flow rate of 45 ml/min. Retention times of 0.90 min for 1-methyl-5-carbomethoxypyrazole (1), 1.5 min for 3-carbomethoxypyrazole (2), and 2.30 min for 1-methyl-3-carbomethoxypyrazole (3) were obtained. These retention times are similar to those previously reported.[1] The peak ratio for 1/2/3 was 2.2:1.34:1.0 (43.8:36.5:19.7%), respectively.

Reaction of Methyl *trans*-β-Chloroacrylate (6) with Distilled Diazomethane in Ether.—Reaction conditions employed were the same as in the reaction of *cis*-6 with distilled ether–diazomethane. Gas–liquid partition chromatography under identical conditions afforded 1-methyl-5-carbomethoxypyrazole (1) and 3-carbomethoxypyrazole (2) in a ratio of 9.87:1.00 (90.8:9.2%), respectively. No 1-methyl-3-carbomethoxypyrazole (3) was detected.

Pyrazoline and Pyrazole Formation When Methyl Acrylate Served as Starting Material.—One gram (1.1×10^{-2} mol) of methyl acrylate was treated with distilled ether–diazomethane ($3.6\text{–}4.3 \times 10^{-2}$ mol) under conditions identical with those described for the reaction of methyl *cis*-β-chloroacrylate (6) with distilled diazomethane in ether. The solvent was removed under reduced pressure and the residue containing pyrazolines was brominated by dropwise addition of 1.0 g (0.55×10^{-2} mol) of Br_2 in 10 ml of dry CCl_4 according to the method of Pechman and Burkard.[2] The reaction temperature was maintained at 0° for 0.5 hr and then the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue was dissolved in 25 ml of dry chloroform. Gas–liquid partition chromatography showed 1-methyl-5-carbomethoxypyrazole (1), 11.6%, and 3-carbomethoxypyrazole (2), 76.8%. No 1-methyl-3-carbomethoxypyrazole (3) was detected. Uncharacterized compounds represented a total of 11.6% of the reaction mixture.

Pyrazole Formation When 3-Carbomethoxy-2-pyrazoline (11) Served as Starting Material.—3-Carbomethoxy-2-pyrazoline was prepared from 2.1 g (2.4×10^{-2} mol) of methyl acrylate under the same reaction conditions as described previously. The solvent was removed under reduced pressure and the residue was crystallized from 95% ethanol, affording 1.8 g (60%) of 3-carbomethoxy-2-pyrazoline (11), mp 61–63° (lit.[2] mp 63–66°). One gram (7.9×10^{-3} mol) of 3-carbomethoxy-2-pyrazoline (11) was treated in distilled ether–diazomethane (2.5×10^{-2} mol) under conditions identical with the reaction conditions described for *cis*-6 with distilled diazomethane in ether. The solvent was removed under reduced pressure and the residue was brominated by addition of 1.0 g (0.55×10^{-2} mol) of Br_2 in 10 ml of dry CCl_4 as above. Gas–liquid partition chromatography showed 1-methyl-5-carbomethoxypyrazole (1), 7.6%, and 3-carbomethoxypyrazole (2), 89.6%. No 1-methyl-3-carbomethoxypyrazole was detected. Uncharacterized compounds represented a total of 2.8% of the reaction mixture.

Registry No.—Diazomethane, 334-88-3; *cis*-6, 3510-44-9; *trans*-6, 5135-18-2.

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Isomeric Transition Metal Complexes of *trans*-2-(2′-Quinolyl)-methylene-3-quinuclidinones[1]

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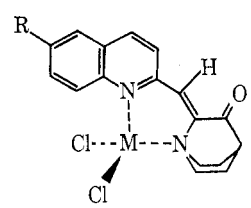
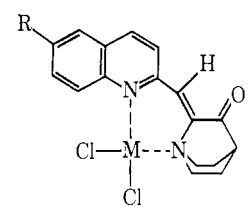
Tetrahedral–square-planar equilibria have been identified and studied with a variety of tetracoordinate nickel(II) complexes in solution.[2] In comparatively fewer instances, both isomers of a given complex have been isolated in pure form.[3] This has been accomplished with bis(alkyldiphenylphosphine)nickel(II) dihalides. It has now been observed that both the tetrahedral and square planar nickel(II) dichloride complexes of the bidendate ligand *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone and of its 6′-methoxy derivative are very easily prepared in pure crystalline form.

