was started at a rate of 200 mL/min. The mixture was stirred vigorously and heated rapidly to 145 °C. At this point (which is considered time 0 for timing purposes) the chlorine flow rate was increased to 800 mL/min. Thoughout the reaction the flow rate was held constant, and the temperature was maintained at 150 ± 3 °C. The reaction is mildly exothermic and, in its early stages, can be kept at this temperature by using an unheated mantle as an insulator. After the conversion is more than 50% complete it becomes necessary to apply heat via the mantle. At a reaction time of 50 min a second portion of 0.56 g (2.7 mmol) of TCNQ was added. At 65 min the temperature began to drop rapidly because of condensing chlorine, and the gas flow was stopped. When the mixture had cooled to ca. 90 °C, it was poured into 1200 mL of hot acetonitrile. The product was crystallized by cooling this solution in ice with stirring. The crystals were collected by suction filtration, washed with ice-cold acetonitrile, and vacuum dried to afford 450.6 g (88%) of 2-chlorostearic acid, mp 63.5–64.5 °C (lit.[13] mp 64.5–65.5 °C). GC analysis of this material (as methyl ester) indicated its purity to be ca. 99%.

Acknowledgment. Technical assistance was provided by Mr. B. A. Banker, Mrs. N. L. Kern, and Mr. J. F. Ward and is gratefully acknowledged.

Registry No. 2-Chlorostearic acid, 56279-49-3; stearic acid, 57-11-4; chlorosulfonic acid, 7790-94-5; methyl 2-chlorostearate, 41753-99-5; TCNQ, 1518-16-7; O_2, 7782-44-7.

(13) Hwang, Y.-S.; Navvab-Gojrati, H. A.; Mulla, M. S. *J. Agric. Food Chem.* **1978**, *26*, 1293.

A Practical Synthesis of 7,7,8,8-Tetracyanoquinodimethane

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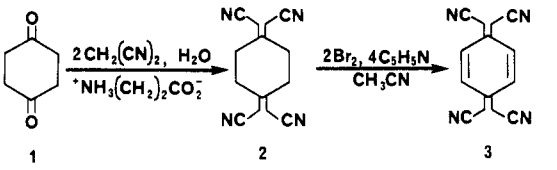
The most commonly used method to prepare 7,7,8,8-tetracyanoquinodimethane (TCNQ, **3**) is the original synthesis reported in 1962 by Acker and Hertler[1] (Scheme I). This procedure is adequate for small-scale work but has shortcomings when applied on a large scale. As a consequence, TCNQ that is sold commercially is characteristically expensive and available only in small lots.[2] In this paper I report an improved procedure that is suitable for laboratory preparation of TCNQ in molar quantities.

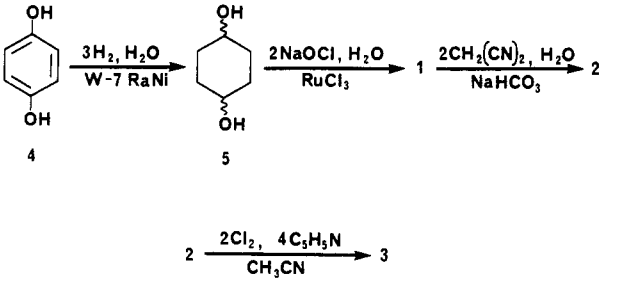
If a synthesis is to be truly practical, it should start with inexpensive commodity chemicals, provide a high overall yield, and be amenable to scale-up. According to the first criterion, 1,4-cyclohexanedione (**1**) is an intermediate rather than a starting material, and its synthesis must be included in the overall route to TCNQ. This diketone is usually prepared by hydrolysis and decarboxylation of diethyl 1,4-dioxocyclohexane-2,5-dicarboxylate, which is, in turn, obtained by self-condensation of diethyl succinate.[3] The average yield for the two steps is 56%, and the procedure is awkward to scale up.[4]

While the conversion of **1** to 1,4-bis(dicyanomethylene)cyclohexane (BDCC, **2**) is rapid and quantitative, the conventional oxidation of **2** to TCNQ suffers from

