiv. wt. of phthalic anhyd., g.	0.968	0.012	0.094	...	1.074
Obs. m. p., °C.	......	0.2	Almost exactly zero		......
Aldehyde test	Very doubtful	None	Very weak test only at very last stage of the reaction	None	No aldehyde found in the reaction mixture itself
Odor	Burnt sugar	Burnt sugar	Burnt glycerol	...	......
Remarks	Detn. of amt. of glycol distilled not made	Diff. in m. p. from product in Trap C thought to be due to glycol	Phthalic anhydride present both as crystals and in solution	...	Inferred that water and resin are only products. Some phthalic anhydride and glycol distilled over

reducing substances were present at all. Judging by the amount of coloration when a known amount of acrolein was added to the rosaniline solution, there could not have been a total of 0.1 g. of aldehyde present in all three traps. No volatile aldehyde was found escaping the liquid-air trap C. No aldehyde was detected in the reaction mixture itself.

Since aldehyde, if present at all, is in so small a proportion that it can scarcely be detected, it is very doubtful whether the mechanism by which resins are formed from glycol and phthalic anhydride is through the formation of an intermediate aldehyde. The only products of the reaction seem to be water and resinous esters, and since the reacting molecules are those of an alcohol and of an acid, it is highly probable that the reaction is that of esterification.

II. Kinetic Isothermal Studies with Time.—As in the case of the reaction of glycerol with phthalic anhydride, this reaction was followed by determining the change of the free acid and of the combined acid with time.

Preparation of Samples.—The reaction was allowed to proceed at atmospheric pressure, keeping the conditions as nearly isothermal as possible, while 124 g. of the ethylene glycol was weighed out into the reaction vessel and heated up to its boiling point, phthalic anhydride was heated in an Erlenmeyer flask slightly above the temperature at which the reaction was to take place to allow for the cooling effect of pouring. When ready to start the reaction, 396 g. of the molten phthalic anhydride was weighed out into the reaction vessel and stirred up with the glycol. Because of the rapid progress of the reaction at the start, so much heat is evolved in a short time that the temperature of the reaction mixture rapidly rises about 40° above the temperature that it had at the instant of mixing. Since the boiling point of glycol is 197.5°, it was necessary to depend upon this quick rise in temperature when mixing the alcohol and acid in order to attain the isothermal conditions for the higher temperature runs.

If it was desired to run the reaction at lower temperatures, it was necessary to cool as rapidly as possible with a jet of compressed air until the right temperature was obtained. In either case, as soon as the desired temperature was reached, the reaction vessel was lowered into a constant temperature oil-bath and the reaction allowed to proceed to completion with the necessary amount of heat supplied to maintain isothermal conditions.

Samples of the reaction mixture were pipetted out from time to time and allowed to cool rapidly, thus freezing the equilibrium at that point. This was done oftener in the earlier stages than in the later stages, because the reaction was proceeding so much more rapidly. The viscosity of the liquid reaction mixture kept increasing as in the case of the glycerol–phthalic anhydride, but finally reached a maximum with no gelation taking place. Since gelation did not take place, it was possible to carry the reaction practically to completion.

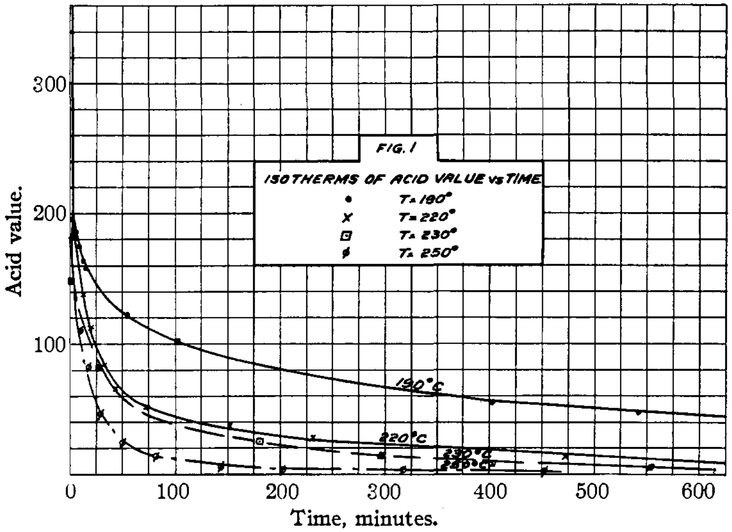

Fig. 1.

