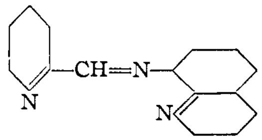
of symmetry.[1] The Schiff base (1) from 8-aminoquinoline and pyridine-2-aldehyde is structurally analogous to 2,2′,2″-terpyridyl and models show a high probability of similar coördination about metallic atoms. Since this molecule is a dissymmetrical tridentate chelate the complex cation should exist in enantiomeric forms. The addition of an alcoholic solution of (1) to aqueous ferrous sulfate was found to give such an intense green color that as little as one part of iron in two million could be detected by the reaction. The iron complex was resolved through the *d*-antimonyl tartrate. The enantiomeric iodides were stable at room temperature but racemized in two minutes at 100°.



I

It is noteworthy that the sequence —N=C—C=N—C—C=N— in (1) is the same as in 2,2′,2″-terpyridyl so that similar possibilities exist for resonance and double bonding of the nitrogen and metal atoms. In the same way it can be inferred that the Schiff bases from pyridine-2-aldehyde and primary amines such as aniline and ethylenediamine should act, respectively, as bidentate and quadridentate molecules similar to 2,2′-dipyridyl and 2,2′,2″,2‴-tetrapyridyl. These compounds are being investigated.

Experimental

8-(α-Pyridylmethyleneamino)-quinoline.—Pyridine-2-aldehyde (5.35 g.) was added to a solution of 8-aminoquinoline (7.0 g.) in ethanol (5.4 ml.) and the mixture warmed for a few minutes on the water-bath. After cooling, ether was added and the product crystallized from ethanol. The minute cream needles melted at 123.5°. *Anal.* Calcd. for $C_{15}H_{11}N_3$: C, 77.2; H, 4.8; N, 18.0. Found: C, 76.2; H, 4.7; N, 18.3.

***d,l*-Bis-(8-(α-pyridylmethyleneamine)-quinoline) Iron (II) Iodide, Dihydrate.**—Ferrous sulfate heptahydrate (1.39 g.) in water (25 ml.) was treated with the tridentate (2.35 g.) in hot methanol (50 ml.) and the mixture heated to 70°. After dilution with 80 ml. of water, the intensely green colored solution was filtered and the iodide precipitated by the addition of sodium iodide. Recrystallized from hot water it gave fine black prisms. The perchlorate, sparingly soluble black needles, could not be oxidized to the iron(III) complex without complete decomposition. *Anal.* Calcd. for $C_{30}H_{26}N_6O_2I_2Fe$: C, 44.4; H, 3.2; N, 10.4; Fe, 6.9; I, 31.3. Found: C, 44.8; H, 3.5; N, 10.6; Fe, 6.9; I, 31.4.

***l*-Bis-(8-(α-pyridylmethyleneamino)-quinoline) Iron(II) Iodide Dihydrate.**—The *d,l*-iodide (2.0 g.) in hot water (40 ml.) was shaken with excess of freshly precipitated silver chloride. Filter pulp was added and the mixture filtered, washing the silver halide precipitate with a little hot water. The volume of the dark green solution was adjusted to 60 ml. and the substance cooled to 4°. Potassium *d*-antimonyl tartrate (0.9 g.) in water (15 ml.) was added with scratching of the sides of the vessel. The fine black precipitate was filtered off, washed with a little ice-water and dissolved in 10% sodium acetate solution (50 ml.) at 35–40°. After filtration the levo iodide was precipitated by the very slow addition of 10% sodium iodide solution. The active iodide which was much less soluble than the *d,l*-iodide was crystallized several times from warm methanol by the addition of ether, to give dark green nodular prisms. A 0.0025% solution in water gave α_D −0.05°, whence $[\alpha]^{20}_D$ −2000°, and $[M]^{20}_D$ −16,000°; a 0.005% solution gave α^{20}_{5461} −0.03°, whence $[\alpha]^{20}_{5461}$ −600°, and $[M]^{20}_{5461}$ −5,000°. *Anal.* Calcd. for $C_{30}H_{26}N_6O_2I_2Fe$: C, 44.4; H, 3.2; N, 10.4; I, 31.3. Found: C, 44.7; H, 3.3; N, 10.5; I, 31.4.

***d*-Bis-(8-(α-pyridylmethyleneamino)-quinoline) Iron (II) Iodide Dihydrate.**—The filtrate from the antimonyl tartrate precipitation was treated very slowly with 10% sodium iodide solution and the resulting precipitate of the impure *d*-iodide crystallized as above from warm methanol and ether.

