benzotriazole in 20 ml. of 3 *N* hydrochloric acid was refluxed for 2 hours. On cooling, 775 mg. of the hydrochloride of 5-amino-6-methoxybenzotriazole separated. After recrystallizing twice from hot water, the free base was obtained by adding aqueous ammonia to a hot concentrated aqueous solution of the hydrochloride. Recrystallized from water, m.p. 157–158°.

Anal. Calcd. for $C_7H_8ON_4$: C, 51.22; H, 4.88; N, 34.15. Found: C, 51.46; H, 4.93; N, 34.40.

4-Amino-5-methoxybenzotriazole (VI).—1-Acetyl-5-methoxybenzotriazole was nitrated according to Fel'dman and Usovskaya.[2] The nitro compound had m.p. 256–257° (lit. m.p. 233–234°). A suspension of 584 mg. (3 mmoles) of the nitro compound and 100 mg. of 10% palladium-on-carbon in 100 ml. of ethanol was stirred for 4 hours in the presence of hydrogen at atmospheric pressure. The catalyst was removed and the filtrate evaporated to dryness. The residue (482 mg.) was recrystallized from 25% ethanol (Nuchar). The 4-amino-5-methoxybenzotriazole separated as dark red needles melting at 202–203°.

Anal. Calcd. for $C_7H_8ON_4$: C, 51.22; H, 4.88; N, 34.15. Found: C, 51.42; H, 4.80; N, 34.12.

Acknowledgment.—This investigation was aided by grants from the American Cancer Society and the Damon Runyon Memorial Fund.

NEW YORK 32, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Dimeric Olefins *versus* Amines from α-Aryl Alkyl Halides with Alkali Amides in Liquid Ammonia. Intermediate Dimeric Halides and Their Dehydrohalogenation. Imines from Amines[1]

BY CHARLES R. HAUSER, WALLACE R. BRASEN, PHILIP S. SKELL, SIMON W. KANTOR AND ALEX E. BRODHAG

RECEIVED SEPTEMBER 29, 1955

Benzyl and benzhydryl chlorides and 9-chlorofluorene are converted to dimeric olefins by alkali amides in liquid ammonia, whereas 2,4,6-trimethylbenzyl chloride yields the corresponding amine. α-Phenylneopentyl bromide forms the corresponding amine, imine and saturated dimeric hydrocarbon. The formation of dimeric olefins is resolved into the self-alkylation of the halide and the dehydrohalogenation of the resulting intermediate dimeric halide. The self-alkylation of benzyl and benzhydryl chlorides furnishes a good method for the synthesis of α,β-diphenylethyl and α,α,β,β-tetraphenylethyl chlorides, respectively. Imines are obtained from amines in two ways. Mechanisms for these various reactions are considered.

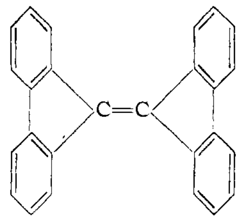
It has long been known that certain halides having a relatively reactive α-hydrogen and no β-hydrogen are converted by bases to dimeric olefins. For example, *o*- or *p*-nitrobenzyl chloride is converted by alcoholic potassium hydroxide to a mixture of the *cis*- and *trans*-nitrostilbenes.[2] More recently Bergstrom and Fernelius[3] reported that even benzyl chloride exhibits this type of reaction to form stilbene with potassium amide in liquid ammonia, while Kharasch and co-workers[4] obtained a quantitative yield of this dimeric olefin with sodium amide in this medium (equation 1). The latter workers also showed that certain other halides, including allyl[5] and methylallyl[6] chlorides, react similarly.

$$2C_6H_5CH_2Cl \xrightarrow[\text{liq. } NH_3]{NaNH_2} \underset{\text{I}}{C_6H_5CH{=}CHC_6H_5} \qquad (1)$$

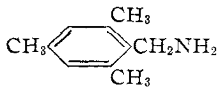
In the present investigation a study of the reactions of certain α-aryl alkyl halides with alkali amides in liquid ammonia was made. It was found that, similar to benzyl chloride, benzhydryl chloride and 9-chlorofluorene produce with sodium amide or potassium amide good yields of the dimeric olefins, II and III,[7] respectively. Moreover, a mixture of benzhydryl chloride and methyl iodide gave the mixed dimeric olefin IV. However, 2,4,6-trimethylbenzyl chloride formed only the corresponding amine V, while α-phenylneopentyl bromide yielded several products including the corresponding amine, imine and the saturated dimeric hydrocarbon VI. Small amounts of imine were obtained also with benzyl chloride and the other halides. The yields of products are summarized in Table I.

$$(C_6H_5)_2C{=}C(C_6H_5)_2$$
II

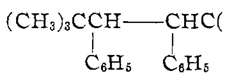
$$(C_6H_5)_2C{=}CH_2$$
IV



III



V



$$(CH_3)_3C\underset{C_6H_5}{CH}\text{——}\underset{C_6H_5}{CH}C(CH_3)_3$$
VI

The reactions listed in Table I were generally carried out by adding the halide to one to two molecular equivalents of the alkali amide. A more thorough study with benzhydryl chloride showed

---

(1) Supported by the Office of Ordnance Research, U. S. Army, and by the Office of Naval Research.

(2) C. A. Bischoff, *Ber.*, **21**, 2072 (1888); P. Walden and A. Kernbaum, *ibid.*, **23**, 1958 (1890).

(3) F. W. Bergstrom and W. C. Fernelius, *Chem. Revs.*, **20**, 435 (1947).