Scheme I



Scheme II



scale limitations in the isolation and purification of the final product. When BDCC is treated with 2 equiv of bromine and 4 equiv of pyridine in acetonitrile solution, TCNQ is formed along with 4 equiv of pyridine hydrobromide, and the two products partially coprecipitate. Water is then added to dissolve the salt and precipitate all of the TCNQ. Unfortunately, TCNQ contains up to 10% of other impurities when it is isolated in this way[5] and must be sublimed or recrystallized. Both purification techniques limit the practicality of large-scale preparations, the latter because of the extremely low solubility of TCNQ.[6]

Our procedure (Scheme II) is designed to overcome all of these limitations. Hydroquinone (**4**) is used as the starting material and is converted to BDCC by a three-step, one-pot procedure using water as the solvent. BDCC is then oxidized to TCNQ by using *chlorine* and pyridine, a modification that allows the purification of TCNQ to be effectively built into the reaction. A detailed account of the synthesis follows.

Hydroquinone can be converted to **1** by a two-step reduction–oxidation sequence in which 1,4-cyclohexanediol (**5**) is an intermediate. The best known procedures for these reactions are catalytic hydrogenation of hydroquinone in alcohol solution and chromic acid oxidation of **5** in acetone or acetic acid.[7] Water is the preferred solvent for the conversion of **1** to BDCC because the product is insoluble and crystallizes directly from the reaction mixture.[1] We reasoned that the isolation of both **5** and **1** would be unnecessary if all three of these steps could be carried out in water. This approach succeeded because of the availability of two rarely used synthetic techniques.

The reduction of hydroquinone in an alkaline 50% water slurry is effected by hydrogenation over W-7 Raney nickel. The unique combination of hydroquinone and the W-7 catalyst was mentioned briefly by Adkins and Billica in 1948[8] but has not been exploited. It is an unusual case in

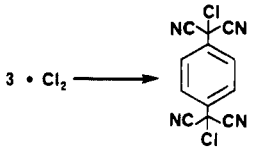
(1) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
(2) The largest quantity supplied by Aldrich Chemical Co. (1982–1983 Catalog) is 10 g at $45.00.
(3) Nielsen, A. T.; Carpenter, W. R. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 288.
(4) A further drawback of this route is that only 32% of the mass of the diethyl succinate is retained in 1.

(5) The major contaminant is an amorphous brown powder that is obtained as a residue from sublimation. This byproduct has not been identified and appears to be polymeric. Interestingly, TCNQ samples that contain this impurity do not show a significant melting point depression but melt with decomposition.
(6) Although acetonitrile is the best recrystallization solvent, as much as 80 mL/g may be required to dissolve TCNQ at the boiling point.
(7) Mussini, P.; Orsini, F.; Pelizzoni, F. *Synth. Commun.* **1975**, *5*, 283. Kern, W.; Gruber, W.; Wirth, H. O. *Makromol. Chem.* **1960**, *37*, 198. Sircar, J. C.; Meyers, A. I. *J. Org. Chem.* **1965**, *30*, 3206. Gogek, C. J.; Moir, R. Y.; Purves, C. B. *Can. J. Chem.* **1951**, *29*, 946. Olberg, R. C.; Pines, H.; Ipatieff, V. N. *J. Am. Chem. Soc.* **1944**, *66*, 1096. Owen, L. N.; Robins, P. A. *J. Chem. Soc.* **1949**, 320.

0022-3263/83/1948-1366$01.50/0

which an aromatic ring can be hydrogenated as easily as a simple olefin. Although Adkins' reduction was run in ethanol, we found that it works as well in water. The mild conditions for this hydrogenation and the absence of a flammable solvent permit large-scale runs to be conducted safely in ordinary equipment. After filtration to remove the catalyst, the resulting aqueous solution of diol **5** is oxidized with sodium hypochlorite and catalytic ruthenium chloride, according to the method invented by Wolfe et al.[9] This elegant oxidation technique has received little use, presumably because alcohol oxidations are not usually carried out in water. It is an ideal method for the present case and affords an aqueous solution of **1** in which sodium chloride is the only major byproduct. Addition of malononitrile followed by adjustment of the pH results in rapid formation and precipitation of BDCC. The overall yield of crystalline **2** for the three steps, based on hydroquinone, is 91%.

