equal volume of aqueous 10% sodium hydroxide solution for 4 hours, to remove any remaining acid. It was then washed and vacuum distilled at 2 mm. of pressure over a 10 cm. packed column. The distillate, which was collected in 26 fractions, seemed to consist of three principal sections.

Section 1	b.p. 113–132°	348 g.
Section 2	b.p. 137–159°	102 g.
Section 3	b.p. 159–177	357 g.
Residue		574 g.

Isolation of 1,1-Diphenyl-1-propene.—Section one was redistilled through an 18″ modified Widmer column. In this manner 225 g. of colorless liquid b.p. 109–111° (2 mm.) was obtained. The index of refraction was not constant but varied from $n^{20}\text{D}$ 1.5720 to 1.5858. It was then refrigerated and a crystalline material separated. This was removed by low temperature filtration (113 g.) and recrystallized from hot alcohol. The melting point of 48° did not change on further recrystallization. A mixed m.p. with 1,1-phenyl-1-propene of m.p. 48–49° was 48–48.5°. It decolorized a solution of bromine. The yield of purified product was 68 g. (5.2% of theory).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.74; H, 7.37.

As a further identification, *ca.* 0.5 g. was oxidized by boiling with a solution of potassium dichromate in water and sulfuric acid. The vapors had a faint odor of acetic acid and reddened blue litmus paper. Glacial acetic acid was then added to improve the solubility, and on further boiling oxidation took place rapidly. The mixture was cooled and extracted several times with benzene. The combined extracts were washed with water and then sodium carbonate solution.

The benzene solution was then dried and evaporated. The oily residue which had the characteristic odor of benzophenone was added to an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine hydrochloride. In a few minutes, a red-orange precipitate of hydrazone was observed. This was filtered, pressed dry and recrystallized from glacial acetic acid. It then melted sharply at 239° (cor.). The 2,4-dinitrophenylhydrazone of benzophenone has this same melting point.[13]

Isolation of 1,1-Diphenylpropene.—The liquid portion from the cold filtration of the 1,1-diphenyl-1-propene was carefully redistilled through a 12-inch column to give 50 g. of a colorless liquid, b.p. 105° (1.6 mm.), $n^{20}\text{D}$ 1.5655; $d^{20}{}_{15}$ 0.9846. It had a bromine number of 6.1, equivalent to 6.6% of diphenylpropene. The physical constants of 1,1-diphenylpropane have been reported as $n^{14}\text{D}$ 1.5657[5] and $d^{24}\text{D}$ 0.9881.[6]

Isolation of 2,2-Diphenyl-1-propanol.—The second section was also carefully refractionated to obtain 55 g. (3.85% of theory) of 2,2-diphenyl-1-propanol, a very viscous liquid having the following properties: b.p. 143–145° (1.8 mm.), $n^{20}\text{D}$ 1.5924.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.59. Found: C, 85.80; H, 7.78.

This alcohol readily gave a phenylurethan which after recrystallization had a m.p. of 148–148.2°. The reported m.p. of this derivative is 148–149°.[8]

Anal. Calcd. for $C_{22}H_{21}O_2N$: C, 79.23; H, 6.40. Found: C, 79.77; H, 6.32.

Isolation of 1,1,2-Triphenylpropane.—Upon redistilling the third section through a 12″ modified Widmer column, a very viscous pale yellow liquid was obtained with the physical constants: b.p. 172° (2 mm.); $n^{20}\text{D}$ 1.5980. On long standing a small crystal was observed in one fraction. Upon seeding the other fractions with this seed, a pale yellow crystalline solid was obtained. This solid after recrystallization from alcohol had a m.p. of 73° which was not altered by further recrystallization (yield 252 g., 13.7%).

The melting point has been reported as 73–75°[6] and 76–77°.[7]

Anal. Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.63; H, 7.50.

