***o*-Toluidide,** $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound crystallizes from fifty per cent. alcohol in lustrous plates which retain a slight yellow color after repeated recrystallization. It is a little more soluble in organic solvents than the *p*-toluidide of the same acid. M. p. 140.5–141° (corr.).

Subst.: 0.2855 g., 0.2681 g.; cc. 0.1 *N* HCl, 17, 16.6.
Calc.: N, 8.75%. Found: N, 8.34%, 8.67%.

***p*-Toluidide,** $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—It is the least soluble in organic solvents of the toluidides studied. It crystallizes in lustrous elongated plates which melt at 143.5–144.5° (corr.).

Subst.: 0.2783 g.; cc. 0.1 *N* HCl, 17.1. Calc.: N, 8.75%. Found: N, 8.61%.

Summary and Discussion.

A comparison of the melting points of tolyl esters of the nitrosulfonic acids of *p*-xylene reveals some peculiarities which are worthy of note, in the light of existing theories. The tolyl esters of the 5-nitro and 6-nitro acids follow the rule of symmetry, *i. e.*, the melting points increase from ortho to meta to para. The melting points of the tolyl esters of the 3-nitro acid, on the other hand, *decrease* from ortho to meta to para. This is especially peculiar in the light of a theory advanced by Smiles,[1] which assigns the lowering of fusion point to intramolecular collision. An examination of the structural formula of the *o*-tolyl ester of the 3-nitro acid shows that the substituting groups are in the most compact arrangement possible, while the melting point is higher than that of any of the other tolyl esters studied, *i. e.*, 151°. No record of esters of similar structure could be found in the literature.

The toluidides are more regular as regards their melting points. The *p*-toluidide of each acid melts at a higher temperature than the *o*-toluidide.

For any given acid the solubility of its derivatives in organic solvents decreases as the melting point increases.

As a rule the derivatives of the 5-nitro acid are less soluble than the derivatives of its isomers.

East Lansing, Mich.

[Contributions from the Chemical Laboratory of the University of Washington.]

THE ACTION OF DIPHENYLUREACHLORIDE ON ORGANIC BASES.

By William M. Dehn and Earl M. Platt.

Received June 28, 1915.

Michler[2] first prepared diphenylureachloride by treating diphenylamine with phosgene in chloroform solution. Its action on ammonia

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[1] "Relation between Chemical Constitution and Some Physical Properties," p. 208.

[2] *Ber.*, **8**, 1665 (1875); **9**, 396 (1876); see also Girard and Wilm, *Bull. soc. chim.*, **25**, 251 (1901); Erdmann and Herth, *J. prakt. Chem.*, [2] **56**, 6 (1897); melts at 189°.

was found by him to yield α,α-diphenylurea at 100°, but diphenylamine, ammonia and carbon dioxide at 150°. Its action on hydrazine hydrate was studied by Toschi[1] who obtained diphenylsemicarbazide and tetraphenylhydrazodicarboxamide. Its action on diethylamine yielded diethyldiphenylurea;[2] on aniline in chloroform solution, triphenylurea;[3] on nitraniline[4] at 120°, *m*-nitrotriphenylurea and *p*-nitrotriphenylurea; on ethylaniline, ethyltriphenylurea;[5] on diphenylamine, tetraphenylurea[6]—this by nitration[7] yielded hexa- and octanitrotetraphenylurea. Other studies of the action of diphenylureachloride on organic bases have not been made.

The following studies were undertaken not only to extend our knowledge of its reactions but also to determine whether this complex halogen derivative and organic bases react in anhydrous ether solutions like previously[8] investigated halogen compounds.

While the mechanism of reaction was found to be the same as with acetyl chloride,[9] benzoyl chloride[10] and other halides, four points of exceptional interest were developed. First, the reactions were found to be sluggish except with piperidine, *p*-toluidine, and some of the lower fatty amines. Second, few additive compounds were obtained. Third, other examples of the noninterchangeability[11] of parts of the pentavalent nitrogen compounds were observed. Fourth, a remarkable example of "steric hindrance" was observed with the toluidines.