(4) M. S. Kharasch, W. Nudenberg and E. K. Fields, THIS JOURNAL, **66**, 1276 (1944).

(5) M. S. Kharasch and E. Sternfeld, *ibid.*, **61**, 2318 (1939).

(6) M. S. Kharasch, W. Nudenberg and E. Sternfeld, *ibid.*, **62**, 2035 (1940).

(7) This dimeric olefin has been obtained in unreported yield from 9-bromofluorene and alcoholic potassium hydroxide (J. Thiele and A. Wanscheidt, *Ann.*, **376**, 278 (1910)) and in 40% yield from 9-chlorofluorene and liquid ammonia at room temperature (L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 379 (1946)).

TABLE I

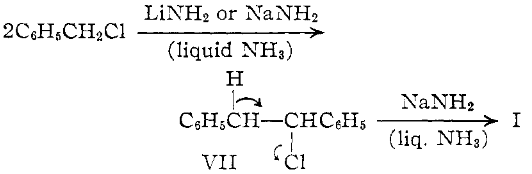
DIMERIC OLEFINS AND OTHER PRODUCTS FROM HALIDES AND ALKALI AMIDES IN LIQUID AMMONIA

Alkyl chloride	Alkali amide	Dimeric product	Yield, %	Other products	Yield, %
Benzyl	$NaNH_2$	*trans*-Stilbene (I)	95	Benzaldehyde imine	3
Benzhydryl	$NaNH_2$ or KNH_2	Tetraphenylethylene (II)	75–93	Benzophenone imine	Trace
9-Fluorenyl	KNH_2	Di-biphenyleneëthylene (III)	90	Fluorenone imine	9
Benzhydryl and methyl[a]	KNH_2	1,1-Diphenylethylene (IV)	40	....	...
2,4,6-Trimethylbenzyl	$NaNH_2$ or KNH_2	....	0	2,4,6-Trimethylbenzylamine (V)	80
α-Phenylneopentyl[b]	KNH_2	α,α'-Di-*t*-butyldibenzyl (VI)	14–27	Pivalophenone imine	9–11
				α-Phenylneopentylamine	0–28
				Neopentylbenzene(?)	18–23

[a] The iodide was used. [b] The bromide was used.

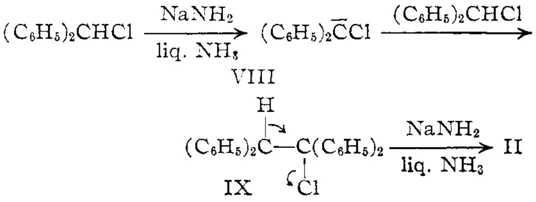
that the yield of the dimeric olefin II is dependent on the mode of addition and on the proportions of reactants. The best yield (93%) of pure product (white) was obtained by slowly adding potassium amide in liquid ammonia to a molecular equivalent of the halide in a mixture of liquid ammonia and ether (inverse addition procedure). When the halide was added to an equivalent of the reagent in the usual manner, the yield was 75–85%, and an appreciable amount of an unidentified yellow product was formed. This mode of addition produced mainly the yellow product when two equivalents of the reagent were employed and the halide added very slowly.

Actually the conversions of benzyl and benzhydryl chlorides to dimeric olefins I and II, respectively, were each resolved into two consecutive reactions. The first reaction involves the self-alkylation of the halide to form the corresponding dimeric halide, and the second, dehydrohalogenation (β-elimination) to give the dimeric olefin. For example, the addition of lithium amide or sodium amide in liquid ammonia to three molecular equivalents of benzyl chloride in liquid ammonia and ether at −70°, produced a 74–79% yield of dimeric halide VII, which on further treatment with the reagent gave a 90% yield of stilbene (equation 2). Even when the halide was added to sodium amide in the usual manner, the dimeric halide VII was obtained in 20–25% yield along with a 40–50% yield of stilbene.



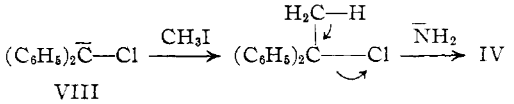
$$2C_6H_5CH_2Cl \xrightarrow[\text{(liquid NH}_3\text{)}]{\text{LiNH}_2\text{ or NaNH}_2} \underset{\text{VII}}{C_6H_5\overset{H}{C}H—\underset{Cl}{C}HC_6H_5} \xrightarrow[\text{(liq. NH}_3\text{)}]{NaNH_2} \text{I} \quad (2)$$

Similarly a 60% yield of dimeric halide IX was obtained from the theoretical amounts of benzhydryl chloride and sodium amide (inverse addition), and subsequently converted in 90% yield to tetraphenylethylene by further treatment with the reagent (equation 3). Evidence that the self-alkylation reaction involves the intermediate formation of carbanion VIII is the production of a transient red-orange color[8] as the reagent was added to two equivalents of the halide to form the colorless dimeric halide IX.



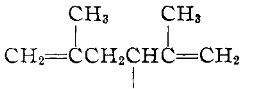
$$(C_6H_5)_2CHCl \xrightarrow[\text{liq. NH}_3]{NaNH_2} \underset{\text{VIII}}{(C_6H_5)_2\bar{C}Cl} \xrightarrow{(C_6H_5)_2CHCl} \underset{\text{IX}}{(C_6H_5)_2\overset{H}{C}—\underset{Cl}{C}(C_6H_5)_2} \xrightarrow[\text{liq. NH}_3]{NaNH_2} \text{II} \quad (3)$$

Presumably the formation of the mixed dimeric olefin IV from benzhydryl chloride and methyl iodide involves the methylation of carbanion VIII to form a mixed dimeric halide which undergoes dehydrohalogenation (equation 4).



