3. *t*-Amylmagnesium chloride was treated with the following substances with the indicated results. (a) Methyl *i*-propyl ketone gave methyl-*i*-propylcarbinol, 50%, the condensation product 2,3,6-trimethyl-3-heptene-5-one, 35 and 2% recovered ketone, *cf.* 2 (k) above. (b) Diethylacetyl chloride gave 2-ethyl-1-butanol, 74%, 3,3-dimethyl-5-ethyl-4-heptanol, 7%, and other products as yet unidentified. (c) Diethylacetaldehyde gave the same alcohols in 67 and 21% yields. (d) Ethylbutylacetyl chloride gave 2-ethyl-1-hexanol, 74% and 3,3-dimethyl-5-ethyl-4-nonanol, 15%. (e) Trimethylacetyl chloride gave neopentyl alcohol, 97%. (f) Lauroyl chloride gave lauryl alcohol, 54%, and 3,3-dimethyl-4-pentadecanol, 17%. (g) Methyl-*t*-butylneopentylacetyl chloride gave methyl-*t*-butylneopentylacetylaldehyde, 78%, and 2,4,4-trimethyl-2-*t*-butyl-1-pentanol, 19%. (h) The aldehyde in (g) was reduced to the primary alcohol, 90%, on prolonged heating. (i) Ethylbutylacetic acid was not changed by prolonged treatment with a large excess of the Grignard reagent. (j) Cinnamaldehyde gave no cinnamyl alcohol. The 1:4 addition product, 4,4-dimethyl-3-phenylhexanal, was found in 10% yield. (k) Mesityl oxide gave a very unmanageable mixture containing unreacted material, methyl-*i*-butylketone, a C_{11} diolefin probably related to 2,4,5,5-tetramethyl-2-heptene-4-ol, impure 4-methyl-3-pentene-2-ol, and 4,4,5,5-tetramethyl-2-heptanone, 16%, formed by 1:4 addition. By the bromoform reaction this saturated ketone gave 3,3,4,4-tetramethylhexanoic acid. (l) Isobutyraldehyde gave isobutyl alcohol, 84%. (m) Isobutyryl chloride, on addition of the Grignard reagent, gave the isobutyrate of isobutyl alcohol, 44%. (n) Acetyl chloride in ethyl ether gave methyl *t*-amyl ketone, 9%, 3,4-dimethyl-3-pentene-2-one, 9%, but no mesityl oxide.

4. *i*-Butylmagnesium chloride and trimethylacetyl chloride gave neopentyl alcohol, 61%, and 2,2,5-trimethyl-3-hexanol, 26%. In a similar reaction the Grignard iodide gave complications.

5. Neopentylmagnesium chloride with trimethylacetyl chloride gave no more than a trace of reduction but gave 2,2,5,5-tetramethyl-3-hexanone in 87% yield.

6. Excess of magnesium in the action of *t*-butylmagnesium chloride with diethylacetyl chloride did not increase the reduction.

STATE COLLEGE, PENNSYLVANIA

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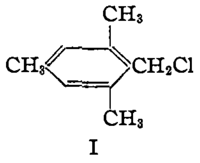
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

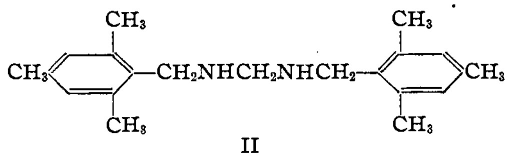
An Abnormal Reaction in the Sommelet Aldehyde Synthesis

BY REYNOLD C. FUSON AND J. J. DENTON

In a study of methods of making mesitaldehyde, hexamethylenetetramine was condensed with α^2-chloroisodurene (I) and the resulting quaternary ammonium salt decomposed in aqueous solution according to the procedure of Sommelet.[1] Instead of the expected aldehyde there was formed a white, solid base which proved to have the formula $C_{21}H_{30}N_2$. A Zerewitinoff determination showed the presence of two active hydrogen atoms. The most probable structure appeared to be that given in formula II.