(a) **Free Acidity.**—The change in free acidity with time was determined and reported both as acid number and as percentage of free phthalic anhydride. Samples weighing 1 g. each were dissolved in 25 cc. of C. P. acetone and titrated with 0.1 *N* potassium hydroxide solution using phenolphthalein as indicator.

As in the case of the glycerol–phthalic anhydride reaction, the free acidity is reduced to at least one-half within the first minute after mixing the hot liquids, after which it proceeds to completion at a greatly diminished rate. The graphical representation of the change in free acidity with time is shown in Fig. 1.

(b) **Saponification Number.**—The method of determining the saponification number differed from the procedure which was used in the first paper[1] in that the samples, after titration for free acidity, were used for the determination of ester number. The samples were refluxed for one hour with 50 cc. of normal alcoholic potassium hydroxide solution. Upon cooling, titration was effected with 0.5 *N* hydrochloric acid until the pink color of the phenolphthalein disappeared; then 0.5 *N* potassium hydroxide solution was run in until the pink color reappeared. The calculation of ester number was made from this titration, which added to the acid number gave the saponification number. Although the saponification number for zero time was calculated as 534.5, actually a lower value was obtained for the earliest time at which the reaction mixture could be sampled. Then as the reaction proceeded, the saponification number increased, finally reaching a more or less constant value. The observed variation in saponification number was probably due to the presence of water, and its subsequent evolution.

(c) **Degree of Esterification.**—The ratio of the amount of combined acid to the total amount of acid gives the degree of esterification—a measure of the completeness of the reaction. The change of this value with time is given in Fig. 2, which shows the rapid increase in esterification at the start of the reaction and the falling off in the rate of increase as the reaction approaches completion.

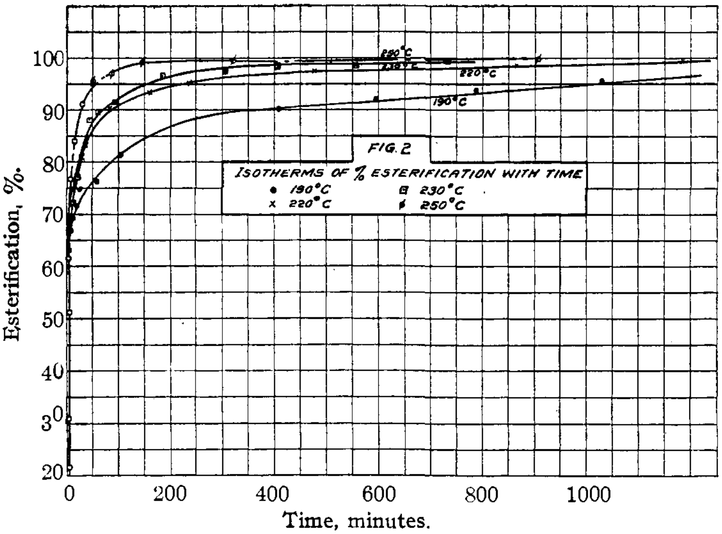

Fig. 2.

(d) **Variation of Other Properties with Time.** 1. **Flow Point.**—The flow point[1] gradually increases as the reaction proceeds, as is shown in Fig. 3, and reaches a maximum of about 80° when the reaction is complete. Since no gelation takes place upon further heating, the flow point can always be taken, but has not been found to increase appreciably.

2. **Viscosity.**—The viscosity of the hot liquid reaction mixture increases, but when the esterification is complete, the viscosity appears to have reached a final value.