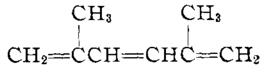
$$\underset{\text{VIII}}{(C_6H_5)_2\bar{C}—Cl} \xrightarrow{CH_3I} (C_6H_5)_2\overset{H_2C—H}{C}—Cl \xrightarrow{\bar{N}H_2} \text{IV} \quad (4)$$

The analogous alkylation–dehydrohalogenation sequence with methylallyl chloride and sodium amide has been demonstrated by Kharasch and coworkers.[6] Thus, they isolated dimeric halide X in low yield (inverse addition procedure), and showed that it produced dimeric olefin XI on further treatment with the reagent.[9]



$$CH_2{=}\overset{CH_3}{C}CH_2CH\overset{CH_3}{\underset{Cl}{C}}{=}CH_2$$

X



$$CH_2{=}\overset{CH_3}{C}CH{=}CH\overset{CH_3}{C}{=}CH_2$$

XI

Also, a similar sequence has been suggested by Kleucker[10] and Hahn[11] for the alkaline conversions of 9-chlorofluorene and *p*-nitrobenzyl chloride to dimeric olefin III and *p,p'*-dinitrostilbene, respectively. However, no experimental evidence was presented.[12]

The present preparations of dimeric halides of IX and VII furnish a convenient method for the synthesis of these compounds. Although the latter halide has been obtained in equally good yield (81%) by the action of thionyl chloride on the corresponding carbinol,[13] the analogous reaction with carbinol XII apparently has not been realized satisfactorily. We have observed that, even under relatively mild conditions, this carbinol is largely converted by thionyl chloride to tetraphenylethyl-

---

[8] This color was similar to that characteristic of diphenyl methide ion; see R. S. Yost and C. R. Hauser, THIS JOURNAL, **69**, 2325 (1947).

[9] A similar dimeric halide was obtained with allyl chloride, but it produced a tetramer instead of the dimeric olefin on further treatment with the reagent; see reference 6.

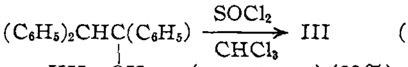
[10] E. Kleucker, *Ber.*, **62B**, 2587 (1929).

[11] G. Hahn, *ibid.*, **62B**, 2485 (1929).

[12] Other early workers considered that these reactions involved the α-elimination of hydrogen halide to form a diradical which dimerized; A. Michael, THIS JOURNAL, **42**, 820 (1920); E. Bergmann and J. Hervey, *Ber.*, **62B**, 893 (1929); C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 709 (1930).

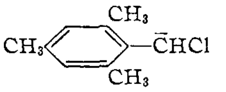
[13] C. R. Hauser, S. W. Kantor and W. R. Brasen, THIS JOURNAL, **75**, 2660 (1953).

ene (equation 5). Halide IX has been reported to be formed by the Friedel–Crafts type of reaction of benzene with chloral hydrate.[14] It should be mentioned that halide IX readily undergoes dehydrochlorination at 60° or above.

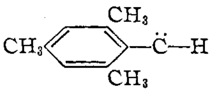


$$\underset{\text{XII}}{}\ (C_6H_5)_2CH\underset{\displaystyle OH}{\underset{|}{C}}(C_6H_5) \xrightarrow[\text{CHCl}_3]{\text{SOCl}_2} \text{III} \quad (\text{room temp.})\ (83\%) \qquad (5)$$

The fact that, in contrast to benzyl chloride, 2,-4,6-trimethylbenzyl chloride fails to undergo self-alkylation to form the dimeric olefin (see Table I) is not surprising since the α-carbon at which alkylation would occur is relatively hindered. The reaction of this halide with the amide ion to form amine V might involve either the SN2 type of displacement or the α-elimination of hydrogen chloride to form diradical or carbene XIV which adds ammonia. Carbanion XIII would be the precursor to carbene XIV. The reaction does not involve solvolysis (SN1) since, in a blank experiment with ammonia alone, the halide was recovered. Moreover, when 11 mole per cent. of amide was used only a 10% yield of amine V was obtained. The fact that a transient purple color is produced on adding the halide to the reagent suggests the intermediate formation of carbanion XIII and/or carbene XIV.



XIII



XIV

Since the related benzyl carbanion appears to be colorless (see Experimental), it seems unlikely that carbanion XIII furnishes the color. The *o*- and *p*-methyl groups might be expected to facilitate the release of chloride ion from carbanion XIII to form the carbene, although this effect is not sufficient to cause the neutral halide molecule to undergo solvolysis under the conditions employed.

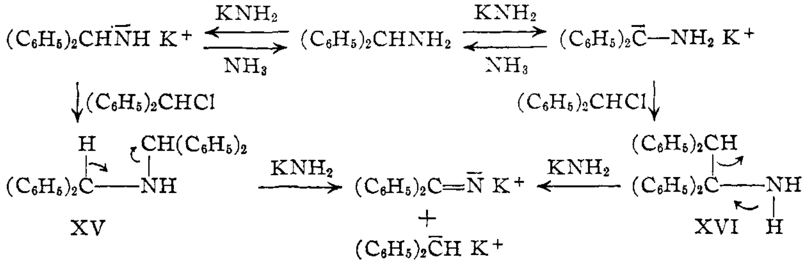
The analogous α-elimination of hydrogen chloride to form an intermediate carbene evidently occurs in the alkaline hydrolysis of chloroform[15] and in the reaction of chloroform with olefins in the presence of a base.[16] Also, α-eliminations accompanied by rearrangement are well known.[17]

The observation that three products and a fourth unidentified compound were formed with α-phenylneopentyl bromide (Table I) is of interest. However this reaction requires further study particularly with regard to the formation of the saturated dimer.[18]

It should be mentioned that the imines, which were obtained in small amounts from most of the halides studied (Table I), were readily isolated as the 2,4-dinitrophenylhydrazones of the corresponding aldehydes or ketones which were produced by hydrolysis of the imine hydrochlorides. The imines presumably arose from amines as considered below.