2-(6′-Methoxy-2′-quinolyl)methylene-3-quinuclidinone was synthesized in the course of a project concerned with antimalarials of the quinolinemethanol class by the base-catalyzed condensation of 6-methoxyquinoline-2-carboxaldehyde[4] with 3-quinuclidinone. In order to prove the anticipated *trans* stereochemistry of the product, its cobalt, nickel, and copper dichloride complexes were prepared. Since these exhibit normal (1710–1720 cm^{-1}) carbonyl stretching frequencies in their infrared spectra, both nitrogen atoms and not the carbonyl oxygen are involved in coordination, whence the *trans* geometry must obtain.



1, M = CO; R = OCH_3
2, M = Ni; R = OCH_3
5, M = CO; R = H
6, M = Ni; R = H



3, M = Cu; R = OCH_3
4, M = Ni; R = OCH_3
7, M = Cu; R = H
8, M = Ni; R = H

The complexes were prepared by combining ethanol solutions of the metal dichlorides with solutions of the ligand. They crystallized out immediately. The cobalt complex 1 is deep green and may be recrystallized without change from chloroform–ethanol. The nickel complex 2 is maroon and has an infrared spectrum (Nujol) identical with that of the cobalt complex. The copper complex 3 is brown-yellow and has an entirely different infrared spectrum from those of complexes 1 and 2. Given the propensity of cobalt(II) to form tetrahedral complexes and of copper(II) to form square-planar complexes,[5] tetrahedral stereochemistry can be assigned to complexes 1 and 2 and square-planar stereochemistry to complex 3. When the maroon nickel complex 2 is recrystallized from methylene chloride–ethanol, it changes color and yields yellow-brown crystals of a complex having an infrared spectrum virtually identical with that of the copper complex 3. On this basis it is assigned the square-planar structure 4.

The isomerization of 2 to 4 is irreversible, the latter evidently being the more stable isomer, and the successful preparation of isomer 2 is contingent on the use of

(1) Synthetic Quinine Analogs II, supported by the U. S. Army Medical Research and Development Command, Contract DADA-17-68-C-80-45. Part I: D. R. Bender and D. L. Coffen, *J. Org. Chem.*, **33**, 2504 (1968).

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a hot solvent in which the complex has low solubility. Boiling absolute ethyl alcohol served admirably up to the time a crystalline sample of isomer **4** was prepared. Thereafter, boiling *n*-butyl alcohol was necessary for further preparations of **2** in the same laboratory.

Since the methoxyl group in the series **1**–**4** is essentially an artifact arising from our interest in quinine analogs, the ligand lacking this additional functional group was also synthesized. Again a single geometrical isomer (*trans*) was obtained, which readily yielded the series of complexes **5**–**8**. The nickel complex **6** undergoes the same facile isomerization to complex **8** described above for the isomeric pair **2** and **4**. Magnetic moments of four of the complexes, **1**, **6**, **7**, and **8**, were measured[6] to confirm the structural assignments made on the basis of infrared spectral data, and, in reasonable agreement[7] with the assigned structures, magnetic moments of 3.98, 3.34, 1.74, and 0.65 BM, respectively, were observed. The small moment observed for complex **8** suggests that it is not entirely diamagnetic. Possibly a small amount of the tetrahedral geometry is admixed with the square-planar geometry.

Experimental Section[8]

***trans*-2-(6′-Methoxy-2′-quinolyl)methylene-3-quinuclidinone.**—A solution of sodium (50 mg) in absolute ethanol (2 ml) was added to a solution of 6-methoxyquinoline-2-carboxyaldehyde[4] (187 mg, 1 mmol) and 3-quinuclidinone[9] (125 mg, 1 mmol) in absolute ethanol (10 ml) and heated under reflux for 2 hr. The solution was cooled and scratched to induce crystallization, and the product was filtered out and washed with water and cold ethanol to give 246 mg (84%) of yellow crystals: mp 185–186°; ir ν_{max} 1700, 1615, 1555, 1495, 1240, 1215, 1090, 1025, and 830 cm^{-1}; nmr ($CDCl_3$) 2.05 (m, 4 H), 2.67 (quintuplet, 1 H), 3.15 (m, 4 H), 3.95 (s, 3 H), 7.08 (d, 1 H), 7.40 (m plus s, 2 H), 8.05 (d, 2 H), and 8.75 ppm (d, 1 H).

Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.65; H, 6.16; N, 9.52. Found: C, 73.80; H, 6.16; N, 9.40.

Cobalt Complex 1.—A solution of cobaltous chloride hexahydrate (81 mg, 0.34 mmol) in ethanol (2 ml) was added to a warm solution of the ligand (100 mg, 0.34 mmol) in ethanol (5 ml). The product was filtered and washed with ethanol, giving 133 mg (92%) of green powder. Recrystallization from chloroform–ethanol gave lustrous green crystals: mp 316° dec; ir ν_{max} 1710, 1620, 1580, 1375, 1245, 1235, 1165, 1130, 1095, 1020, 938, 867, 819, 764, 754, and 688 cm^{-1}. An nmr spectrum was precluded by low solubility.

Anal. Calcd for $C_{18}H_{18}Cl_2CoN_2O_2$: C, 50.96; H, 4.28; Cl, 16.72; N, 6.60. Found: C, 51.22; H, 4.30; Cl, 17.04; N, 6.73.

Nickel Complex 2.—A hot solution of nickelous chloride hexahydrate (81 mg, 0.34 mmol) in ethanol (1 ml) was added to a boiling solution of the ligand (100 mg, 0.34 mmol) in 1-butanol (1 ml). The product was filtered and washed with ethanol, giving 131 mg (91%) of maroon needles: mp 310° dec; ir ν_{max} 1710, 1620, 1580, 1375, 1245, 1235, 1165, 1130, 1095, 1020, 938, 868, 816, 764, 755, and 687 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}Cl_2N_2NiO_2$: C, 50.99; H, 4.28; Cl, 16.73; N, 6.61. Found: C, 51.06; H, 4.32; Cl, 16.44; N, 6.43.

Copper Complex 3.—A solution of cupric chloride dihydrate (58 mg, 0.34 mmol) in ethanol (2 ml) was added to a warm solution of ligand (100 mg, 0.34 mmol) in ethanol (5 ml). The product was filtered and washed with ethanol, giving 138 mg (95%) of small khaki crystals: mp 297–298°; ir ν_{max} 1720, 1645, 1625, 1500, 1380, 1245, 1135, 1090, 1025, 910, 888, 875, 850, 833, 819, 781, 772, 755, and 690 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}Cl_2CuN_2O_2$: C, 50.42; H, 4.23; Cl, 16.54; N, 6.53. Found: C, 50.47; H, 4.05; Cl, 16.33; N, 6.39.

Nickel Complex 4.—The nickel complex **2** (131 mg) was taken up in boiling methylene chloride (25 ml), giving a brown solution. This was concentrated with gradual addition of ethanol, causing the isomeric complex to separate in yellow-brown plates. The product was filtered and washed with ethanol, giving 120 mg (92%): mp >360°; ir ν_{max} 1720, 1645, 1625, 1500, 1380, 1245, 1135, 1090, 1025, 910, 885, 871, 850, 835, 818, 782, 763, 757, and 690 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}Cl_2N_2NiO_2$: C, 50.99; H, 4.28; Cl, 16.73; N, 6.61. Found: C, 51.21; H, 4.02; Cl, 16.92; N, 6.57.

***trans*-2-(2′-Quinolyl)methylene-3-quinuclidinone.**—A solution of sodium (347 mg) in absolute ethanol (10 ml) was added to a solution of quinoline-2-carboxaldehyde[10] (1.572 g, 0.01 mol) and 3-quinuclidinone[9] (1.612 g, 0.01 mol) in absolute ethanol (25 ml) and heated under reflux for 0.5 hr. The solution was cooled and treated with water (50 ml) to induce crystallization, and the product was filtered out and washed with alcohol to give 2.187 g (83%) of yellow crystals: mp 150–151°; ir ν_{max} 1710, 1640, 1240, 1170, 1090, 830, 810, and 758 cm^{-1}; nmr ($CDCl_3$) 2.03 (m, 4 H), 2.67 (quintuplet, 1 H), 3.08 (m, 4 H), 7.36 (s, 1 H), 7.63 (m, 3 H), 8.08 (d, 2 H), and 8.71 ppm (d, 1 H).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.46; H, 6.10; N, 10.52.