3. **Density.**—The density at 25.0–25.0° was determined using a pycnometer with specially distilled mineral spirits (sp. gr. 0.7779) as an inert liquid. The results are included in Table II. The variation of density with time is found to be quite irregular, although there is a definite upward trend throughout the reaction. The same type of variation has also been found, by careful check, to exist in the case of the resinous product of the reaction of phthalic anhydride and glycerol.[6]

4. **Color.**—The color change is even less than that of the glycerol–phthalic anhydride reaction. The resin is clear, colorless and transparent at the start and remains so up to the end, when it resembles glass.

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[6] An error has been found in our previous paper [This Journal, 51, 509 (1929)]. In Table IIb the density data should read: time 3420 sec., *d*, 1.376; 3980 sec., *d*, 1.390; 5740 sec., *d*, 1.420; 9720 sec., *d*, 1.400.

5. Refractive Index.—The refractive index of the resinous product was found to be within the limits of 1.560 and 1.570.

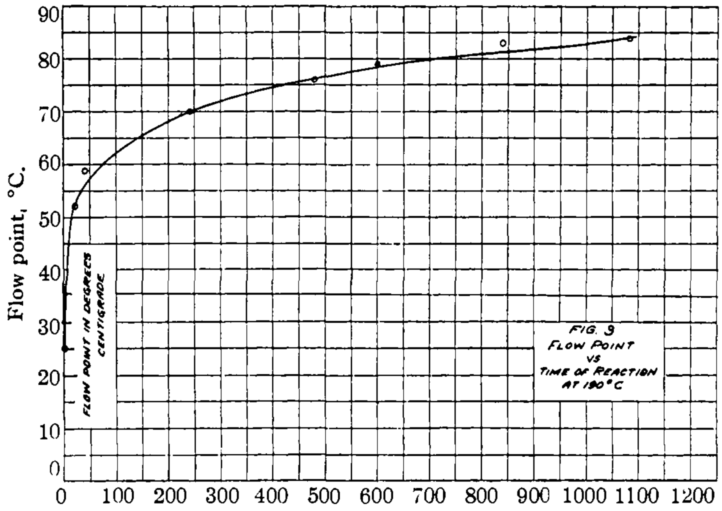

Fig. 3.

Table II shows a comparison of the variations of different properties of a set of standard samples taken from time to time with the temperature at 190°.

TABLE II

PROPERTIES OF SAMPLES (T, 190°)

Time, min.	Free acid, %[a]	Acid no.	Ester no.	Sap. no.	Ester, %	Sp. gr.	Refr. index
0	70.48	(534.5)		(534.5)	0	...	...
3	25.44	196	292	488	60	...	...
4	25.13	185	313	498	63	1.315	...
8	23.07	175	350	525	67	1.311	..
12.25	21.47	162.5	374	536	69.8	1.313	...
17.25	21.07	159.5	399	558	71.5	1.319	...
23.25	18.36	139	415	554	75.0	1.326	...
57	16.25	123	403	526	76.5	1.323	...
100	13.25	100.3	450	550	81.5	1.323	...
404	7.28	55	520	575	90.5	1.323	1.560
544	6.25	48	531	579	92.0	1.366	...
784	4.77	36.0	564	600	94.0	1.325	...
1024	3.84	29.0	570	599	95.25	1.339	...
1525	3.55	26.8	550	577	96.0	...	...
2965	1.68	12.7	551	564	97.7	..	...
3910	1.04	7.9	552	560	98.5	...	...
5565	0.61	4.6	494	499	99.0	...	1.570

Percentage of free acid calculated as phthalic anhydride.

Table III

Isotherms of Free Acidity and Percentage of Esterification Change with Time (*T*, 220°)

Time, min.	Acid no.	Ester no.	Sap. no.	Ester, %
0	(534.5)	0	(534.5)	0
1.5	183	295	480	62
3.0	181	314	495	63.5
13.5	139	347	486	73
21.5	111	432	543	81.4
31.5	81	454	535	83
45.5	64.4	484	548	88.3
73.5	52.5	494	546	90.5
158	36.8	523	560	93.6
233	28	540	568	95
473	13.1	550	563	97.6
863	4.98	510	518	98.5
1133	3.44	602	605	99.5