A 0.0025% solution in water gave α_D +0.05°, whence $[\alpha]^{20}_D$ +2000°. *Anal.* Calcd. for $C_{30}H_{26}N_6O_2{\cdot}I_2Fe$: C, 44.4; H, 3.2; N, 10.4; I, 31.3. Found: C, 44.7; H, 3.3; N, 10.5; I, 31.4.

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[1] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).

Thermal Decomposition of Chlorate–Chloride Mixtures

BY A. VANDEN BOSCH AND A. H. W. ATEN, JR.

RECEIVED MARCH 2, 1953

As a result of kinetic measurements Glassner and Weidenfeld have recently suggested[1] that the formation of potassium perchlorate during the thermal decomposition of potassium chlorate should be due to a transfer of atomic oxygen from the chlorate ion to a chloride ion. If this assumption were correct, decomposition of ordinary chlorate in the presence of radioactive chloride would lead to the formation of labeled perchlorate.

We have performed experiments of this type, using sodium chlorate and sodium chloride because we encountered difficulties in the rapid recrystallization of potassium perchlorate formed in this way. A mixture of 5 g. of $NaClO_3$ with 0.6 to 0.8 g. of NaCl was kept at 505° during 30 minutes. The $NaClO_3$ had been dried at 120° and the NaCl had been irradiated with a mixed beam of slow and fast neutrons and contained both Cl^{34} and Cl^{38}. As irradiation of the chloride crystals is reported to influence the course of the chemical reaction[1] the NaCl was melted before use. The reaction mixture was dissolved in water, perchlorate was precipitated as $KClO_4$ by addition of KNO_3 and chloride was isolated as AgCl. Activities were measured with a mica window counter and corrections for the natural activity of potassium and for self-absorption were applied, although these were of minor importance. In four experiments at the end of the reaction period the mixture contained 15–22% of the total chlorine as ClO_4^-, 76–82% as Cl^- and 2–4% as ClO_3^-. For the ratio of the specific activities of the chlorine in ClO_4^- and in Cl^- from the reaction mixture the following successive figures were found: 0.013, 0.015, 0.004, 0.010.

In case the mechanism of Glasner and Weidenfeld were correct and if all the chloride ions in the mixture have an equal chance of participating in the reaction, this ratio should have been > 1. At the start of the reaction the perchlorate would have originated from the undiluted labeled chloride. However, as the reaction proceeded, the original radioactive chloride would have been diluted by new inactive chloride formed in the decomposition of the chlorate and therefore at the end the specific activity of the Cl^- in the reaction mixture should be lower than the specific activity of the chlorine in the perchlorate. (Both in our experiments and in those of Glasner and Weidenfeld part of the chloride may have remained solid from the start of the reaction, but at least an appreciable fraction must have been present in the melt. Incomplete melting of the chloride might have lowered the ratio to a value slightly less than unity, but not to a small fraction of 1.)

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[1] A. Glasner and L. Weidenfeld, THIS JOURNAL, **74**, 2464 (1952).

Finally we may point out that our figures do not only disprove this theory but that they also show that during the reaction an exchange of labeled chlorine between Cl^- and ClO_3^- or between Cl^- and ClO_4^- does not occur to an appreciable extent.

We are glad to thank the Foundation for Fundamental Research of Matter (F.O.M.) and the Netherlands Organization for Pure Research (Z.W.O.) for their support of this investigation. Thanks are also due to the personnel of the Philips' cyclotron who performed the necessary irradiations. We also wish to express our gratitude to the Technische Commissie van het Belgisch-Nederlands Cultureel Accoord, who enabled one of us (A. Vanden Bosch, Laboratorium voor Physische Chemie, Rijksuniversiteit, Ghent) to take part in this investigation.