The rationale for using chlorine–pyridine in the oxidation of **2** to TCNQ relates to the solubility of pyridine hydrochloride. This salt, unlike the bromide, remains in solution at the end of the reaction, allowing TCNQ to precipitate in pure form. An aqueous workup, which precipitates other impurities, is thus unnecessary, and pure TCNQ is obtained by simple filtration of the reaction mixture. The substitution of chlorine for bromine in this reaction is not straightforward, because TCNQ reacts with chlorine (but not bromine) to form a 1,6-addition product (**6**).[1] For example, use of chlorine in the procedure of ref



6

1 affords **6** as the major product. Reversal of the chlorine–pyridine addition order results in impure TCNQ owing to formation of polymeric byproducts. Our method requires a carefully controlled, simultaneous addition of chlorine and pyridine in a perfectly matched 1:2 molar ratio. Also, the addition must be stopped precisely at the end of the reaction in order to avoid formation of **6**. The reaction is purposely run very rapidly (total time = 10 min), and the relative addition rates are manipulated such that the end of reaction is indicated by a sudden color change, similar to a titration endpoint (see Experimental Section). TCNQ is obtained in 88% yield, and its purity is approximately 99%.[10] This optimized result is achieved only by an unusually stringent experimental technique that leaves little margin for error. Once mastered, the procedure is highly reproducible and easily scaled up.

The overall yield of pure TCNQ, based on hydroquinone, is 80%. All of the reactions are rapid and mildly exothermic, and the two product-isolation procedures are simple filtrations. We routinely use this synthesis to prepare TCNQ in 200-g batches.

Experimental Section

General Methods and Materials. Hydroquinone was purchased from MCB, Inc. Nickel–aluminum Raney-type alloy and ruthenium trichloride hydrate were purchased from Alfa Products Co. Malononitrile was obtained from Aldrich Chemical Co. and was redistilled before use. Pyridine and acetonitrile were ACS reagent grade chemicals supplied by Fisher and MCB, respectively, and were used without further purification. Chlorine gas was Matheson "high purity" grade.

W-7 Raney nickel was prepared according to the procedure of Billica and Adkins,[11] except that the catalyst was stored under water instead of ethanol. After completion of the digestion and decantation of the water as directed, the solid was transferred to a Büchner funnel and washed with 1250 mL of water. (The washing procedure must be continuous so that the catalyst remains submerged in water at all times.) The slurry was then transferred to a wide-mouth jar and stored in a refrigerator.[12] **Caution**: The catalyst is exceedingly pyrophoric if it is allowed to dry. Although care must be taken to avoid spilling small particles that could dry out and start fires, the usual fire hazards associated with Raney nickel are avoided in this case because of the absence of flammable solvents.

Sodium hypochlorite of approximately a 2.5 M concentration was prepared by bubbling chlorine gas at a flow rate of 3 L/min into a stirred solution of 500 g of sodium hydroxide in 2 L of water. The solution temperature was maintained at −10–0 °C throughout the addition. After 25 min, continuous monitoring with a pH meter was begun. The chlorine flow was stopped when the pH fell to 11.5. The sodium hypochlorite concentration was determined by a standard iodometric titration in aqueous acetic acid.

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

1,4-Bis(dicyanomethylene)cyclohexane. A slurry of 140 g (1.27 mol) of hydroquinone in 160 mL of water was placed in a vented, glass autoclave liner and deoxygenated by bubbling with argon. Approximately 10 g of W-7 Raney nickel slurry in water was added, followed by 0.35 mL of 50% sodium hydroxide solution. The resulting mixture was hydrogenated in a rocking autoclave at an average temperature of 70 °C and an initial pressure of 700 psi.[13] The reaction was rapid and mildly exothermic and was allowed to proceed for 2.5 h to ensure completion. The reaction mixture was allowed to stand until the catalyst settled, and the bulk of the solution was removed from the liner by decantation. The catalyst was separated from the remaining portion by suction filtration and washing.