I



II

Evidence has now been accumulated which establishes the correctness of this formula. The action of acetic anhydride yielded an acetyl derivative which was identified as N-α^2-isodurylacetamide ($CH_3CONHCH_2C_9H_{11}$). Similarly, benzoylation led to the formation of N-α^2-isodurylbenzamide ($C_6H_5CONHCH_2C_9H_{11}$). The structures of these two amides were confirmed by synthesis from the parent amino compound, α^2-isodurylamine ($C_9H_{11}CH_2NH_2$).

This amine (isolated as the hydrohalide) was prepared in three different ways. Mesitonitrile, made from bromomesitylene by the Rosenmund–

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(1) Sommelet, *Compt. rend.*, **157**, 852, 1443 (1913).

von Braun method,[2] gave a high yield of the amine when hydrogenated at high pressure in the presence of Raney nickel. This synthesis is remarkable in that it involves hydrogenation of a highly hindered nitrile. A second method was that of Delépine[3] which consisted in decomposing the quaternary ammonium salt from α^2-chloroisodurene and hexamethylenetetramine by means of alcoholic hydrogen chloride. Finally, α^2-chloroisodurene was transformed into the amine by the Gabriel phthalimide method. The N-α^2-isodurylphthalimide was hydrolyzed by heating with a mixture of hydrobromic acid, glacial acetic acid and acetic anhydride.

That the product obtained by the Sommelet procedure was in fact N,N'-di-α^2-isodurylmethanediamine (II) was proved by the discovery that it could be made readily by allowing either formaldehyde or hexamethylenetetramine to act upon the hydrochloride of α^2-isodurylamine. Moreover, hydrolysis of the diamine (II) with dilute hydrochloric acid gave formaldehyde (identified as its methone derivative) and the hydrochloride of α^2-isodurylamine.

While no satisfactory mechanism has been developed for the normal course of the Sommelet synthesis of aldehydes from the corresponding alkyl halides, it is clear that it involves at least one step which is inhibited by the mesityl radical.

Experimental

The Quaternary Ammonium Salt from Hexamethylenetetramine and α^2-Chloroisodurene.—A mixture of 25 g. of the chloride, 21 g. of the tetramine and 250 cc. of chloroform was heated under reflux for three hours. The mixture was cooled and the salt collected on a filter; yield, 44 g. Attempts to purify it by recrystallization were unsuccessful. Analysis showed the salt to be somewhat impure.

Anal. Calcd. for $C_{16}H_{25}N_4Cl$: Cl, 11.49. Found: Cl, 11.96.

Decomposition of the Salt

A. With Water.—A solution of 41.7 g. of the crude salt in 250 cc. of distilled water was heated under reflux for four hours. The N,N'-di-α^2-isodurylmethanediamine (II) was collected on a filter and recrystallized from alcohol; m. p. 151.5–152°; yield, 15.8 g.

Anal. Calcd. for $C_{21}H_{30}N_2$: C, 81.20; H, 9.75; N, 9.03, mol. wt., 310. Found: C, 81.64; H, 9.66; N, 8.83; mol. wt. (in boiling chloroform), 350. In the Zerewitinoff determination 0.1503 g. (0.5×10^{-3} mole) gave 1.1×10^{-3} mole of gas.

N,N'-Di-α^2-isodurylmethanediamine was also made by treating the hydrochloride of α^2-isodurylamine with formaldehyde. A mixture of 1.86 g. of the hydrochloride and 50 cc. of distilled water was heated until solution was effected. Then 1 cc. of concentrated ammonium hydroxide was added followed by 0.4 g. of formalin, which had previously been diluted to 50 cc. with distilled water. The mixture was heated under reflux for twelve hours and cooled. The yield of diamine was 0.8 g.; m. p. 151.5–152°.

Finally, the diamine was made by heating for two hours an aqueous solution of equimolecular amounts of the amine hydrochloride and hexamethylenetetramine.