Imines from Amines.—Certain amines were found to be converted to the corresponding imines merely on standing with potassium amide in liquid ammonia under nitrogen. Thus, 9-aminofluorene, benzhydrylamine and benzylamine gave the corresponding imines in yields of 47, 3 and 0.5%, respectively. In the first and last cases, the reaction was stopped after one hour, and in the second case, after only 15 minutes. No other product was found, the balance of the original amine being recovered. Evidently the carbanion, the presence of which was indicated by deeply colored solutions in the first and second cases, underwent dehydrogenation, perhaps by the β-elimination of hydride ion. Air oxidation, which has been observed[19] with certain carbanions, was avoided by the use of nitrogen, while oxidation by the trace of ferric ion employed in the preparation of the potassium amide could hardly account for the 47% yield of imine from 9-aminofluorene.

A much larger conversion of benzhydrylamine to its imine, accompanied by the formation of other products, was realized by treating the amine with excess potassium amide in liquid ammonia, followed by benzhydryl chloride. This reaction produced the imine in 78% yield along with diphenylmethane (72%) and tetraphenylethane (16%). The two main products may have arisen through either nitrogen or carbon-alkylation of the anion of benzhydrylamine as indicated below,[20] while the tetraphenylethane may have been formed by subsequent coupling of the resulting potassium diphenylmethide with the original benzhydryl chloride.



Intermediate XV, which would have resulted from the nitrogen-alkylation, was prepared and shown to undergo with potassium amide the β-elimination indicated to form benzophenoneimine and diphenylmethane. The imine was isolated as benzophenone (73%), and the hydrocarbon, as its carbonation product diphenylacetic acid (80%). Although the β-elimination represented for intermediate amine XVI[21] from the carbon-alkylation was not independently established (because of the difficulty of preparing this compound by the usual

---

[14] M. Van Laer, *Bull. soc. chim. Belg.*, **28**, 346 (1919).

[15] J. Hine, THIS JOURNAL, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[16] W. von E. Doering and A. K. Hofmann, *ibid.*, **76**, 6162 (1954).

[17] See C. R. Hauser, *ibid.*, **62**, 933 (1940).

[18] This study is being made by Dr. P. S. Skell of the Pennsylvania State University.

[19] See C. B. Wooster and J. G. Dean, THIS JOURNAL, **57**, 113 (1935).

[20] See C. R. Hauser, I. C. Flur and S. W. Kantor, *ibid.*, **71**, 294 (1949).

[21] Pinck and Hilbert suggested an intermediate analogous to XVI leading to the formation of fluorenone imine and fluorene in the reaction of 9-chlorofluorene with ammonia at room temperature (see reference 7).

methods), such a reaction might be expected since the corresponding carbinol, $\alpha,\alpha,\beta,\beta$-tetraphenylethanol, has been shown by other workers[22] to undergo an analogous β-elimination with alcoholic potassium hydroxide to form benzophenone and diphenylmethane.

Experimental[23]

Dimeric Olefins I, II and III, and Imines from Halides with Alkali Amides. (A) General Procedure.—Sodium amide[24] or potassium amide[8] (0.1–0.2 mole) in 200–400 ml. of liquid ammonia was prepared. To the stirred suspension or solution was added during 5–10 minutes, 1–2 molecular equivalents of the halide in 75–100 ml. of dry ether, and the stirring continued for one hour. The reaction mixture was decomposed with excess solid ammonium chloride, and after the ammonia had evaporated, water and ether or benzene were added. The organic layer was washed with water, dilute hydrochloric or phosphoric acid, and again with water. After drying and removing the solvent, the residual dimeric olefin crystallized. The crude product (95%) from benzyl chloride was recrystallized once from methanol to give stilbene, m.p. 120–122°, reported m.p. 124.[25] The crude yellow product (80–90%) from benzhydryl chloride was recrystallized from benzene–methanol to give tetraphenylethylene (II), m.p. 219–222°, reported m.p. 223–224°.[26] Samples of this olefin were ozonized to form benzophenone and brominated to give the tetrabromide,[27] m.p. and mixed m.p. 248°. The crude product (90%) from 9-chlorofluorene was recrystallized three times from chloroform–methanol to give dibiphenylene-ethylene (III), m.p. 185–187°, reported m.p. 187°.[28]

The acid extracts from the reaction mixtures usually were allowed to stand until the imine salt had hydrolyzed (cloudiness), the resulting aldehyde or ketone then being isolated as the 2,4-dinitrophenylhydrazone. On extracting the reaction mixture from 9-chlorofluorene with hydrochloric acid, the imine salt precipitated, and was removed and hydrolyzed to form fluorenone (9%), m.p. 81–82°, reported m.p. 83–83.5°.[29]

When a solution of 0.25 mole of benzhydryl chloride in 50 ml. of ether was added during 35 minutes to a stirred solution of 0.25 mole of potassium amide (to produce a red-orange color that faded to yellow as the last of the halide was added), there was obtained a yellow product from which a 75% yield of slightly yellow tetraphenylethylene, m.p. 220–221°, was isolated by two recrystallizations from benzene and acetone as described below under (B).

