[Contribution from the Chemical Laboratory of New York University]

Trimerization of Benzonitrile with Sodium

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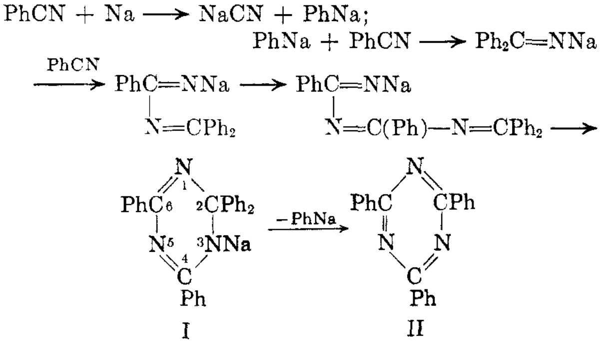
The formation of kyaphenin (2,4,6-triphenyl-s-triazine) by the action of sodium on benzonitrile has been reinvestigated. The yield of kyaphenin from 2,2,4,6-tetraphenyl-2,3-dihydrotriazine sodium salt by elimination of phenylsodium is significantly increased by treatment with carbon dioxide, sulfur dioxide, or benzonitrile. Methylation of 2,2,4,6-tetraphenyl-2,3-dihydrotriazine sodium salt yields two isomeric *N*-methyl derivatives. An attempt has been made to interrelate and interpret these reactions.

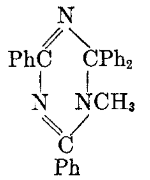
Benzonitrile may be trimerized to kyaphenin, 2,4,6-triphenyl-s-triazine (II) by the action of acids[2] or sodium.[3] While the acid trimerization can be explained simply, the reaction with sodium evidently proceeds in a more complex manner. Lottermoser[3] identified a tetraphenyldihydrotriazine (I, Na = H) as the main product, as well as sodium cyanide and small amounts of II, in the reaction of benzonitrile with sodium in boiling benzene. The initial stage of this reaction was clarified by Anker and Cook[4]; and Swamer, Reynolds, and Hauser[5] formulated the sodium trimerization as follows:

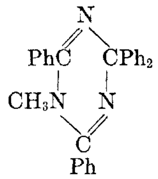


We have studied these reactions further, especially the reactions of I. The treatment of benzonitrile with sodium in boiling benzene for 4 hr. yielded 80–85% of I and 1–3% of II, in agreement with Lottermoser[3] except that the time required for complete reaction was greatly reduced by use of sodium dispersion. However, further heating in boiling benzene or at higher temperatures in other solvents did not result in improved yield of II, indicating that spontaneous elimination of phenylsodium does not occur under the conditions employed.

The yield of II was increased considerably by treatment of I with carbon dioxide or with sulfur dioxide (Table I). The simple assumption that this might be due to equilibrium shift by reaction with phenylsodium to form sodium benzoate or sodium benzenesulfinate is contradicted by the fact that treatment of I with carbon dioxide at elevated temperature under 100 atm. of carbon dioxide pressure prevented completely the formation of II beyond the 1–3% normally obtained in the absence of carbon dioxide.

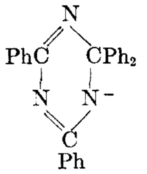
Treatment of I with methyl iodide yielded two isomeric *N*-methyl derivatives for which the structures 2,2,4,6-tetraphenyl-3-methyl-2,3-dihydro-1,3,5-triazine (III) and 2,2,4,6-tetraphenyl-5-methyl-2,5-dihydro-1,3,5-triazine (IV) are suggested. The

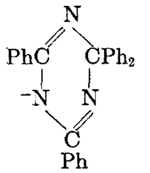

III, m.p. 191°

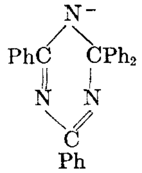

IV, m.p. 210°

evidence offered in support of the suggested structures, in addition to elementary analysis, molecular weight, and mixed melting point determinations is as follows: both show substantially zero value in determination of active hydrogen while I (Na = H) yielded one mole of methane in a control determination; ultraviolet absorption curves (Fig. 1) show significant differences and, for III, maxima indicating conjugation of double bonds, presumably to be ascribed to the *N*-ring. The participation of both nitrogen atoms in alkylation of analogous cyclic amidines has been reported, for example, in the case of 4(5) methylimidazole, which yields 1,4- and 1,5-dimethylimidazoles on treatment with methyl iodide.[6]

It seems therefore that the anion of I may be represented as a resonating system (V a,b,c) with


Va


Vb


Vc

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[1] Present address: American Cyanamid Co., Stamford, Conn.