That diphenylureachloride is less reactive than alkyl or acyl halides toward bases, is to be expected. However, that it is immediately reactive with piperidine and some of the lower fatty amines, but absolutely nonreactive, except at elevated temperatures, with other bases such as *o*-toluidine, etc., is irreconcilable with the usual conceptions of the ionic theory.[12] Moreover—since the reactions, here as before, were promoted

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[1] *Gazz. chim. ital.*, **44**, I, 443 (1914). Melts at 154° and 215°, respectively.

[2] Michler, *Ber.*, **9**, 711 (1875). Melts at 54°.

[3] Michler, *Ber.*, **9**, 398, 715 (1875); Gebhardt, *Ber.*, **17**, 2093 (1884); Steindorff, *Ber.*, **37**, 963 (1894); Reudler, *Rec. trav. chim.*, **33**, 35 (1914). Melts at 136°.

[4] Lellmann and Bonhöffer, *Ber.*, **20**, 2121 (1887). These melt at 155° and 176°, respectively.

[5] Michler, *Ber.*, **9**, 712 (1875); Kaufmann, *Ber.*, **14**, 2185 (1881). Melts at 80°.

[6] Michler, *Ber.*, **9**, 710 (1875); **12**, 1166 (1879); Strohmann, *J. prakt. Chem.*, [2] **55**, 264 (1897). Melts at 183°.

[7] Reudler, *Rec. trav. chim.*, **33**, 35 (1914).

[8] THIS JOURNAL, **33**, 1588, 1598 (1911); **34**, 286, 290, 1399, 1409 (1912); **36**, 2091 (1914).

[9] *Ibid.*, **34**, 1409 (1912).

[10] *Ibid.*, **36**, 2091 (1914).

[11] *Ibid.*, **36**, 2095 (1914).

[12] Evidences of certain nonionic organic reactions, as well as a more rational explanation of such reactions were previously given. *Am. Chem. J.*, **40**, 91–97 (1908); THIS JOURNAL, **31**, 1220–22 (1909); **33**, 1589–92 (1911); **34**, 287, 291, 1400–2, 1410–11 (1912); **36**, 2093–96 (1914).

by sunlight or by heat, and gave rise to additive products or dissociated molecules of such additive products—little dependence can be placed in the ionic theory to account for the mechanism of this type of reaction. However, the best evidence obtained to cast doubt on an ionic explanation of these reactions was found in the noninterchangeability[1] of parts of the additive, pentavalent-nitrogen compound. This phenomenon is illustrated by equations:

$$(1)\quad Ph_2NCO.Cl + H.NC_5H_{10} \longrightarrow Ph_2NCO.NC_5H_{10}.HCl$$

$$(2)\quad Ph_2NCO.NC_5H_{10} + HCl \longrightarrow \text{no reaction.}$$

That is, *diphenylureachloride easily adds one molecule of piperidine to form diphenylpiperidylurea hydrochloride, but this additive compound could not be formed by the addition of hydrogenchloride to diphenylpiperidylurea.*

An ionic explanation of the first reaction may be indicated in the equation:

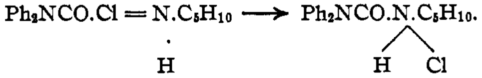
$$(3)\quad Ph_2NCO + Cl + H + NC_5H_{10} \longrightarrow Ph_2NCO.NC_5H_{10}.HCl$$

but, in the second reaction, similar ionic dissociation would be necessary, at least an ionic dissociation of hydrogen chloride[2] must be assumed:

$$(4)\quad HCl \longrightarrow H + Cl$$

Now since this last reaction in aqueous solutions is real and known, reaction (2) may be expected to yield the same product as in reaction (1) but, as a matter of fact, such product is not obtained, hence it may be concluded: (*a*) an ionic dissociation of hydrogen chloride does not take place in anhydrous ether solution and (*b*) an ionic explanation of the anomalous phenomena of Equations 1 and 2 is untenable. A more satisfactory explanation is expressed in the equation:

(5)



$$Ph_2NCO.Cl = \underset{\underset{H}{\cdot}}{N}.C_5H_{10} \longrightarrow Ph_2NCO.\underset{H\ \ Cl}{\underset{\wedge}{N}}.C_5H_{10}.$$

As enunciated before, the possibility of reaction in such cases is conditioned both by a tendency to coalesce and by a tendency to undergo molecular rearrangement.