Hydrolysis.—A mixture of 3 g. of the diamine, 25 cc. of concentrated hydrochloric acid and 75 cc. of distilled water was distilled slowly until 40 cc. of distillate had been collected. The distillate was poured into a solution of 2 g. of methone in aqueous alcohol buffered by sodium acetate. The methone derivative of formaldehyde crystallized from alcohol; m. p. 186–188°; yield, 0.8 g.

B. With Hydrochloric Acid.—A mixture of 15.4 g. of the salt, 200 cc. of alcohol and 30 cc. of concentrated hydrochloric acid was slowly evaporated almost to dryness on a steam cone. Alcohol and acid were added in the same amounts as before and the evaporation was repeated. This procedure was carried out a third time. The solid residue was washed thoroughly with 200 cc. of cold water to remove the ammonium chloride, collected on a filter and recrystallized twice from distilled water. This procedure gave 7 g. of α^2-isodurylamine hydrochloride in the form of long white needles.

Anal. Calcd. for $C_{10}H_{16}NCl$: N, 7.54; Cl, 19.12. Found: N, 7.12; Cl, 18.81.

N-α^2-Isodurylacetamide.—A solution of 3 g. of N,N'-di-α^2-isodurylmethanediamine in 30 cc. of acetyl chloride was heated under reflux for two hours, cooled and poured on ice. After being allowed to stand overnight the amide was collected on a filter, dried and recrystallized from alcohol; m. p. 186.5–187°. The yield was nearly quantitative.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.97; N, 7.33; mol. wt., 191.2. Found: C, 75.19; H, 8.79; N, 7.14; mol. wt. (in boiling chloroform), 191, 179.

N-α^2-Isodurylacetamide was also made from the hydrochloride of α^2-isodurylamine by treatment with acetic anhydride.

N-α^2-Isodurylbenzamide.—A mixture of 3 g. of N,N'-di-α^2-isodurylmethanediamine and 20 cc. of benzoyl chloride was heated for four hours between 120° and 150°. It was cooled and poured into dilute sodium carbonate solution. After the solution had been heated to destroy excess benzoyl chloride it was cooled and the amide collected on a filter. After treatment with decolorizing charcoal and two recrystallizations from alcohol, the product melted at 153.5–154°; yield, 4.3 g.

Anal. Calcd. for $C_{17}H_{19}NO$: C, 80.58; H, 7.57; N, 5.53. Found: C, 80.43; H, 7.74; N, 5.17.

The benzamide was also made from the amine hydrochloride and benzoyl chloride by the Schotten–Baumann method.

Mesitonitrile.—A mixture of 31.8 g. of bromomesitylene, 17.3 g. of cuprous cyanide and 20 cc. of dry pyridine was heated at 220–230° for eighteen hours. The hot mixture

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[2] *Cf.* Newman, THIS JOURNAL, **59**, 2472 (1937).

[3] Delépine, *Bull. soc. chim.*, [3] **13**, 355 (1895).

was poured into a dilute solution of ammonium hydroxide and allowed to stand. The crude solid was purified by further treatment with ammonium hydroxide and with decolorizing charcoal, and recrystallized from ligroin; m. p. 50–52°[4]; yield, 18.2 g.

α^2-Isodurylamine Hydrochloride

A. From Mesitonitrile.—A mixture of 10 g. of the nitrile, 130 cc. of absolute alcohol and 2 g. of Raney nickel was treated with hydrogen for about two hours at 150° and 2200 lb. pressure. After removal of the catalyst by filtration the solution was concentrated to a small volume and hydrochloric acid added. The amine hydrochloride crystallized from water in the form of long, white needles melting at 315°, with decomposition. The yield was nearly quantitative.

Anal. Calcd. for $C_{10}H_{16}NCl$: N, 7.54; Cl, 19.12. Found: N, 7.47; Cl, 19.21.

B. From Potassium Phthalimide and α^2-Chloroisodurene.—A mixture of 20 g. of the chloride and 33 g. of the potassium salt was heated for four hours at 170–180°. The solid product was digested with dilute sodium hydroxide, collected on a filter and washed with water until the wash water was no longer basic to litmus. The N-α^2-isodurylphthalimide was crystallized from glacial acetic acid and then from alcohol. It formed small white needles melting at 209.5–210°. The yield of once recrystallized material was 21 g.