The combined solutions and washings were neutralized by addition of a few drops of concentrated hydrochloric acid and were placed in a 2-L round-bottomed reaction flask fitted with a mechanical stirrer, thermometer, and addition funnel. A solution of 1.26 g (5.0 mmol) of ruthenium trichloride hydrate in 70 mL of water was added. This mixture was stirred while a total of 1157 mL (2.96 mol) of 2.56 M sodium hypochlorite solution[14] was added dropwise over a period of 45 min. The reaction was mildly exothermic and was maintained at 30–40 °C by means of a cooling bath. The hypochlorite was added at the fastest rate that would maintain the opaque, dark brown color of the reaction mixture. (Formation of a clear, yellow solution indicates that the addition is too rapid. At the end of the reaction, the yellow color is produced by very small additions of hypochlorite, and persists for several minutes.) Destruction of any remaining oxidizing agent was effected by addition of 35 mL of methanol, and the solution was decolorized by stirring with 350 g of chromatographic grade alumina (Merck No. 1077). The alumina was removed by filtration, and the solution was returned to the reaction flask. It was stirred vigorously while 200 g (3.0 mol) of malononitrile and 35 mL of saturated sodium bicarbonate solution were added. Formation and precipitation of the product was complete after 30 min. The solid was collected by filtration, washed thoroughly

(8) Adkins, H.; Billica, H. R. *J. Am. Chem. Soc.* **1948**, *70*, 695.
(9) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *Chem. Commun.* **1970**, 1420.
(10) This product is equivalent to the recrystallized TCNQ of ref 1. It should be noted that TCNQ used for organic semiconductor studies normally requires additional purification. See: Gemmer, R. V.; Cowan, D. O.; Poehler, T. O.; Bloch, A. N.; Pyle, R. E.; Banks, R. H. *J. Org. Chem.* **1975**, *40*, 3544.
(11) Billica, H. R.; Adkins, H. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 176.
(12) Contrary to the published reports,[8,11] we have observed no significant loss in activity when this catalyst is stored under water. Also, a single portion of catalyst can be reused for many successive reductions of hydroquinone.
(13) An autoclave was used only to accommodate the scale of this reaction. Small-scale reductions can be conducted at room temperature in a Parr apparatus and require approximately 6 h for completion.
(14) If ordinary household bleach (0.7 M NaOCl) is used, the reaction occurs more slowly, and the final solution volume is excessive.

with water, and vacuum dried. BDCC was obtained as 240.2 g (91%) of off-white powder, mp 198–206 °C. For characterization purposes, a small sample was recrystallized from acetonitrile with 78% recovery to afford pure **2**, mp 215-217 °C (lit.[1] mp 216–217 °C).