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[13] Shriner and Fuson, "Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

BROOKLYN, N. Y. RECEIVED JUNE 10, 1950

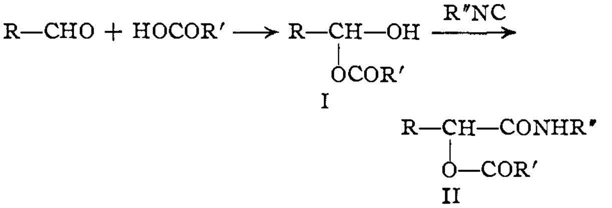
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Passerini Reaction. III. Stereochemistry and Mechanism[1,2]

BY ROBERT H. BAKER AND DAVID STANONIS

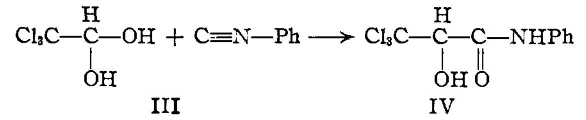
Certain aldehydes and unsymmetrical ketones produce with *l*-menthoxyacetic acid and phenyl isocyanide the diastereomeric *l*-menthoxyacetoxyanilides. Methods of separation of these are described. The kinetics of a typical Passerini reaction has been found to be third order, first order in each of the reactants. A mechanism is postulated which shows the reaction to be related to the second order Beckmann rearrangement.

Passerini[3] proposed that the mechanism of formation of α-acyloxyanilides (II) from phenylisocyanide, an aldehyde and an acid involved two steps. First, the acid was supposed to attack aldehyde to form I and then this reacted with isocyanide to form II.



$$\mathrm{R{-}CHO + HOCOR' \longrightarrow \underset{I}{R{-}\underset{\substack{|\\ OCOR'}}{CH}{-}OH} \xrightarrow{R''NC} \underset{II}{R{-}\underset{\substack{|\\ O{-}COR'}}{CH}{-}CONHR''}}$$

Evidence cited to support this scheme was the fact that chloroaldehyde or ketone hydrates would react without acid to produce the hydroxyanilide, IV,[4] and that certain optically active acids in



$$\mathrm{\underset{III}{Cl_3C{-}\overset{H}{\underset{\substack{|\\ OH}}{C}}{-}OH} + C{\equiv}N{-}Ph \longrightarrow \underset{IV}{Cl_3C{-}\overset{H}{\underset{\substack{|\\ OH}}{C}}{-}\underset{\substack{\|\\ O}}{C}{-}NHPh}}$$

ketone solutions showed anomalous rotations.[5] The weakness in the argument lies in the lack of a reasonable explanation of how such intermediates as I or III could react with isocyanide to yield II or IV. We have previously pointed out that the anomalous rotation is not compelling evidence of the formation of intermediates of type I,[6] and we point out later in this paper an alternate interpretation of the aldehyde hydrate reaction.

Earlier[6] we have sought to make use of the Passerini reaction in the production of optically

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[1] This investigation was supported by a grant from the Abbott Fund of Northwestern University.

[2] Presented at the Philadelphia Meeting of the American Chemical Society, April, 1950.

[3] M. Passerini, *Gazz. chim. ital.*, **51**, 126 (1921).

[4] M. Passerini, *ibid.*, **52**, 432 (1922).

[5] M. Passerini, *ibid.*, **55**, 726 (1925).

[6] R. H. Baker and L. E. Linn, THIS JOURNAL, **70**, 3721 (1948).

active hydroxyanilides or their esters. Both (+)2-methylbutanoic acid and (−)menthoxyacetic acid were used on phenyl isocyanide and benzaldehyde or 2-octanone. Whereas the crystalline products of these reactions were apparently pure diastereomers, this has been shown in the present paper to be due to preferential crystallization. Products derived from three unsymmetrical ketones and (−)menthoxyacetic acid have been hydrolyzed before removing any crystals and have invariably yielded inactive hydroxyanilides. The aldehyde diastereomers have been separated by chromatography but hydrolysis has always been attended by racemization. The ketone derivatives are usually separable by crystallization and hydrolysis provides a means of obtaining the active hydroxyanilides.