Table IV

Isothermal Data (*T*, 230°)

Time, min.	Acid no.	Ester no.	Sap. no.	Ester, %
0	(534.5)	0	(534.5)	0
1.5	148	252	400	63
2.5	120	286	406	70.5
6	120	328	448	73.2
12	116	342	458	74.6
19	114	385	499	77
43.5	61.4	448	509	88
57.5	55	460	515	89.4
93.5	40.6	500	541	91.5
183	24.6	525	550	96.6
303	13.6	540	554	97.6
403	8.6	530	539	98.7
553	6.6	540	547	98.9
733	3.5	535	539	99.5

Table V

Isothermal Data (*T*, 250°)

Time, min.	Acid no.	Ester no.	Sap. no.	Ester, %
0	(534.5)	0	(534.5)	0
7	145	302	447	67.5
12	114	390	514	76.8
18	82.4	430	512	84
30	46.5	469	515	91
50	24.2	485	519	95.5
86	15.4	533	548	97.5
146	5.7	530	536	99.4
203	2.46	540	543	99.5
320	2.70	545	548	99.5
455	2.10	547	549	99.6
905	2.01	550	532	99.8
1085	1.99	535	537	99.8

III. The Effect of Temperature.—The reaction of ethylene glycol and phthalic anhydride was studied not only at 190°, but also by making runs as nearly isothermal as possible at 220, 230 and 250°; the results are given in Tables III, IV and V, respectively. The isotherms of free acidity are plotted in Fig. 1 and show that the effect of carrying out the reaction at a higher temperature is to reduce the amount of free acid more rapidly than at a lower temperature. The isotherms of the percentage of esterification given in Fig. 2 show the effect of increasing the speed of the reaction by increasing the temperature.

The resinous product of the reaction is completely volatilized at 400°. In the case of the glycerol-phthalic anhydride reaction, it was shown[1] that plotting on semi-log paper the time to attain gelation against the reciprocal of absolute temperature resulted in a straight line. Since no gelation occurs in the ethylene glycol–phthalic anhydride reaction, it is not possible to use this transition point as a measure of a particular stage in the reaction. However, any definite percentage of esterification furnishes a suitable measure of the extent to which the reaction has taken place. Thus, taking 95% esterification, although other percentage esterifications may be taken equally well, it is possible by referring to Fig. 2 to set up a relationship between temperature and the time necessary to reach a definite percentage of esterification. The interpolated values of time necessary to produce 95% esterification at each temperature are given in Table VI.

TABLE VI

INTERPOLATED TIMES

Temp., °C.	Temp., °Abs.	$1/T \times 10$	Time at which esterification = 95% (obtained from Fig. 2), min.
190	463	216	1000
220	493	203	220
230	503	199	145
250	523	191	55

Plotting these data in Fig. 4 again shows a linear relationship for the log time *vs.* the reciprocal of the absolute temperature.

Discussion

The data of the ethylene glycol–phthalic anhydride reaction again show that in the formation of polyhydric alcohol–polybasic acid esters, the principal reaction is that of esterification, no intermediate aldehyde formation occurring. The change in all the properties is progressive and continuous, making it plausible that the esterification takes place according to the chance meeting of the individual alcohol and acid radicals, resulting in a mixture of esters instead of the formation of simple mono- or di-esters.

The ethylene glycol–phthalic anhydride reaction differs from that of glycerol–phthalic anhydride in that the reaction can be carried practically to completion without gelation, although the kinetic data of the two reactions give similarly shaped curves. This marked change in physical properties of the resinous product by simply substituting a dihydric alcohol for a trihydric alcohol is significant in theories of resin formation. The importance of the number of reacting groups on the inter-reacting molecules is clearly shown.