In the first place, the tendency to coalesce by means of residual or partial valencies[3] involves different affinity constants of the reacting

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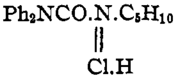
[1] This same noninterchangeability was previously observed with benzoyl chloride compounds. THIS JOURNAL, **36**, 2095 (1914).

[2] For a discussion and the literature of nonionic dissociation of hydrogen chloride see Mellor's "Statics and Dynamics," p. 290. Since neither the solvent nor sunlight promotes reaction (2) above, Baly's contention that these alone are the "openers of chemical reactivity" cannot hold, see THIS JOURNAL, **37**, 986 (1915).

[3] This assumption of preliminary molecular coalescence gathers support from consideration of the fact that only such *unsaturated* compounds react. See Nef, ***Ann.***, **298**, 202 (1898). It may be observed that application of the methylene theory of dissociation is entirely inapplicable to these reactions.

compounds, hence, as actually found, different speeds of reaction or complete inhibition of reaction are met with. Such varied systems of molecular aggregation may tend to undergo simple reversible reaction or a non-reversible molecular rearrangement. Thus, while the following may be formed:



$$\begin{array}{c} Ph_2NCO.N.C_5H_{10} \\ \| \\ Cl.H \end{array}$$

it is conceivable that the hydrogen atom is held by the chlorine atom so tenaceously[1] that molecular rearrangement is impossible.

Since energy is required to promote molecular rearrangements, it may be assumed that, owing to varied affinity constants, in different cases, more or less resistance or inertia will be met with before yielding the non-reversible, pentavalent-nitrogen, molecular compound. Now, as a matter of fact, such resistence or inertia is met with, for light or heat energy is required to start and advance certain reactions. For instance, some of the reactions take place at room temperature without applying direct sunlight; some are resistent to direct sunlight but may be promoted by moderate heat; finally, others are promoted only by extreme heat. Whatever may be the cause of these varied resistences in different cases, it must be observed that the ionic theory is helpless to account for the progress of the reaction.

A Case of "Steric Hindrance."

The toluidines showed different speeds of reaction with diphenylureachloride. When equimolecular quantities in equal ether volumes were prepared, the *p*-toluidine gave a rapid precipitation of wart-like masses of needles. The *m*-toluidine yielded a small quantity of ball-like masses which was slowly added to during 4 months' standing in sunlight. The *o*-toluidine yielded, after 5 months' standing in sunlight, mere traces of microscopical prismatic needles.

When heated on the water bath or in sealed tubes, ether solutions of diphenylureachloride and each of the toluidines yielded in a few hours the respective tolyldiphenylurea. The formation of such tolyldiphenylurea was easily observed to be most rapid with *p*-toluidine and least rapid with the *o*-toluidine. In other words, *p*-toluidine yields the tolyldiphenylurea by application of light or of heat. The *m*-toluidine yields the tolyldiphenylurea, slowly by application of light, but rapidly by application of heat. The *o*-toluidine yields the tolyldiphenylurea only by application of heat.

What is the cause of these resistences to the advance of the reactions, particularly in the case of *o*-toluidine? Of course, in the case of *o*-toluidine

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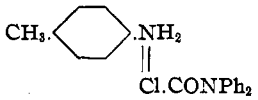
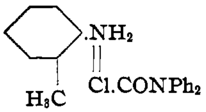
[1] It must be remembered that hydrogen chloride is not decomposed below 1000° by heat alone.

Victor Meyer's steric hindrance or retardation hypothesis[1] suggests itself; however, since the validity of this hypothesis has been questioned and disproven by Baly and Stewart,[2] Rosanoff and Prager,[3] and others, some other hypothesis must be sought, to explain the effects of heat and light on these reacting mixtures. Baly and Stewart[4] advance a hypothesis of "nascent carbonyl group," to account for differences of speed of reaction observed with various ketones. However, such a hypothesis is inapplicable to these reactions of diphenylureachloride since no "pseudo-nascent" hydrogen atom exists in the reacting substances, since the carbonyl group probably is unimportant in these reactions[5] and since no such tautomerism is involved.