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Preparation of N-Alkyl-2-methylcyclohexylamines

BY L. E. CRAIG AND I. J. RESSA

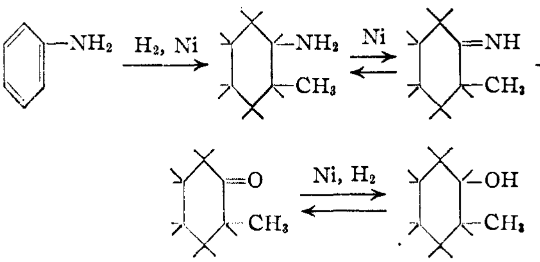
RECEIVED FEBRUARY 2, 1953

Adkins and Cramer[1] found that N-ethylcyclohexylamine is produced in excellent yield when aniline is hydrogenated in ethanol in the presence of a nickel catalyst. This apparent nickel-catalyzed alkylation of an amine with an alcohol was subsequently confirmed[2] by heating cyclohexylamine and ethanol at 200° under hydrogen at 75 atm. and in the presence of the nickel catalyst, N-ethylcyclohexylamine being produced as the main product along with small amounts of cyclohexylamine, N,N-diethylcyclohexylamine and dicyclohexylamine. The reaction was studied as a preparative method with several amines and alcohols, but no appreciable reaction was found to occur with cyclohexylamine, methanol and isopropyl alcohol.

This paper reports the preparation of N-alkyl-2-methylcyclohexylamines in good yields by ring-hydrogenation of *o*-toluidine in various alcohols. The reaction conditions used and the products obtained are summarized in Table I; the physical properties of the novel 2-methylcyclohexylamines and derivatives are summarized in Table II. The catalyst was a commercially available nickel-on-kieselguhr catalyst, Harshaw Ni-0104T 1/8". One experiment was carried out with Raney nickel catalyst with results comparable to those with the nickel-on-kieselguhr catalyst, but no other catalysts were investigated.

The hydrogenations in methanol and ethanol produced both N-alkyl- and N,N-dialkyl-2-methylcyclohexylamines, the latter being the main product in methanol. Two isomers, undoubtedly *cis–trans* isomers, of N,N,2-trimethylcyclohexylamine were isolated; this is the only case where *cis–trans* isomers were isolated, although such isomers of all the 2-methylcyclohexylamines are possible.

The 2-methylcyclohexanol produced in hydrogenations in methanol and ethanol formed constant-boiling mixtures with certain of the amines. It was necessary to remove the 2-methylcyclohexanol before isolation and purification of the products by fractional distillation. It seems probable that the 2-methylcyclohexanol is formed from 2-methylcyclohexylamine and water by nickel-catalyzed reactions of the types



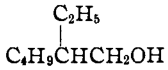
(I)

The formation of the imine is in accord with the mechanism suggested by Winans and Adkins[2] for the formation of secondary amines from primary amines in the presence of hydrogenation catalysts.

As evidence for the over-all reaction I, cyclohexylamine and water at 180° in the presence of the nickel catalyst were found to give cyclohexanol. The addition of a mutual solvent, tetrahydrofuran, was found to be beneficial, 62% of the cyclohexylamine reacting to give cyclohexanol in 84.8% yield.

TABLE I

HYDROGENATIONS OF *o*-TOLUIDINE IN ALCOHOL

Alcohol	Alcohol, ml.	*o*-Toluidine, moles	Catalyst, g.	Temp., °C.	Time, hr.	Products (% yield)
CH_3OH	1000	5	50	200	29	2-Methylcyclohexanol (8.8)
						2-Methylcyclohexylamine (4.8)
						N,2-Dimethylcyclohexylamine (6.0)
						cis- (or *trans*)-N,N,2-Trimethylcyclohexylamine (33.5)
						trans- (or *cis*)-N,N,2-Trimethylcyclohexylamine (6.5)
						Unreacted *o*-toluidine (7.7)
C_2H_5OH	400	2	20	180	16	2-Methylcyclohexanol (15.8)
						N-Ethyl-2-methylcyclohexylamine (49.1)
						N,N-Diethyl-2-methylcyclohexylamine (17.1)
$(CH_3)_2CHOH$	200	0.5	5	180	14	N-Isopropyl-2-methylcyclohexylamine (67.8)
n-C_4H_9OH	200	0.5	5	180	10	N-Butyl-2-methylcyclohexylamine (64.3)
						2-Methylcyclohexylamine (35.4)
						N-(2-Ethylhexyl)-2-methylcyclohexylamine (14.2)
 $C_4H_9\overset{C_2H_5}{\overset{\mid}{C}}HCH_2OH$	500	1	30	200	9	Unreacted *o*-toluidine (9.9)

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[1] H. Adkins and H. I. Cramer, THIS JOURNAL, **52**, 4349 (1930).

[2] C. F. Winans and H. Adkins, *ibid.*, **54**, 306 (1932).