This stereochemical evidence is of little importance in interpreting the reaction mechanism except possibly to point to the fact that there is little difference in ease of formation of the two possible diastereomeric activated complexes.

Considerable evidence has been expended in this Laboratory to find conditions and reactants which would afford kinetic analysis of the reaction. In ordinary practice with no solvent and at 0–25° there are side reactions between the acid and isocyanide which produce formamidine salts and amides.[6] During the present work it has been found that with menthoxyacetic or benzoic acid in preparative runs these side reactions may be avoided to the extent of obtaining 90–98% yields of Passerini product by operating at −20°. It was also possible to avoid side reactions even at 37° when a fast reacting system, cyclohexanone, phenyl isocyanide and benzoic acid each 0.2 molar in carbon tetrachloride was used. This system at various temperatures was used and the remaining acid in aliquots titrated to obtain third order kinetics, first order in each of the three reactants. Typical results are presented in Table I and a typical run in Table II. Reactions were followed only up to the time when product began to precipitate, about 50% of the acid having disappeared.

TABLE I

THIRD ORDER RATE CONSTANTS OF THE REACTION OF CYCLOHEXANONE WITH BENZOIC ACID AND PHENYL ISOCYANIDE

Original molalities of reactants in carbon tetrachloride				Av. $k \times 10^{-4}$ sec.$^{-1}$ moles^{-2}liters^2
Ketone	Acid	Isocyanide	T, °C.	
0.20	0.20	0.20	27	1.65
.20	.20	.20	27	1.61
.20	.20	.20	27	1.74
.20	.20	.50	27	1.61
.50	.20	.20	27	1.35
.20	.20	.20	0	0.38
.20	.20	.20	0	0.36
.20	.20	.20	37.1	2.86
.20	.20	.20	37.1	2.64

TABLE II

DATA ON EXPERIMENT NO. 2, TABLE I

Time, min.	Ml. NaOH	k
0	28.33	
200	27.64	1.56
353	25.73	1.58
442	24.83	1.73
1180	21.59	1.55
1780	19.48	1.59
2640	17.10	1.67
	Av.	1.61

The integrated forms of the equations used for the calculation of the third order rate constants were, for equal concentrations of reactants

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

and for the other cases

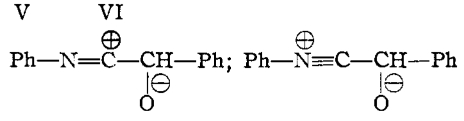
$$k = \frac{1}{t(b-a)^2}\left[\frac{x(b-a)}{a(a-x)} + \ln\frac{b(a-x)}{a(b-x)}\right]$$

The energies of activation, calculated from three of the experiments at different temperatures using the familiar Arrhenius equation were 9.1, 9.1 and 9.2 kcal.

The effects of dilution and solvent can be seen in the following reactions at 27° of phenyl isocyanide, cyclohexanone and benzoic acid. With these reagents each 0.2 molar in ether for 10 hours 5% of the acid had reacted but in carbon tetrachloride 18% had disappeared. By comparison, the mixture with no solvent was 97% complete in a like period of time. This is some evidence that benzoate anion is not involved. This was further tested in the no solvent reaction by incorporating sodium benzoate. Two homogeneous mixtures, identical except that the second one contained an added 10 mole per cent. of sodium benzoate, were allowed to stand for 50 minutes. Titrations of the remaining acid showed that 67 and 61%, respectively, had reacted. This result is indicative of the fact that the rate is not appreciably altered by changing the anion concentration.