When this last reaction was repeated employing 0.25 mole of potassium amide and 0.125 mole of benzhydryl chloride, the only product isolated was an unidentified bright yellow solid (7 g.), m.p. 120–121°.

(B) Inverse Addition Procedure. Tetraphenylethylene (II) from Benzhydryl Chloride.—The apparatus consisted of two, one-liter, standard taper, three-necked round-bottomed flasks. The bottom of the special upper flask was equipped with a bent glass tube terminating in a male standard taper joint seated in one of the side necks of the lower flask. This connecting tube could be opened or closed by a 6-mm. stopcock. Each flask was fitted with a mechanical stirrer and condenser. A glass stopper closed the third neck of the upper flask.

Potassium amide (0.25 mole) in 300 ml. of liquid ammonia was prepared in the upper flask and added during 10 minutes to a rapidly stirred suspension[30] of 50.75 g. (0.25 mole) of benzhydryl chloride in 50 ml. of dry ether and 300 ml. of liquid ammonia contained in the lower flask. During the addition, each portion of the amide solution imparts to the reaction mixture a red-orange color which fades to gray after a few seconds. The final gray suspension was heated on the steam-bath to remove ammonia, and 500 ml. of 2 *M* hydrochloric acid was added. The ether was then removed on the steam-bath and the resulting aqueous suspension filtered. The solid was washed with 2 *M* hydrochloric acid, followed by water, dried and recrystallized in the following manner. It was dissolved in 200 ml. of hot benzene and, after filtering, the solution was diluted with 120 ml. of acetone. The volume was then reduced to approximately 200 ml. by heating on the steam-bath. The process of adding acetone and reducing the volume was repeated twice. After most of the benzene had been removed in this way, the resulting acetone suspension was diluted with 200 ml. of methanol and the volume again reduced to 200 ml. The mixture was chilled, the solid collected on a filter, and washed with methanol to give 38.7 g. (93%) of white tetraphenylethylene, m.p. 221–221.5°.

Mixed Dimeric Olefin IV from Benzhydryl Chloride and Methyl Iodide.—A solution of 0.10 mole each of benzhydryl chloride and methyl iodide in 75 ml. of dry ether was added to 0.11 mole of potassium amide in 200 ml. of liquid ammonia, and the reaction mixture worked up essentially as described above in the general procedure. The residue, obtained on removing the solvent from the ether extract of the reaction mixture, consisted of an unidentified solid and an oil which, on distillation, gave a 40% yield of 1,1-diphenylethylene (IV), b.p. 144–145° at 13 mm., reported b.p. 143–144° at 15 mm.[31] A sample of this olefin was oxidized with potassium permanganate to give benzophenone. Another sample was converted to diphenylvinyl bromide,[32] m.p. and mixed m.p. 50–51°.

Amine from 2,4,6-Trimethylbenzyl Chloride.—A solution of 0.10 mole of 2,4,6-trimethylbenzyl chloride[33] in 100 ml. of dry ether was added to 0.11 mole of potassium amide in 300 ml. of liquid ammonia essentially according to the general procedure described above. A transient purple color was produced until the last of the halide was added when a white precipitate remained. There was isolated an 80% yield of 2,4,6-trimethylbenzylamine (V), b.p. 98.5–100° at 6 mm., which readily absorbed carbon dioxide from the air. The amine was more readily isolated as its hydrochloride. The benzoyl derivative of the amine melted at 153–154°, reported m.p. 153.5–154°.[34]

The yield of amine V was approximately the same when the reaction was carried out similarly with a 10% excess of sodium amide, but when only 11 mole per cent. of sodium amide was employed, the yield was only 10%, 84% of the halide being recovered.

In a blank experiment, the halide was stirred with liquid ammonia for one hour after which 90% of the halide was recovered.

Products from α-Phenylneopentyl Bromide.—A solution of this halide in ether was added to two molecular equivalents of potassium amide in liquid ammonia (to produce an orange-red color) and, after stirring for 5 hours, the reaction mixture was worked up as described in the general procedure. The ether solution of the reaction products was extracted with 2 *M* hydrochloric acid, followed by water, then dried and the solvent removed. The neutral residue was distilled to give hydrocarbon, b.p. 66–68° at 12 mm. (apparently neopentylbenzene, 18–23%), leaving a solid residue which was recrystallized from methanol to give a 14–27% yield of α,α'-di-*t*-butyldibenzyl (VI), m.p. 180–181°. This melting point was not depressed by admixture with an authentic sample of this compound, m.p. 180–181°.[35]

Anal. Calcd. for $C_{22}H_{30}$: C, 89.8; H, 10.25. Found: C, 89.4; H, 10.50.

A sample of this hydrocarbon failed to undergo ozonization and it was recovered quantitatively.

The acid extract of the ether solution of the reaction products was allowed to stand until the imine had hydrolyzed

---

[22] C. F. Koelsch, This Journal, **53**, 1147 (1931); D. Y. Curtin and S. Leskowitz, *ibid.*, **73**, 2631 (1951).

[23] Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

[24] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., p. 122.

[25] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2079 (1938).

[26] J. Schmidlin, *Ber.*, **39**, 4203 (1907).

[27] See J. F. Norris, This Journal, **38**, 709 (1916).

[28] See Pinck and Hilbert, ref. 7.

[29] E. H. Huntress, E. B. Hershberg and I. S. Cliff, This Journal, **53**, 2720 (1931).