Cobalt Complex 5.—A solution of cobaltous chloride hexahydrate (0.237 g, 0.001 mol) in ethanol (12 ml) was added to a warm solution of the ligand (0.264 g, 0.001 mol) in ethanol (10 ml). The product was filtered and washed with ethanol, giving 0.379 g (96%) of green powder. Recrystallization from $CHCl_3$–ethanol gave deep green crystals: mp 325° dec; ir ν_{max} 1710, 1640, 1590, 1370, 1240, 1210, 1165, 1090, 1015, 935, 855, 832, 807, 788, 760, and 745 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}Cl_2CoN_2O$: C, 51.80; H, 4.09; N, 7.11; Cl, 17.99. Found: C, 51.80; H, 4.02; N, 7.05; Cl, 18.18.

Nickel Complex 6.—A hot solution of nickelous chloride hexahydrate (0.095 g, 0.4 mmol) in absolute ethanol (1.5 ml) was added to a warm solution of the ligand (0.106 g, 0.4 mmol) in *n*-butyl alcohol (4 ml). The resulting maroon solution was quickly cooled in a cold-water bath. The product was filtered and vacuum dried, giving 0.141 g (89%) of maroon crystals: mp 310° dec; ir ν_{max} 1720, 1645, 1595, 1370, 1245, 935, 868, 855, 835, 810, 790, 780, 760, and 743 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}Cl_2N_2NiO$: C, 51.83; H, 4.09; Cl, 18.00; N, 7.11. Found: C, 51.88; H, 4.03; Cl, 18.15; N, 7.11.

Copper Complex 7.—A solution of cupric chloride dihydrate (0.085 g, 0.5 mmol) in ethanol (4 ml) was added to a warm solution of the ligand (0.132 g, 0.5 mol) in ethanol (7 ml). The product was filtered and washed with ethanol, giving 0.189 g (95%) of small gold crystals: mp 233° dec; ir ν_{max} 1720, 1640, 1595, 1495, 1370, 1240, 1090, 908, 855, 828, 783, 766, and 755 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}Cl_2CuN_2O$: C, 51.20; H, 4.04; Cl, 17.80; N, 7.03. Found: C, 51.03; H, 3.96; Cl, 17.96; N, 6.90.

Nickel Complex 8.—The nickel complex **6** (50 mg) was dissolved in boiling chloroform (35 ml), giving a rose-colored solution. This was concentrated with concurrent addition of absolute ethanol, causing the isomeric complex to separate in yellow-brown crystals. The product was filtered and washed with ethanol, giving 43 mg (86%): mp >360°; ir ν_{max} 1710, 1645, 1595, 1500, 1370, 1238, 1160, 1140, 1085, 1020, 915, 886, 860, 830, 810, 780, 755, and 738 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}Cl_2N_2NiO$: C, 51.83; H, 4.09; Cl, 18.00; N, 7.11. Found: C, 51.81; H, 4.08; Cl, 17.96; N, 7.04.

(6) Magnetic susceptibilities were measured at room temperatures with a Gouy balance using solid samples in glass tubes. The apparatus was calibrated with mercury tetrathiocyanato cobaltate. For a detailed description, see B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958). No allowance was made for diamagnetic contributions in calculating magnetic moments from the observed susceptibilities.

(7) See ref 5, p 636–637.

(8) Melting points are uncorrected. Infrared spectra were measured as Nujol mulls on a Perkin-Elmer Infracord Model 137; stronger bands are listed. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

(9) Obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis., as the hydrochloride.

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Registry No.—*trans*-2-(6′-Methoxy-2′-quinolyl)-methylene-3-quinclidinone, 22058-77-1; *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone, 22058-81-7; **1**, 22143-13-1; **2**, 22058-78-2; **3**, 22058-79-3; **5**, 22058-80-6; **6**, 22143-14-2; **7**, 22058-82-8.