[2] A. Cook and D. Jones, *J. Chem. Soc.*, 278 (1941).

[3] A. W. von Hofmann, *Ber.*, 1, 198 (1868); A. Lottermoser, *J. prakt. Chem.*, 54, 132 (1896).

[4] R. Anker and A. Cook, *J. Chem. Soc.*, 323 (1941).

[5] F. Swamer, G. Reynolds, and C. Hauser, *J. Org. Chem.*, 16, 43 (1951).

[6] H. Gilman, *Organic Chemistry*, John Wiley and Sons, Inc., New York, 1953, vol. IV, p. 792.

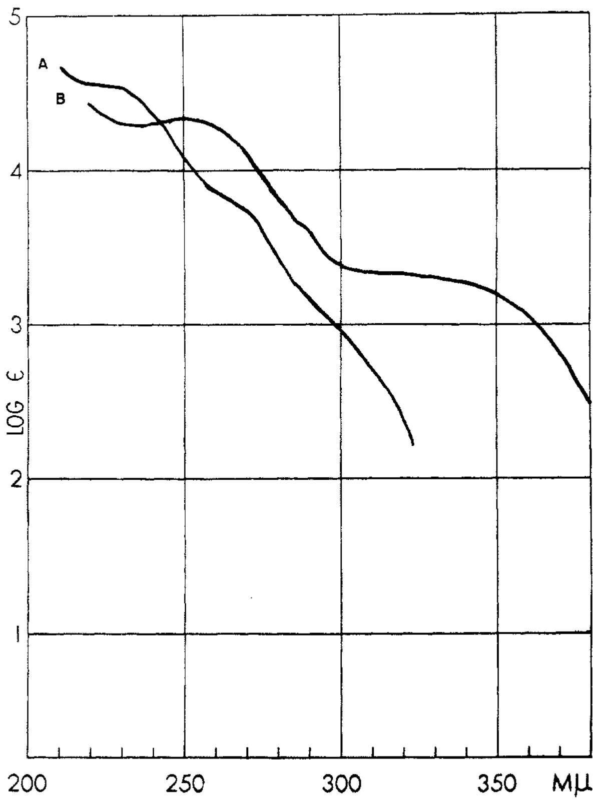

Fig. 1. Ultraviolet spectrum of: A, 2,2,4,6-tetraphenyl 5-methyl 2,5-dihydro-s-triazine; B, 2,2,4,6-tetraphenyl 3-methyl 2,3-dihydro-s-triazine.

resulting stabilization which impedes the aromatization of I to II by spontaneous loss of phenylsodium. We suggest that reaction of this anion with carbon dioxide and with sulfur dioxide forms in each case two carbamate or sulfinate ions RCO_2^- and RSO_2^- (R = V a and V b) in proportions which depend upon the contribution of each end-form to the resonance hybrid, as well as symmetry and steric factors. The resulting loss of resonance stability and increased electron density in the vicinity of carbon atom 2 is followed by transition to II by loss of benzoate or benzenesulfinate ion. This is probably undergone most readily by the unsymmetrical ion (R = V a), which would be expected to form in the lesser amount. The yield of II has not exceeded 23% in the experiments reported here by us or previously by others.

In further study of the report of von Hofmann[3] in which II was shown to form by the action of sodium on boiling benzonitrile, the action of benzonitrile on I in boiling benzene and xylene was investigated (Table I). As with carbon dioxide and sulfur dioxide the yield of II was again significantly increased, suggesting that analogous adducts of I with benzonitrile may be postulated as RC(Ph)=NNa (R = V a and V b). Kyaphenin (II) would form from the unsymmetrical adduct (R= V a) with separation of sodium diphenylketimine to start a fresh trimerization cycle in the manner suggested previously.[5] It may be noted that the postulated formation of additional II from freshly formed sodium diphenylketimine in the second and succeeding cycles does not increase the over-all yield of II significantly. This is to be anticipated in view of the approximately 3:1 ratio of symmetrical to unsymmetrical adduct formed in each cycle, which results rapidly in substantially complete consumption of freshly formed sodium diphenylketimine to yield the symmetrical adduct (R = V b) which does not aromatize.