[30] Benzhydryl chloride, m.p. 20.5°, freezes in this solution.

[31] A. Stieglitz, *Ber.*, **55**, 2042 (1922).

[32] E. Hepp, *ibid.*, **7**, 1410 (1874).

[33] G. Vavon, J. Bolle and J. Calvin, *Bull. soc. chim. France*, [5] **6**, 1025 (1939).

[34] R. C. Fuson and J. J. Denton, This Journal, **63**, 655 (1941).

[35] This sample was kindly furnished by Professor A. H. Blatt of Queens College; see J. B. Conant and A. H. Blatt, *ibid.*, **50**, 556 (1928).

(became cloudy), and the resulting mixture was then extracted with ether. The ether solution gave, on distillation, a 9–11% yield of pivalophenone, which was identified as the oxime, m.p. and mixed m.p. 164–165°, reported m.p. 165–166°.[36] The acidic solution from which the ketone had been removed was made basic to give 0–28% yields of the α-phenylneopentylamine which was identified as the benzoyl derivative, m.p. and mixed m.p. 148–149°. The amine employed in the preparation of the benzoyl derivative used as the authentic sample in this mixed melting point determination was synthesized by the reduction of the oxime of pivalophenone.[36]

Dimeric Halide VII from Benzyl Chloride.—A solution of 381 g. (3.0 mole, 50% excess) of benzyl chloride in 100 ml. of dry ether and 500 ml. of liquid ammonia was placed in the lower flask (2 liter) of the apparatus described above for the Inverse Addition Procedure. This solution was cooled to −70° in a Dry Ice–acetone-bath, and a suspension of 1.0 mole of lithium amide[37] in 500 ml. of liquid ammonia was added during 15 minutes from the upper flask of the apparatus. No color was produced. The gray suspension was stirred for 15 minutes, and the cooling bath then removed. The ammonia was evaporated on the steam-bath, ether being added to keep the mixture fluid. Hydrochloric acid (2 *M*) was added and the ether layer washed twice with 6 *M* hydrochloric acid, followed by 10% sodium bicarbonate, and dried over calcium chloride. After removal of the solvent, the residue was distilled to give 154 g. (1.2 moles) of benzyl chloride, b.p. 66° at 20 mm., and 171 g. (78.6%) of α-chlorobibenzyl (VII), b.p. 110–111° at 0.4 mm.; reported b.p. 127–129° at 0.5 mm.[13] $n^{25}\text{D}$ 1.5815.

Anal. Calcd. for $C_{14}H_{13}Cl$: C, 77.60; H, 6.04; Cl, 16.36. Found: C, 77.82; H, 6.16; Cl, 16.49.

When the reaction was carried out as described above using sodium amide in place of lithium amide the isolation of the dimeric halide was complicated because of contamination with stilbene and high boiling material. In working up this reaction, the oil remaining after unreacted benzyl chloride had been removed was diluted with half its volume of 30–60° petroleum ether and cooled. The solid which crystallized from this solution was recrystallized from chloroform–methanol yielding 7 g. (8%) of stilbene, m.p. and mixed m.p. 121–122°. The mother liquor from the first crystallization was freed of solvent and distilled to yield 160 g. (74%) of α-chlorobibenzyl (VII), b.p. 124–126° at 1 mm., $n^{25}\text{D}$ 1.5825, and high boiling residue. Analysis of the halide indicated that it was contaminated with about 6% of stilbene.

When the dimerization of benzyl chloride was carried out by addition of the halide to a suspension of sodium amide or lithium amide the products were stilbene 40–50% and α-chlorobibenzyl 20–25%.

Dehydrohalogenation of VII.—A solution of 21.6 g. (0.1 mole) of VII in 50 ml. of anhydrous ether was added during 5 minutes to a suspension of 0.11 mole of sodium amide in 200 ml. of liquid ammonia. A purple color was produced. After stirring for 15 minutes ammonium chloride was added (color discharged) and the liquid ammonia evaporated. Ether and water were added and the ether layer washed with 2 *M* hydrochloric acid and 10% sodium bicarbonate. The solvent was removed and the solid residue crystallized from a mixture of benzene and 60–90° ligroin to yield 16.2 g. (90%) of stilbene, m.p. and mixed m.p. 120–121°.

Dimeric Halide IX from Benzhydryl Chloride.—A stirred suspension[30] of 100 g. (0.5 mole) of benzhydryl chloride in 300 ml. of dry ether and 300 ml. of liquid ammonia was cooled to −70°. To this was added, during 15 minutes, a suspension of 0.25 mole of sodium amide in 300 ml. of liquid ammonia as described above for VII. A transient red-orange color was produced during addition of the reagent. The resulting grayish mixture was stirred for one hour and the cooling bath removed to allow evaporation of the ammonia. Water was added to the thick suspension and the crude product was collected by filtration. After washing with ether the product was dried rapidly by drawing through it a stream of dry air. Recrystallization from toluene, taking care to keep the temperature of the solvent below 50°, gave 55 g. (60%) of pure 1,1,2,2-tetraphenylethyl chloride (IX).

Anal.[38] Calcd. for $C_{26}H_{21}Cl$: Cl, 9.61. Found: Cl, 9.62.

An attempt to determine the melting point of this halide resulted in its rapid dehydrohalogenation at about 60° to give tetraphenylethylene, m.p. 219–221°.

Dehydrohalogenation of IX.—The halide (9.2 g., 0.01 mole) was treated with sodium amide as described above for VII to give 7.5 g. (90%) of tetraphenylethylene, m.p. and mixed m.p. 221–221.5°.