However, if we assume in cases of *p*- and *o*-toluidines the following initial additions:





it is conceivable that the two complexes, while not necessarily possessing different steric hindrances, may possess different tendencies to rearrange. The centers of gravity of the two toluidine molecules being differently located may possibly influence the nitrogen affinities so that the nitrogen atom of *o*-toluidine does not exert sufficient attraction on the $CONPh_2$ group to bring about a molecular rearrangement.

This interesting phenomenon will be studied anew, especially by way of comparison of the effects of the toluidines on the following types of halogen derivatives:

H.X Bz.X Ac.X R.X $Ph_2CO.X$, etc.

Method of Study.

The anhydrous ether solutions of diphenylureachloride were treated with the respective anhydrous bases in equimolecular quantities. Bottles containing these mixtures were tightly corked and set aside for observation. Provided water was rigorously excluded and sufficient ether to dissolve the materials was used, the formation of a precipitate indicated either the additive compound, the hydrochloride of the original base, or a mixture of the two. Such precipitates always indicated a reaction, hence speeds of reaction could roughly be estimated by mere observation of the quantities of the precipitate. In some cases the ether solu-

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[1] *Ber.*, **27**, 510, 1580, 3146 (1894); **28**, 1254 (1895); **29**, 836 (1896); Kellas, *Z. physik. Chem.*, **24**, 221 (1897); Eckstand, *J. prakt. Chem.*, **38**, 267 (1888).

[2] *J. Chem. Soc.*, **89**, 489, 502, 514, 618 (1906).

[3] THIS JOURNAL, 30, 1895, 1908 (1908).

[4] *J. Chem. Soc.*, **89**, 491 (1906).

[5] Compare the action of alkyl halides on toluidines.

tions were heated in sealed tubes or under return condensers to promote reactions.

The precipitates were filtered off, washed with anhydrous ether and dried in desiccators. They were then either analyzed for chlorine to determine the general composition of the mixture, or were treated with water to hydrolyse and to dissolve the hydrochlorides. The aqueous solutions were extracted with ether, dried with calcium chloride, and concentrated. In this manner, the Ph_2NCO-substituted products of the bases were obtained pure.

The original ether solutions were shaken with dilute hydrochloric acid to remove unchanged bases; the ether extracts were dried with calcium chloride and concentrated. In this manner, mixtures of unchanged diphenylureachloride and the Ph_2NCO-substituted derivatives of the bases were obtained. When the former was nearly quantitatively transformed by the original reaction, or when the latter was difficultly soluble in ether, separations were easy. In cases of lower aliphatic bases, however, oily residues were obtained; these could not be made to yield pure Ph_2NCO-substituted products.

Primary Amines.

***p*-Toluidine.**—Diphenylureachloride in anhydrous ether was treated with a slight excess of *p*-toluidine and heated in a sealed tube at 70° for four hours. A mass of crystals formed. The mixture was treated with dilute hydrochloric acid so as to separate the unchanged toluidine; more ether was added and the mixture was thoroughly shaken. The ether solution was separated, dried with calcium chloride and concentrated, when transparent prismatic needles melting at 130° were obtained.

Calc. for $CH_3C_6H_4NH.CON(C_6H_5)_2$: N, 9.27%. Found. N, 9.47%.

p-Tolyldiphenylurea is very soluble in chloroform and ether, less soluble in alcohol and benzene and insoluble in water.

When 1 g. of diphenylureachloride and 0.4 g. of *p*-toluidine were brought together in anhydrous ether solutions, such solutions remained clear at first, then clouded, and during four months in direct sunlight, precipitated 0.2 g. of wart-like masses of needles. These were separated and were found to melt above 200°, to dissolve rapidly in water with a spinning motion.[1]

Calc. for $CH_3C_6H_4NH_2.(C_6H_5)_2NCOCl$: Cl, 10.47%.
Calc. for $CH_3C_6H_4NH_2.HCl$: Cl, 24.70%. Found: 17.45.