The kinetics and other facts about the reaction are satisfied by a two step mechanism, the first of which is reversible and similar to the cyanohydrin reaction.[7] The rate-determining step would involve the acid and the transitory intermediate.[8]

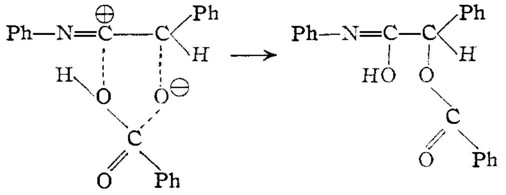
(Step 1) $\underset{\mathrm{V}}{\mathrm{PhNC}} + \underset{\mathrm{VI}}{\mathrm{PhCHO}} \rightleftarrows$



$\mathrm{Ph{-}\overset{\oplus}{N}{=}C{-}\underset{O^{\ominus}}{CH}{-}Ph}$; $\mathrm{Ph{-}\overset{\oplus}{N}{\equiv}C{-}\underset{O^{\ominus}}{CH}{-}Ph}$

VIIa VIIb

(Step 2) VII + PhCOOH ⟶



VIII IX

The details of the latter step are shown in the conversion of the activated complex (VIII) to the enol (IX) of the Passerini product.

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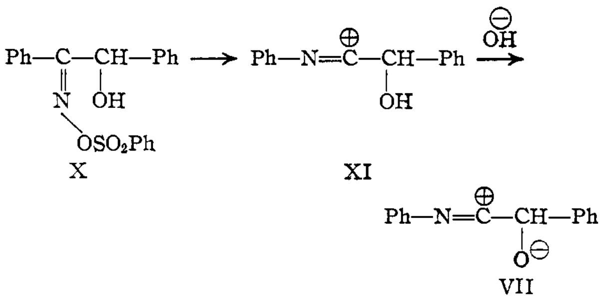
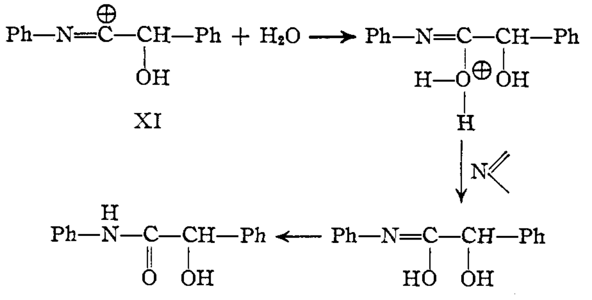
(7) R. H. Baker and A. H. Schlesinger, THIS JOURNAL, **67**, 1499 (1945).

(8) Essentially this mechanism has been presented without supporting evidence by M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 116.

Some evidence supporting Step 1 has already been cited.[7] The remarkable similarity of the reactivity of the various aldehydes and ketones in this and the cyanohydrin reaction is added evidence of a similar mechanism. Like the first step in the cyanohydrin reaction it would be expected to be reversible, actually Werner's[9] conversion of β-benzoin oxime into phenyl isocyanide and benzaldehyde by benzenesulfonyl chloride and alkali probably goes by a mechanism identical with the reverse of Step 1.[10] Assuming that the oxime forms the benzenesulfonamide, X, solvolysis would lead to phenyl migration to nitrogen and removal of proton by base would lead to our intermediate, VII,[11] and eventually to isocyanide and aldehyde.



There remains only the mechanism of the rate-controlling step in the Passerini reaction. The fact that α-substituted acids react much more slowly or not at all[6] suggests an attack of the intermediate on the carbonyl group of the acid. That it is the undissociated acid and not the anion is supported by the fact that added benzoate anion fails to increase the rate. These facts are satisfied by the formulation of Step 2. Incidentally, the reaction with water instead of acid as in the case of chloral could be interpreted as a solvation of essentially the same type. This latter reaction is probably similar to Werner's[9] conversion of the sulfonamide X to mandelanilide by the weaker base pyridine and, apparently, water.



Experimental[12]

Reagents.—Phenyl isocyanide, prepared by the Hofmann method, was distilled, b.p. 35–37° at 1.5 mm., and was stored at Dry Ice temperature. We have been unable to confirm the high yield of the compound reported to be obtained by Malatesta's modification.[13] Other reagents were distilled or crystallized before use.