Reaction of Carbinol XII with Thionyl Chloride.—A solution of 8.75 g. (0.025 mole) of 1,1,2,2-tetraphenylethanol (XII) in 30 ml. of chloroform was added to 30 ml. of thionyl chloride and the solution allowed to stand at room temperature for one hour. After pouring onto crushed ice the chloroform solution was separated, washed with water and diluted with three volumes of 30–60° petroleum ether to precipitate a white solid which was found to contain no halogen. Recrystallization gave 6.9 g. (83%) of tetraphenylethylene, m.p. 219.5–221°. A mixed melting point with a sample of tetraphenylethylene (m.p. 221–221.5°) was not depressed.

Imines from Amines by Means of Potassium Amide.—To a stirred solution of 0.2 mole of potassium amide in 200 ml. of liquid ammonia under nitrogen atmosphere was added a solution of 0.1 mole of 9-aminofluorene in 50 ml. of ether. The resulting red mixture was stirred for one hour. Ammonium chloride was added followed by water and shaken with 100 ml. of 2 *M* hydrochloric acid. The resulting precipitate of the imine hydrochloride was removed by filtration and hydrolyzed with hot water to give a 47% yield of fluorenone, m.p. 81–82°. The acid filtrate was made basic to recover 46% of 9-aminofluorene.

Similarly benzhydrylamine gave, within 15 minutes, a 3% yield of the corresponding imine which was isolated as benzophenone 2,4-dinitrophenylhydrazone, m.p. 240–240.5°, reported m.p. 238°.[39] Benzylamine gave, with sodium amide in liquid ammonia during one hour, a 0.5% yield of the imine isolated as benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 238–239°, reported m.p. 237°.[40]

Reaction of Benzhydrylamine with Potassium Amide and Benzhydryl Chloride.—To a stirred solution of 0.15 mole of potassium amide in 200 ml. of liquid ammonia under nitrogen atmosphere was added 9.15 g. (0.05 mole) of benzhydrylamine. After 10 minutes a solution of 10.14 g. (0.05 mole) of benzhydryl chloride in 100 ml. of anhydrous ether was added. The resulting mixture was stirred for one hour and worked up as described above in the general procedure. The ether extract of the reaction mixture was extracted twice with 2 *M* hydrochloric acid, the layers being separated immediately. Crystals separated in the combined acid extract, but they soon disintegrated producing a cloudy mixture, from which was obtained benzophenone, isolated as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 239–240°; yield 78% based on benzhydrylamine. The ether solution (after the acid extractions) was washed with water, dried over anhydrous potassium carbonate and the solvent distilled. The residue, containing crystals, was treated with a little absolute methanol, the crystals filtered off and washed with methanol. The solid was evidently tetraphenylethane (16%), m.p. and mixed m.p. 210–211° after two recrystallizations from chloroform–methanol, reported m.p. 211°.[41] A mixed melting point with tetraphenylethylene (m.p. 222–223°) was 191–217°. The methanol was distilled from the filtrate and the residue, which solidified in an ice-bath, was distilled giving diphenylmethane, b.p. 125–126° at 7.5 mm., reported b.p. 129° at 11 mm.,[8] yield, 72% based on benzhydryl chloride. A sample of this diphenylmethane was oxidized with chromic anhydride in anhydrous acetic acid to give benzophenone.

Similarly, the reaction of benzyl chloride (0.1 mole) and benzylamine (0.1 mole) with sodium amide (0.3 mole) was carried out under nitrogen atmosphere. The products were stilbene (95%), benzaldehyde imine (1.2%) and the benzylamine was recovered.

Dibenzhydrylamine (XV).—A solution of 24 g. (0.131 mole) of benzhydrylamine and 32.4 g. (0.131 mole) of benzhydryl bromide in 60 ml. of acetonitrile was heated for 2 hours on the steam-bath. A crystalline solid began to pre-

---

[36] A. Brodhag and C. R. Hauser, THIS JOURNAL, **77**, 3028 (1955).

[37] C. R. Hauser and W. H. Puterbaugh, *ibid.* **75**, 1068 (1953).

[38] This analysis was carried out gravimetrically in this Laboratory since a sample sent to a commercial laboratory decomposed in transit.

[39] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p. 256.

[40] See reference 39, p. 237.

[41] H. Biltz, *Ann. Chem. Justus Liebigs*, **296**, 221 (1897).

cipitate within 5 minutes. After standing overnight the mixture was poured into 6 *M* hydrochloric acid. The secondary amine (which does not form a hydrochloride in aqueous solution) was filtered, sucked dry and taken up in ether. Some of the solid, presumably benzhydrylamine hydrochloride, did not dissolve and was discarded. The solvent was removed, and the residue washed with methanol and recrystallized twice from acetone–methanol to yield 22.3 g. (49%) of dibenzhydrylamine, m.p. 138–139°, reported 136°.[42] Recrystallization from ethanol did not raise the melting point.

Anal. Calcd. for $C_{26}H_{23}N$: C, 89.35; H, 6.63; N, 4.01. Found: C, 89.75; H, 6.77; N, 3.92.

The picrate recrystallized from ethanol melted at 206–207° dec., reported 212°.[42]

Anal. Calcd. for $C_{32}H_{26}N_4O_6$: N, 9.68. Found: N, 9.60.