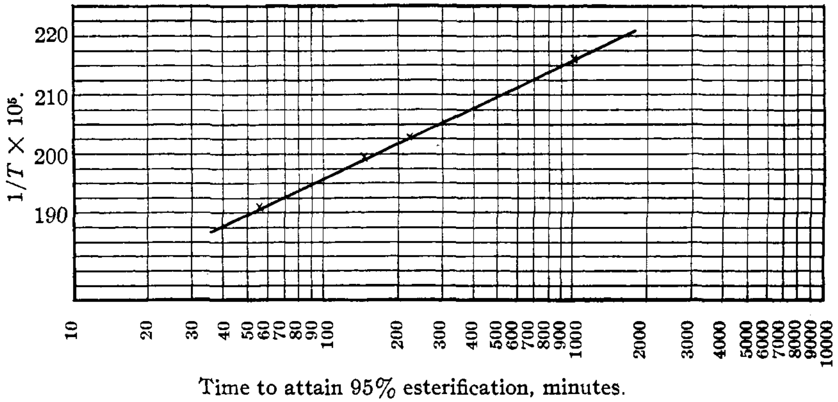

Fig. 4.—Relationship of time to attain definite percentage esterification *vs.* reciprocal of absolute temperature.

Linear relationship between the reciprocal of the absolute temperature and the log of the time necessary to reach a definite percentage of esterification points out how these poly-ester reactions obey Arrhenius' equation[7] relating to the effect of temperature on chemical reactions

$$\log_e \frac{k_1}{k_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since the reaction at each temperature has been carried to the same end-point

$$k_1 \infty \frac{1}{t_1} \text{ and } k_2 \infty \frac{1}{t_2}$$

therefore

$$\log_e \frac{t_2}{t_1} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Applying this equation to the data given in Table VI, it is possible to calculate the heat of activation for the reaction, the order of magnitude of which is characteristic of many chemical reactions, *viz.*, 22,600 calories.

Summary

1. The glycol–phthalic anhydride reaction is similar to the glycerol–phthalic anhydride reaction in that: (a) the reaction proceeds by esterifica-

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[7] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, Vol. II, p. 900.

tion, since water and resin are the only products. No intermediate aldehyde is formed. (b) The reaction, when carried on at a temperature at which both reactants are liquid, goes very rapidly at the start, evolving heat and is apparently about one-half complete within one minute of mixing. (c) As the reaction proceeds under isothermal conditions, the free acidity decreases, and the percentage esterification and the flow point increase. (d) The properties and appearance of the resinous products are similar except that the phenomenon of gelation possessed by the product of the glycerol–phthalic anhydride reaction is not possessed by the product of the ethylene glycol–phthalic anhydride reaction.

2. The glycol–phthalic anhydride reaction is dissimilar to the glycerol–phthalic anhydride reaction in that: (a) gelation of the resinous product does not take place at any temperature at which the reaction is carried out. The product remains fusible and soluble. (b) The reaction may be carried practically to completion, because gelation does not interfere with its normal course.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

SOME NEW DERIVATIVES OF DIPHENYLCARBAMINE CHLORIDE

BY THEODORE W. EVANS[1] AND WILLIAM M. DEHN

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Recently the probable –OM rather than the –NM linking in salts of cyclic imides was shown. Since the reactions of metallic sodium on aniline and acetanilide are remarkably different, it was thought that the constitution of sodium acetanilide is $C_6H_5{-}N{=}CONaCH_3$, rather than $C_6H_5{-}N{-}NaCOCH_3$. When this salt is treated with RI, etc., the R or other group is known to be linked to nitrogen; however, this linking can result from either of the two forms of the salt, from the –NNa form by direct substitution and from the –ONa form by initial addition, followed by a splitting off of sodium chloride, as indicated in the equation

$$C_6H_5N{=}CONaCH_3 + RI \longrightarrow C_6H_5NRICONaCH_3 \longrightarrow C_6H_5NRCOCH_3 + NaI$$

Since diphenylcarbamine chloride[2] reacted with many bases to yield additive compounds, it was anticipated that it would react with this salt to give some indication of addition. This was found to be the case.

When the sodium salt of acetanilide is suspended in toluene, treated with its equivalent of diphenylcarbamine chloride dissolved in toluene,

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[1] The material presented in this paper is part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] Platt and Dehn, THIS JOURNAL, 37, 2122 (1915).