In confirmation of the hypothesis that introduction of high electron-density (anionic) groups as carboxylate, sulfinate, and benzaldimino is necessary to effect aromatization, I was treated with further reagents to yield *N*-substitution products (Table II). No significant amounts of II were obtained in any case. Separation of isomers was not attempted; the compounds reported are probably the symmetrical forms corresponding to V b.

TABLE I

EFFECT OF CO_2,[a] SO_2,[a] AND C_6H_5CN[b] ON FORMATION OF II FROM I

Reagent	Time, Hr.	Temp., °C.	% Conversion
None	114	138	1
CO_2	3	80	4
	22	80	10
	4	138	12
	23	138	23
	48	138	23
SO_2	24	138	10
C_6H_5CN	5	82	7
	4	185	10
	24	138	21
	117	138	22

Percentage conversions are based on [a] benzonitrile and [b] sodium tetraphenyldihydro-s-triazine.

TABLE II

N-DERIVATIVES FROM SODIUM TETRAPHENYLDIHYDRO-S-TRIAZINE (I)[a]

Reagent	Time, Hr.	Temp., °C.	% yield	Formula	M.P., °C.
$(CH_3)_2SO_4$[b]	20	80		$C_{28}H_{23}N_3$	210
$ClCO_2C_2H_5$[c]	3	25	30	$C_{30}H_{25}O_2N_3$	155–156
C_6H_5COCl[d]	3	25	20	$C_{34}H_{25}ON_3$	232–233

[a] Heptane was used as solvent. [b] Product was identified by comparison with that obtained using methyl iodide. [c] Mole Weight calcd., 459; found by saponification No., 454. [d] % N calcd., 8.55; found, 8.51 (Dumas).

EXPERIMENTAL

Sodium tetraphenyldihydro-s-triazine (I). A mixture of sodium (3.0 g., 0.13 mole) and 150 ml. of dry thiophene-free benzene was placed in a 500-ml. three-necked flask fitted with a mercury-sealed stirrer, thermometer, dropping funnel, and reflux condenser with drying tube. The sodium was used as a 50% dispersion in kerosine, average particle size 15μ. The mixture was heated to 80° and benzonitrile (24 g., 0.23 mole) in 50 g. of benzene was added with stirring over 1 hr. Heating and stirring were continued for 3 hr. during which a dark red precipitate of I formed in suitable condition for use in further reactions. Assay of the reaction mixture was made as follows: after cooling to room temperature in an atmosphere of nitrogen the solids were separated by filtration, allowed to air slake and then washed with water to remove sodium cyanide. The remaining insoluble solid was recrystallized from alcohol and yielded 19 g. (85%) of 2,2,4,6-tetraphenyldihydrotriazine, m.p. 190–191° in agreement with Lottermoser.[3] The benzene filtrate was distilled to remove the benzene and the residue was recrystallized from alcohol to yield 0.54 g. (3%) of II, m.p. 229–230° in agreement with that reported previously.[3,5]

Reaction of I *with carbon dioxide.* A portion of I was prepared (as above) from 0.23 mole of benzonitrile and 0.13 mole of sodium, using xylene as solvent. The mixture was heated to reflux and dry CO_2 was introduced through a fritted glass bubbler with stirring for 23 hr. The reaction-mixture, which contained suspended solids, was treated as in the preceding paragraph. The xylene solution yielded 2.72 g. of II, and the xylene-insoluble solids gave 1.34 g. after water washing and recrystallization from alcohol. The total yield of II was 4.06 g. (22.6%) based on the benzonitrile used. The procedures for other experiments with carbon dioxide and with sulfur dioxide differed from the above only in the solvent used and the reaction time and temperature.

Reaction of I *with benzonitrile.* A portion of I was prepared as above from 30 g. (0.26 mole +11% excess) of benzonitrile and 3 g. (0.13 mole) of sodium, using xylene as solvent. The excess of benzonitrile was added to ensure complete disappearance of the sodium in the first stage of the reaction. A further quantity of benzonitrile (0.195 mole) was then added and the mixture was refluxed with stirring for 24 hr. For this operation it appeared advantageous to partially fill the reaction vessel with glass beads, whose grinding action promotes the reaction between solid and liquid reactants. Subsequent treatment of the reaction mixture as described above yielded 4.09 g. of II (20.5%).