Reaction of XV with Potassium Amide.—Dibenzhydrylamine (7.98 g., 0.02 mole) and potassium amide (0.06 mole) in 300 ml. of liquid ammonia and 300 ml. of dry ether was stirred for 30 minutes (red-orange color) and ammonia was then removed on the steam-bath as 300 ml. of dry ether was added. Powdered Dry Ice was added, and after stirring for 30 minutes, water was added and the layers separated. The aqueous layer was acidified to precipitate diphenylacetic acid, which after recrystallization from methanol and water melted at 147–148°. A mixed melting point was the same, yield 3.2 g. (80%). The ethereal layer was extracted with 6 *M* hydrochloric acid and the acid solution warmed on the steam-bath for one hour to hydrolyze the imine hydrochloride. The resulting ketone was taken up in ether, recovered from this solvent and crystallized from 30–60° petroleum ether to give 2.65 g. (73%) of benzophenone, m.p. and mixed m.p. 47.5–48.5°.

DURHAM, NORTH CAROLINA

---

(42) S. Goldschmidt and L. Reichel, *Ann. Chem. Justus Liebigs*, **456**, 152 (1927).

[CONTRIBUTION NO. 185 FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS & CO.]

Relative Reactivity of the Isocyanate Groups in Toluene-2,4-diisocyanate

BY DONALD M. SIMONS AND ROBERT G. ARNOLD

RECEIVED JUNE 29, 1955

The greater reactivity of the *p*-isocyanate group in toluene-2,4-diisocyanate is demonstrated. 4-Methyl-3-nitro-, 2-methyl-5-nitro-, 3-amino-4-methyl- and 5-amino-2-methylcarbanilide have been prepared.

During the course of some work in this Laboratory it became desirable to demonstrate unequivocally which isocyanate group in toluene-2,4-diisocyanate (TDI) is the more reactive. Bayer[1] and Siefkin[2] state that an alkyl or alkoxy group *ortho* to an isocyanate exerts a rate-retarding effect but cite no experimental evidence.

Rate studies performed on *o*- and *p*-tolyl isocyanate–amine systems showed that *p*-tolyl isocyanate is the more reactive and one would be justified in suspecting that this is also true for the *p*-isocyanate group in TDI. However, to demonstrate the absence of any anomalous effects in TDI itself, the greater reactivity of the *p*-isocyanate group was demonstrated by the following procedure. TDI (one mole) was treated with aniline (one mole) in tetrahydrofuran solution and the residual isocyanate group then hydrolyzed with hydrochloric acid. Fractional recrystallization of the product gave 68% of theory of a compound which proved to be identical with an authentic sample of 3-amino-4-methylcarbanilide as judged by melting point, mixed-melting point and infrared spectra.

Experimental

Reaction of TDI and Aniline.—TDI (0.2018 mole) in one liter of anhydrous tetrahydrofuran was cooled to −25° and a solution of aniline (0.2017 mole) in 500 ml. of tetrahydrofuran (also cooled to −25°) added slowly with stirring. After the addition was complete the mixture was warmed to room temperature and allowed to stand overnight. The mixture was then poured into one liter of 6 *N* hydrochloric acid with sufficient cooling to keep the temperature at 25–30°. After standing for 3 hours the mixture was neutralized with potassium carbonate and the organic layer separated. (The potassium chloride concentration is high enough to salt out the tetrahydrofuran.) Removal of the solvent *in vacuo* gave 51.0 g. of solid. Repeated fractional recrystallization of this product from ethanol gave eventually two fractions of sufficient purity to identify.

	M.p., °C.	Mixed melting point[a]	Wt., g.	Nitrogen, %
Fract. A	198–199.5	197.5–198.5	22.7	17.5
Fract. B	193–195	193–195	10.3	17.1

[a] With an authentic sample of 3-amino-4-methylcarbanilide, m.p. 200–201°.

The infrared spectra of the two fractions were identical with that of an authentic sample of 3-amino-4-methylcarbanilide and were different from that of the isomeric 5-amino-2-methylcarbanilide. The combined weight of the two fractions represented a yield of 68%. The remaining 32% of the material consisted predominantly of a mixture of the two isomeric carbanilides which could not be separated readily.

3-Amino-4-methylcarbanilide and 5-Amino-2-methylcarbanilide.—These substances were prepared from the corresponding nitrotoluidines and phenyl isocyanate followed by hydrogenation.

The appropriate nitrotoluidine (0.20 mole) was dissolved in 300 ml. of dry dioxane, and phenyl isocyanate (0.20 mole) in 50 ml. of dioxane added. The solution was refluxed about 30 minutes, cooled and the product filtered off and recrystallized from alcohol–tetrahydrofuran. The nitro group was reduced by dissolving the carbanilide (15 g.) in 700 ml. of hot alcohol–tetrahydrofuran and hydrogenating at 60° with 200 lb. of hydrogen and about 5 g. of Raney nickel. After removal of the catalyst the product was obtained by evaporating part of the solvent *in vacuo* and cooling the residue in an ice-bath.

TABLE I

Carbanilide	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	M.p., °C.
4-Methyl-3-nitro-	$C_{14}H_{13}O_3N_3$	15.5	15.4	218–219
2-Methyl-5-nitro-	$C_{14}H_{13}O_3N_3$	15.5	15.7	[a]
3-Amino-4-methyl-	$C_{14}H_{15}ON_3$	17.4	17.3	200–201
5-Amino-2-methyl-	$C_{14}H_{15}ON_3$	17.4	17.0	>200[a]

[a] M.p. dependent upon rate of heating.

---

(1) O. Bayer, *Angew. Chem.*, **59**, 257 (1947).

(2) W. Siefkin, *Ann.*, **562**, 75 (1949).