Rate Experiments.—The following quantities of carbon tetrachloride solutions were mixed, 4 ml. of 0.50 *M* benzoic acid, 2.0 ml. of 1.0 *M* phenyl isocyanide, and 2.0 ml. of 1.0 *M* cyclohexanone. The solution was quickly made up to a volume of 10 ml. and placed in the thermostat. One-ml. aliquots were withdrawn at stated times, diluted with 10–15 ml. of water and titrated with 0.00640 *M* sodium hydroxide. Typical data are presented in Table II. The crude product obtained from some residues had m.p. 151–152°.[14]

Reaction of Ketones and Aldehydes with *l*-Menthoxyacetic Acid and Phenyl Isocyanide.—The purity of the acid has been previously described.[6] Reactions were run by mixing equimolar proportions of the three reagents and allowing to stand at −20°, specific rotations were taken in acetone at nearly 1% concn.

Methyl Ethyl Ketone.—After 18 days the solid was removed and separated into two fractions of essentially the same rotations and m.p. by crystallization from petroleum ether, $[\alpha]^{25}\mathrm{D}$ −47°, m.p. 131.5–132.5°.

Anal. Calcd. for $C_{23}H_{25}NO_4$: C, 70.90; H, 9.07; N, 3.61. Found: C, 70.65; H, 9.56; N, 3.46.

Alkaline saponification of the above active material gave **(+)-2-hydroxy-2-methylbutananilide**, $[\alpha]^{24}\mathrm{D}$ +44, m.p. 103–104.5°. The (−)enantiomorph, $[\alpha]^{23}\mathrm{D}$ −9.8, m.p. 109.5–110° was obtained by saponifying the material in the mother liquors from the above reaction. An aliquot of the original homogeneous reaction mixture was saponified to racemic material in 75% over-all yield, m.p. 111–113°.[15]

Methyl Propyl Ketone.—After 8 months the crystals were removed and subjected to fractional crystallization from petroleum ether. The top fraction, 20% yield, had $[\alpha]^{27}\mathrm{D}$ −64°, m.p. 122°. Three fractions of intermediate rotations and finally one, 6% yield, with $[\alpha]^{26}\mathrm{D}$ −47° were obtained.

Anal. (top fraction) Calcd. for $C_{24}H_{37}NO_4$: C, 71.43; H, 9.22; N, 3.47. Found: C, 71.11; H, 9.50; N, 3.60.

Saponification of the top fraction gave **(+)2-hydroxy-2-methylpentananilide**, $[\alpha]^{33}\mathrm{D}$ −43, m.p. 88°. The crude enantiomorph was obtained by saponification of the most soluble fraction, $[\alpha]^{27}\mathrm{D}$ +30°, m.p. 82.5°.

Anal. Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.75. Found: C, 69.47; H, 8.22; N, 6.67.

3-Methylcyclohexanone.—The crystalline material obtained in 95% yield after one month could not be separated by fractional crystallization. Four crops of crystals, m.p. 105–110° from ether-petroleum ether varied in $[\alpha]^{23}\mathrm{D}$ from −60 to −58°.

Anal. Calcd. for $C_{26}H_{39}NO_4$: C, 72.69; H, 9.15; N, 3.26. Found: C, 72.40; H, 9.12; N, 3.24.

Saponification of an aliquot of the original mixture produced inactive **3-methylcyclohexanol-1-carboxanilide**, m.p. 138.5–143°; lit.[14] 142–143°.

Isobutyraldehyde.—After 6 months the product was washed with sodium bicarbonate and dried. The oil so obtained solidified after several months; 98% yield, m.p. 43–56°, $[\alpha]^{27}\mathrm{D}$ −59°.

Anal. Calcd. for $C_{23}H_{35}NO_4$: C, 70.92; H, 9.06; N, 3.60. Found: C, 71.20; H, 9.53; N, 3.30.

A 1-g. sample of this petroleum ether was chromatographed on alumina and eluted with hot benzene to give 380 mg. of oil, $[\alpha]^{30}\mathrm{D}$ −65°. Repetition of the process twice more produced $[\alpha]^{30}\mathrm{D}$ −81° and then −90°.