Evidently about 50% of the crystalline mixture was *p-tolyldiphenylurea hydrochloride*.

***m*-Toluidine.**—The equimolecular mixture was heated at 115° for four hours. Crystals melting at 130–180° were obtained. After treating

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[1] This Journal, 34, 1400 (1912); 36, 2093 (1914).

with dilute hydrochloric acid and extracting with ether, as with *p*-toluidine, transparent prismatic needles, melting at 125–126° were obtained.

Calc. for $CH_3C_6H_4NHCON(C_6H_5)_2$: N, 9.27%. Found: N, 9.16 and 9.51%.

m-Tolyldiphenylurea crystallizes from alcohol in transparent rhombic plates.

When 1 g. of diphenylureachloride and 0.4 g. of *m*-toluidine were brought together in ether solution, 0.2 g. of precipitate was formed after standing in four months' sunlight. The precipitate consisted of brown-red balls and gave the spinning motion on water.

o-Toluidine.—After heating the reacting mixture in a sealed tube at 115° for four hours, a crystalline mass, melting at 121–126°, was obtained. After purifying, rectangular plates and tufts of needles melting at 119° were obtained. Since they contained 9.35% of nitrogen, pure *o-tolyldiphenylurea* was obtained.

An ether solution of the reacting substances, exposed to four months' sunlight, yielded only 1 mg. of brown ball-like masses.

Phenylhydrazine.—Equimolecular quantities of diphenylureachloride and phenylhydrazine in anhydrous ether solution were heated under a return condenser for two hours. A crystalline mass, increasing on standing, was formed. These crystals, incompletely soluble in water and containing merely traces of chlorine, after treatment with water and recrystallization from absolute alcohol, gave rhombic plates which melted at 149–150°.

Calc. for $C_6H_5NHNHCON(C_6H_5)_2$: N, 13.86%. Found: N, 13.92%.

That this is *1,4,4-triphenylsemicarbazide* is concluded from a comparison of melting points. Rape and Labhardt[1] prepared 2,4,4-triphenylsemicarbazide, melting at 128°. H. Richter[2] prepared 1,1,4-triphenylsemicarbazide, needles melting at 193°. Therefore the indicated structure is the most probable.

When 1 g. of diphenylureachloride and 0.47 g. of phenylhydrazine were permitted to stand in anhydrous ether in sunlight for two months, 0.45 g. of a crystalline mass, melting[3] at 227° and containing 7.15% of chlorine, was obtained.

Calc. for $C_6H_5N_2H_3.HCl$: Cl, 24.53%.
Calc. for $(C_6H_5N_2H_3)_2HCl$: Cl, 14.03%.
Calc. for $C_6H_5N_2H_3.(C_6H_5)_2NCOCl$: Cl, 10.14%.

That the mixture contained 1,4,4-triphenylsemicarbazide or its *hydrochloride* is evident.

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[1] *Ber.*, 33, 247 (1900).

[2] Dissertation.

[3] Phenylhydrazine forms two hydrochlorides: $C_6H_5N_2H_3.HCl$, melting at 240° (Broche, *J. prakt. Chem.*, [2] 50, 114 (1894)) or at 243–246° (Autenrieth, *Ber.*, 29, 1656 (1896)); $(C_6H_5N_2H_3)_2HCl$, melting at 225° (Allain le Canu, *Compt. rend.*, 129, 105 (1899)); (Schmitz and Dumont, *Chem. Ztg.*, 21, 511).

***p*-Tolylhydrazine.**—Only a little precipitate was formed in two months.

Diphenylhydrazine (asym.).—Similar results.

Benzylphenylhydrazine (asym.).—After heating for 20 hours under return condenser, a considerable quantity of transparent crystals was obtained.

α-Naphthylamine.—A heavy precipitate containing a dye was obtained in direct sunlight.

Benzidine.—Sheaves of needles.

***p*-Aminophenol.**—Heating for 4 hours at 200° yielded a blue-black dye.

***o*-Chloroaniline.**—In sunlight for two months, a little gray precipitate was obtained; heated for 4 hours at 200°, a dark-brown solid was obtained.