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.14; N, 5.02. Found: C, 77.56; H, 6.41; N, 5.06.

Hydrolysis.—A mixture of 7.0 g. of N-α^2-isodurylphthalimide, 50 cc. of hydrobromic acid (sp. gr., 1.36), 40 cc. of glacial acetic acid and 10 cc. of acetic anhydride was heated under reflux for sixteen hours. The solid from the reaction mixture was collected on a filter and the filtrate was evaporated to a small volume. The solid which formed in the latter was combined with the main product and the resulting mixture was thoroughly washed with warm water. The solid residue was discarded and the aqueous solution was evaporated to a small volume. The α^2-isodurylamine hydrobromide separated from the aqueous solution in white needles; yield, 2.8 g. Benzoylation of this solid gave a compound causing no depression in the melting point of an authentic sample of N-α^2-isodurylbenzamide.

Summary

An attempt to prepare mesitaldehyde from α^2-chloroisodurene and hexamethylenetetramine by the method of Sommelet led to anomalous results. The product has been shown to be N,N′-di-α^2-isodurylmethanediamine ($C_9H_{11}CH_2$-$NHCH_2NHCH_2C_9H_{11}$).

URBANA, ILLINOIS RECEIVED DECEMBER 13, 1940

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[4] Küster and Stallberg, *Ann.*, **278**, 207 (1893).

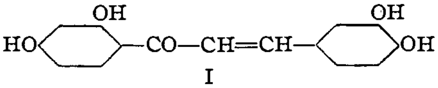
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Anthochlor Pigments. The Pigment of *Coreopsis Douglasii*

BY T. A. GEISSMAN

Certain yellow flowers, notably in the *Compositae*, are characterized by the fact that upon treatment with alkali (for example, by exposure to ammonia vapor) they turn red. The majority of yellow flowers are pigmented by carotenoids or flavone derivatives or mixtures of these[1] and give color changes with alkali which are generally no more than a deepening of the normal shade of yellow. The color change to red is characteristic of a class of pigments which has been termed "anthochlor"[1] and whose existence in a number of species of *Compositae* has been demonstrated by Gertz.[2] While information concerning the chemical constitution of the anthochlor pigments would be of great interest in connection with studies on the phytosynthetic and genetic relationships between the coloring matters of flowers, very little is known about them.

The yellow *Dahlia variabilis* is among the species shown by Gertz to contain anthochlor. Recently Price,[3] following the work of Schmid and his collaborators[4] who isolated apigenin from this flower, has shown that *Dahlia* contains the chalcone butein (I), possibly as a glycoside.[5]



I

Butein was first obtained by Perkin and Hummel[6] in the course of isolating butin (the isomeric flavanone) from the flowers of *Butea frondosa.*

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(1) Klein, *Sitzb. Akad. Wiss., Wien*, **129**, 341 (1920); **130**, 247 (1921).

(2) Gertz, *Kgl. Physiograf. Sällskap. Lund, Förh.*, **8**, 62, 71, 215 (1938); *C. A.*, **34**, 473 (1940).

(3) Price, *J. Chem. Soc.*, 1018 (1939).

(4) Schmid and Waschkan, *Monatsh.*, **49**, 83 (1928); Schmid and Seebald, *ibid.*, **60**, 32 (1932); Schmid and Hacheck, *ibid.*, **62**, 317 (1932).

(5) Klein ("Handbuch der Pflanzenanalyse," Julius Springer, Vienna, 1932, Bd. III/2; p. 858) designates apigenin as the anthochlor of *Dahlia*. Since apigenin is a typical flavone which in the free or glycosidic condition gives only yellow salts with alkalies and since butein gives a deep red coloration with alkalies such as is shown by the flowers themselves, it is clear that butein is the true anthochlor, as this term is used.

(6) A. G. Perkin and Hummel, *J. Chem. Soc.*, **85**, 1459 (1904).