Saponification of the original product with alcoholic sodium hydroxide or hydrolysis on an alumina column by elution with U. S. P. ether produced the known inactive **2-hydroxy-3-methylbutananilide**, m.p. 129–131°; lit.[16] 133°.

Benzyloxyacetaldehyde.—This gave oils which could not be separated into purer diastereomers by chromatography over alumina or Norit. The purest fraction, $n^{22}\mathrm{D}$ 1.5249 had $[\alpha]^{24}\mathrm{D}$ −64°.

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(9) A. Werner and A. Piguet, *Ber.*, **37**, 4295 (1904); A. Werner and Th. Detscheff, *ibid.*, **38**, 69 (1905).

(10) I am indebted to Dr. Peter A. S. Smith, University of Michigan for a discussion which brought to light these relationships.

(11) Contrary to Werner's impression the β-oxime (low melting) has phenyl *anti* to N-hydroxyl. This is shown by its oxidation to β-benzil monoxime which is rearranged to benzoylformanilide, J. Meisenheimer, *Ber.*, **54**, 3206 (1921).

(12) Microanalyses by the Misses P. Craig, J. Anderson, V. Hobbs, M. Nielsen and M. Hines.

(13) L. Malatesta, *Gazz. chim. ital.*, **77**, 238 (1947).

(14) M. Passerini, *ibid.*, **53**, 410 (1923), reports 155–156°.

(15) The reported m.p. is 112.5°, E. Winzheimer, *Chem. Zentr.*, **80**, II, 1370 (1909).

(16) C. A. Bischoff, *Ber.*, **30**, 2315 (1897).

Anal. Calcd. for $C_{26}H_{37}NO_5$: C, 71.90; H, 7.98. Found: C, 72.47; H, 8.54.

Saponification of this oil gave optically inactive 2-hydroxy-3-benzyloxypropanilide, m.p. 77–78.5°.

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.82; H, 6.32; N, 5.16. Found: C, 70.73; H, 6.42; N, 5.22.

Methyl Cyclopropyl Ketone.—After 17 months at −20° and 1 month at 25° the odor of isocyanide was still quite strong and a work up of the product failed to detect any product other than traces of the isocyanide polymer.

EVANSTON, ILLINOIS RECEIVED JANUARY 14, 1950

[A CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

The Action of *t*-Butyl Hypochlorite on Organic Compounds. II. Aromatic Aldehydes[1]

BY DAVID GINSBURG

The action of *t*-butyl hypochlorite on a number of aromatic aldehydes has been investigated. In methoxy-, dimethylamino- and hydroxyaldehydes, nuclear chlorination takes place, whereas in other aldehydes, the hydrogen of the aldehyde group is substituted by chlorine and the corresponding acid chloride is formed.

In continuation of previous experiments, the reaction of aromatic aldehydes with *t*-butyl hypochlorite was studied. The only reference in the published literature to such a reaction was a note by Clark[2] who reported—without experimental details—that benzaldehyde is converted to benzoyl chloride.[2a] Indeed, in some cases, *t*-butyl hypochlorite has been known to effect substitution of hydrogen by chlorine.[3]

Table I summarizes the results obtained. In most cases, the products could be identified by their physical constants. Where this was impossible, an exact proof was provided; the pertinent results are recorded in the Experimental Section.

It can be seen from the table that, on the whole, the hydroxyl, methoxyl and dimethylamino groups activate the nucleus (nuclear chlorination) whereas hydrogen, chlorine or the methyl group activate the aldehyde group (formation of the acid chloride). When the *methoxyl* group is present, the chlorine enters para to it. If the para position is occupied, ortho chlorination occurs.[4]

The *hydroxyl* group is usually ortho directing but in the case of salicylaldehyde, the chlorine atom enters para to the hydroxyl group and not in the other ortho position. In vanillin, it can be seen that the directive influence of the hydroxyl group outweighs that of the methoxyl group since 5-chlorovanillin is obtained. Veratraldehyde conforms to the behavior of the monomethoxy aldehydes, yielding 6-chloroveratraldehyde.