***p*-Bromoaniline.**—Two months' direct sunlight gave a quantity of wedge-shaped crystals.

***p*-Anisidine.**—Heating for 4 hours at 200° yielded a deep-red, gummy oil.

Isobutylamine.—Sheaves of needles; a refractory oil.

Hexylamine.—Crystals softening at 183° and melting at 230°; original ether solution yielded a refractory oil.

Heptylamine.—A refractory oil.

Secondary Amines.

Piperidine.—A voluminous precipitate was formed at once. The crystals melted at 213°, and were soluble in water.

Calc. for $(C_6H_5)_2NCOCl.NC_5H_{11}$: Cl, 11.19%.
Calc. for $NC_5H_{11}.HCl$: Cl, 29.17%. Found: Cl, 15.70.

Therefore the crystals contained 75% of *diphenylpiperidylureahydrochloride*. Its presence was further indicated by spinning motions produced when the crystals were floated on water. After treating with water, etc., hexagonal and rhomboidal plates melting at 122° were obtained.

Calc. for $(C_6H_5)_2NCO.NC_5H_{10}$: C, 77.09%; H, 7.19%. Found: C, 77.17%; H, 7.31%.

Evidently *triphenylpiperidylurea* (*triphenylcyclopentamethyleneurea*) was formed. A toluene solution of this compound treated with a toluene solution of hydrogen chloride failed to yield any precipitate (of the hydrochloride) even though standing for five months in sunlight.

Diisobutylamine.—Rhombic plates melting at 240°; ether solution yielded hydroscopic needles melting at 60°.

Diisoamylamine.—Crystals melting at 147–230°; refractory oil.

Diphenylamine.—Amorphous precipitate.

Phthalimide.—Heating for two hours at 220° in xylene solution gave no evidence of a reaction.

Tertiary Bases.

Quinoline.—A quantity of amorphous precipitate.

Pyridine—A red-black precipitate.

Picoline.—A chocolate-colored precipitate.

Triethylamine.—Transparent prismatic needles.

Triisobutylamine.—Cubes and spindle-shaped crystals.

Triisoamylamine.—Minute needles.

Diethylaniline.—A small amount of dirty brown precipitate.

Tribenzylamine.—Cubic masses and boat-shaped prisms.

Some of these compounds will be further investigated.

Summary.

1. Diphenylureachloride reacts sluggishly with most bases; such reactions are promoted by sunlight or by heat.

2. Additive products are first formed; these yield by action of heat, water, etc., the Ph_2NCO-substituted products of the base.

3. Evidences for the nonionic nature of these reactions are given.

SEATTLE, WASHINGTON.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE COMPARATIVE BEHAVIOR OF THIOUREA AND UREA TOWARDS ACETIC ANHYDRIDE.

BY EDWARD F. KOHMANN.

Received July 5, 1915.

During the course of work in this laboratory, Professor Treat B. Johnson asked the author to determine whether there would be any formation of hydantoin if thiourea were used instead of ammonium thiocyanate in the reaction described by Johnson and Nicolet[1] for the preparation of 2-thio-3-benzoyl hydantoin.[2] Exactly the same conditions were employed, as well as the same reagents in the same proportions, as described for the preparation of the hydantoin, with the exception that the ammonium thiocyanate was replaced by an equivalent quantity of thiourea. Although no trace of a thiohydantoin was detected, a small amount of a substance was obtained which could be crystallized from water or alcohol in the form of colorless slender prisms. As this substance had a melting point of 165° it was concluded that it must be acetyl thiourea. In order to definitely establish this point it was decided to prepare acetyl thiourea for comparison and the method of Nenki[3] with slight modifications, was adopted.

Nenki assigned to this derivative a melting point of 11.5° which he

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[1] THIS JOURNAL, 33, 1973 (1911); *Am. Chem. J.*, 49, 202 (1913).

[2] A discussion of this reaction and its application with anhydrides other than acetic will follow in a future paper by Bernard H. Bailey.

[3] *Ber.*, 6, 599 (1873).