Methylation of I. A portion of I was prepared from benzonitrile (0.23 mole) and sodium (0.13 mole) in refluxing heptane with the aid of glass beads. After cooling the reaction mixture to 30° under nitrogen, methyl iodide (16.5 g., 0.116 mole) in 10 ml. of heptane was added over 1 hr. with stirring at 30–40°, and the stirring continued for 0.5 hr. The mixture was filtered to remove solid reaction products and the heptane filtrate was discarded. The separated solid was thoroughly washed with five 200-ml. portions of benzene and the combined benzene washes were applied to a column of 385 g. of alumina (Alcoa F-20), 1″ × 4′. The chromatogram was developed with benzene and yielded: II, m.p. 229–230°, 0.533 g. (3%); III, m.p. 191°, 0.920 g. (3.95%); IV, m.p. 210°, 3.173 g. (13.6%).

Anal. Calcd. for $C_{28}H_{23}N_3$: C, 83.8; H, 5.7; N, 10.5; mol. wt., 401. Found (III): C, 83.5; H, 5.9; N, 10.6; mol. wt., 403. (IV): C, 84.3; H, 5.3; N, 9.9; mol. wt., 401.

Active hydrogen: Calcd. for I (Na = H): 1 mole CH_4/mole subst.; found, 0.9 mole CH_4. III and IV both yielded 0.0 mole CH_4.

Mixed melting points: III–IV, 167–180°; III–I (Na = H), 155–170°; III–II, 175–205°.

Further derivatives of I. Treatment of I with other reagents under the conditions described above yielded *N*-substitution products (Table II). When heated alone or in solvents at elevated temperatures (without prior purification) these failed to yield further isolable amounts of II. The melting points and analyses shown were determined after recrystallization of the principal (probably symmetrical) isomer.

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[CONTRIBUTION FROM THE GRADUATE SCHOOL OF ARTS AND SCIENCES, UNIVERSITY OF BUFFALO]

Reaction of Cyanogen with Organic Compounds. XII. Glycols and Glycol Monoethers[1]

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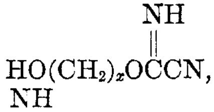
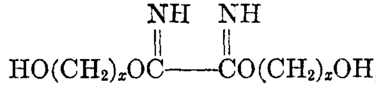
Ethylene glycol, 1,2-propanediol, 1,3-propanediol, and 2,3-butanediol, as well as the methyl, ethyl, and butyl monoethers of ethylene glycol, react with cyanogen in the presence of hydrogen chloride to yield moderately stable symmetrical oxaldiimidate dihydrochlorides. Neither 1,2-, 1,3-, nor 1,4-butanediol reacts with cyanogen under these conditions. In the presence of aqueous potassium cyanide, cyanogen and the glycol monoethers produce stable cyanoformimidates. Potassium carbonate and ammonium hydroxide are equally effective catalysts. With catalytic amounts of sodium, glycol monoethers and cyanogen produce stable oxaldiimidates. 2-Methoxyethylcyanoformimidate reacts with methyl Cellosolve to form the oxaldiimidate. Other combinations of glycol ethers and cyanoformimidates have thus far been unreactive.

This investigation is part of a series dealing with the reaction of cyanogen with bifunctional compounds. In previous papers we have described the behavior of aliphatic and aromatic diamines,[4,5] amino mercaptans,[6] and amino alcohols.[7] Although published information concerning the reaction of cyanogen with monohydroxy alcohols is scanty,[8,9] the studies referred to above indicated that glycols might logically form any of the following type products: cyanoformimidates,  $HO(CH_2)_xO\overset{NH}{\overset{\|}{C}}CN$, oxaldiimidates,  $HO(CH_2)_xO\overset{NH}{\overset{\|}{C}}—\overset{NH}{\overset{\|}{C}}O(CH_2)_xOH$, bi-

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[1] Parts of this paper are from a thesis submitted by A. B. Whitehouse in partial fulfillment of the requirements for the Ph.D. degree, June 1957.

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(4) H. M. Woodburn and R. C. O'Gee, *J. Org. Chem.*, **17**, 1235 (1952).

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(7) H. M. Woodburn and E. L. Graminski, *J. Org. Chem.*, **23**, 819 (1958).

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