The *dimethylamino* group in *p*-dimethylaminobenzaldehyde (occupied *p*-position!) directs the chlorine atom into the *ortho*-position.

m- and *p*-nitrobenzaldehydes were not attacked by *t*-butyl hypochlorite. Also the carboxyl group exerts a deactivating influence. Thus, benzoic, *p*-toluic and *p*-nitrobenzoic acids were recovered unchanged from the mixture with *t*-butyl hypochlorite.

The *solvent* influences the course of the reaction. In a non-polar solvent such as carbon tetrachloride, also the aldehydes containing a methoxyl group yield the acid chlorides.

Clark's observation that benzaldehyde yields benzoyl chloride upon chlorination with *t*-butyl hypochlorite was duplicated but only under the condition that the *t*-butanol formed in the reaction was removed *in vacuo* (at low temperature); otherwise benzoic acid becomes the main reaction product. This is also the case for anisaldehyde. The formation of benzoic (and anisic) acid is not due to hydrolysis at elevated temperature, as it occurs not only in 90% acetic acid, but also in carefully dried carbon tetrachloride. The following formulas account for these observations:

$$\text{(a)}\quad \mathrm{RCHO} + t\text{-}\mathrm{BuOCl} \longrightarrow \mathrm{RCOCl} + t\text{-}\mathrm{BuOH}$$
$$\text{(b)}\quad \mathrm{RCOCl} + t\text{-}\mathrm{BuOH} \longrightarrow \mathrm{RCOOH} + t\text{-}\mathrm{BuCl}$$

The chlorination reaction (a) is practically instantaneous. If aniline is added to the reaction mixture soon after the chlorinating agent, a nearly quantitative yield of benzanilide or *p*-anisanilide is obtained. Equally, if, after the addition of the chlorinating agent the *t*-butanol formed is removed *in vacuo*, a high yield of the acid chloride is obtained. If, however, the reaction mixture is heated for some time, the final product is the aromatic acid and, during the heating, *t*-butyl chloride distils off continually.

Experimental[5]

General Chlorination Procedure.—The aldehyde (0.04 mole) is dissolved or suspended (in cases of low solubility) in the solvent (10 ml.) used for the reaction (see table) and *t*-butyl hypochlorite (5 ml.) added with stirring. Usually there is an induction period (30–120 seconds) before a strong exothermic reaction sets in. The reaction mixture is concentrated and the product is isolated by either crystallization or distillation. The products are purified so easily, that in all probability no isomers are formed in addition to those indicated in the table.

Example: Chlorination of Benzaldehyde in Carbon Tetrachloride.—The general procedure was followed: benzaldehyde (4.3 g.) was treated with *t*-butyl hypochlorite (4.4 g.). Immediately after all the hypochlorite had been added, excess aniline was added to the reaction mixture. A nearly quantitative yield of benzanilide (7.5 g.), m. p. 161°, was obtained. The m. p. was not depressed on admixture with an authentic sample. When the *t*-butanol was removed *in*

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[1] Paper I in this series, Ritter and Ginsburg, THIS JOURNAL, **72**, 2381 (1950).

[2] Clark, *Chem. News*, **143**, 265 (1931).

[2a] It has been brought to our attention by one of the Referees that there are three dissertations in the M.I.T. library on this subject: Bixley, M.S. Thesis, M.I.T. (1927); Clark, Ph.D. Thesis, M.I.T. (1930); Sumner, Ph.D. Thesis, M.I.T. (1934).

[3] For references, *cf.* Ref. 1.

[4] Differences in the directing influence of methoxyl and hydroxyl groups have been observed in other instances, *e.g.*, in bromination (*cf.*, E. Bergmann, *J. Chem. Soc.*, 1284 (1948)) and in the Friedel-Crafts reaction (*cf.* Ch. Weizmann, Haskelberg and Berlin, *ibid.*, 398 (1939)).

[5] All melting and boiling points are uncorrected.