4-(4-Nitrophenylazo)benzoic Acid. Improved Synthesis of Its Acid Chloride and Spectroscopic Properties of Its Esters[1]

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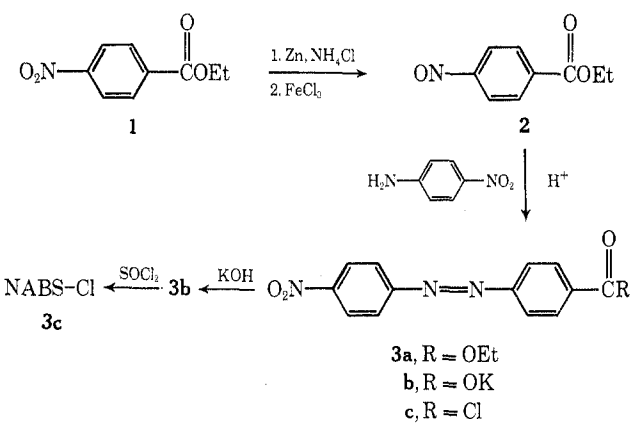
The synthesis of 4-(4-nitrophenylazo)benzoyl chloride (NABS–Cl)[2] and its use in the formation of esters was described[3] in 1955. Since then, NABS–Cl has been employed advantageously for the derivatization of other aliphatic[4] and aromatic[5] alcohols, thiols,[6] sugars,[7] amines,[8] and amino acid methyl esters;[9] NABS–hydrazide has been prepared and used to prepare derivatives of aldehydes and ketones.[10] The esters are usually solid,[11] their bright red-orange color makes them highly suitable for chromatographic purification,[4,12] and their molecular weight[13] may be determined from the ultraviolet absorption of the NABS chromophore. These properties make NABS–Cl a desirable reagent in the isolation and characterization of natural products.[12,14]

Synthesis of NABS–Cl.—In connection with work on the structure of sirenin,[14a] it became necessary to synthesize NABS–Cl in quantity as shown in Scheme I. Our attempts to obtain the 65–70% yield reported[3] for the conversion of **1** into **2** on the original 5-g scale resulted in an average yield (ten experiments) of 15%; larger scale reactions gave even lower yields. Other attempts[5a] to increase the scale of the reaction have also resulted in lower yields of **2**. A 65% yield is claimed[5a] using modified conditions, but these also failed in our hands. Consequently we examined this reaction in detail and now report conditions which reliably lead to 60–65% yields on up to a 40-g scale. In particular, vigorous stirring, closely controlled temperature, and a nitrogen atmosphere are required. Also, the use of ammonium chloride[15] in place of the originally recommended acetic acid reduced the acid-catalyzed side reactions of the intermediate ethyl *p*-hydroxylaminobenzoate, which was then oxidized to **2** using a decreased quantity of ferric chloride in the cold.

SCHEME I



No major changes were required in the subsequent steps. The crude, thoroughly dried NABS ester **3a** was purified by chromatography on alumina, and the most effect purification of the final NABS chloride (**3c**) was accomplished by vacuum sublimation.

Ultraviolet Absorption of NABS Esters.—The light-activated isomerization of substituted *trans*-azobenzenes to a photostationary equilibrium mixture of *cis* and *trans* isomers has been established.[16] In the presence of ordinary laboratory fluorescent light, solutions of *trans*-*p*-phenylazobenzoates (PAB esters) of aliphatic[17] and aromatic[5b] alcohols are isomerized, and the isomers are chromatographically separable.[17] Consequently, *trans*-4-(4-nitrophenylazo)benzoates (NABS esters) would be expected to behave similarly, and thus special precautions would be necessary to exclude light during handling of the solutions when precise chromatographic and spectroscopic determinations were being made.

About 3×10^{-3} *M* solutions of NABS ethyl ester (**3a**) were exposed to laboratory fluorescent light and the absorbance at 330 nm was noted as a function of time. A variety of solvents—benzene, ether, ethyl acetate, ethanol, and acetic acid—was used, and in each case photostationary equilibrium was reached after 2 hr with about a 5% decrease in absorbance.

The equilibrium mixture, showing a yellow spot at R_f 0.14 and a red-orange spot at R_f 0.37 on silica gel–benzene thin layer chromatography, can be thermally isomerized[6a] at room temperature in the dark for 30 hr to an all-*trans* solution which shows only

(1) Supported in part by the National Science Foundation.

(2) Abbreviated from its German name, 4-nitroazobenzolcarbonsaure-4-chlorid: A. Butenandt, R. Beckmann, and D. Stamm, *Z. Physiol. Chem.*, **324**, 84 (1961).

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