7,7,8,8-Tetracyanoquinodimethane. A 500-mL, round-bottomed, four-necked flask (or three-necked flask with a Y adapter) was fitted with a mechanical stirrer, thermometer, 5-mm-i.d. gas introduction tube extending to near the bottom of the flask, and a 50-mL buret positioned for liquid addition into an open neck. The flask was charged with 25.0 g (0.120 mol) of crude BDCC from the above preparation and 300 mL of acetonitrile, and the buret was filled with 39.0 mL (0.483 mol) of pyridine. The gas tube was connected to a chlorine cylinder by PVC tubing that included an in-line rotameter (glass ball) calibrated to supply chlorine at a rate of 620 mL/min. The gas tube was temporarily removed from the flask during the initial phase of the procedure. The stirrer was started, and the contents of the flask were warmed to 40–50 °C. The heating mantle was removed, and the gas flow was started at the precalibrated rate. (On a reaction of this scale, this flow rate has been found experimentally to supply 0.24 mol of chlorine in almost exactly 10 min and corresponds to an "effective" flow rate of ca. 550 mL/min.) When the gas flow had stabilized, the tube was reinserted into the reaction flask, and a stopwatch was started at the same instant. After 15 s, the pyridine addition was started at a flow rate of exactly 4 mL/min (1 mL/15 s). Throughout the reaction, the chlorine and pyridine additions were continuously regulated to maintain precisely constant rates, and the temperature was held between 40 and 50 °C by occasional application of a cooling bath. Initial precipitation of the product occurred at 4–5 min. At a reaction time of 8 min (when 31 mL of pyridine had been added) the pyridine addition rate was increased to 8 mL/min for 1 min. The addition of the entire 39 mL of pyridine was thus completed at the 9-min point. The chlorine addition was continued for 30 s, when a rapid color change from dark brown to orange was observed.[15] This color change serves as a visual endpoint for the reaction; as soon as it occurs the chlorine tube must be removed from the solution immediately. The reaction mixture was allowed to stir for an additional 5 min, and the color slowly reverted from orange to brown. The end-point color was then restored by reintroduction of the chlorine tube for 15 s. The reaction mixture was cooled to 0 °C, and the precipitated product was collected by suction filtration, washed with 150 mL of cold acetonitrile, and vacuum dried. TCNQ was obtained as 21.6 g (88%)[16] of orange-bronze crystals: mp 287–289 °C (lit.[1] mp 289–291 °C); estimated purity 99%.[17]

Note: This procedure is best conducted with two operators. One operator normally regulates the chlorine flow and temperature while the other controls the pyridine addition. Mastery of the technique may require one or two practice runs. The 25-g run described here is a convenient scale for demonstration purposes. We normally carry out the reaction on 10 times this scale with no change in procedure or results. The average yield for ten consecutive 250-g runs was 87 ± 1%.

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Registry No. BDCC, 1518-15-6; TCNQ, 1518-16-7; hydroquinone, 123-31-9; malononitrile, 4341-85-9.

(15) Optimum yields of TCNQ are obtained when chlorine is in *very* slight excess during the simultaneous addition. This is why the pyridine addition is started after a 15-s delay. However, the end-point color change can only be observed when pyridine is in excess. The increase in the pyridine addition rate near the end of the reaction serves to "set" the color for the end-point change. The slight excess of pyridine late in the reaction is not detrimental.

(16) The yield in this reaction is 95% if recrystallized BDCC is used. However, this results in a lower overall yield with no difference in TCNQ purity.

(17) This purity value was obtained by two independent methods: (1) measurement of the percent residue after sublimation and (2) comparison of the UV extinction coefficient with that of a purified standard.

Correlation Analysis: Hammett Substituent Constants and Hydroxyl Proton NMR Chemical Shifts of Triarylcarbinols

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Correlation analysis, the study of the relationships between the parameters known as substituent constants that appear in linear free energy expressions (e.g., the Hammett equation) and various directly measurable quantities, has been a subject of intense interest among chemists. Extensive reviews of the many aspects of this field have appeared in two recently published volumes.[1,2] In particular, many efforts have been made to establish a linear correlation (eq 1) between Hammett σ constants and NMR chemical shifts (δ).

$$\delta = a + b\sigma \quad (1)$$

In a recent review,[3] Tribble and Traynham list 182 published relationships purporting to be linear correlations of Hammett σ constants and proton NMR chemical shifts. However, the significance of most of these correlations is questionable. One reviewer[4] has stated, "To support any serious claim that there is a *precise* parallel between δ and σ, the linear correlation must be extremely good,...and should summarize the data so as to give r [the linear correlation coefficient] >0.95". In fact, only 40% of the relationships cited by Tribble and Traynham satisfy this criterion.

In addition, most of the aforesaid correlations may be faulted for yet another reason: the observed variation of the chemical shift with change in the σ constant is so small that any apparent trend may be more fortuitous than real. Thus, in the aforementioned listing, the magnitude of this variation (b in eq 1) exceeds 0.40 in only 27, and 1.00 in only 9 of the 182 relationships.

The investigation herein reported was undertaken in the hope of discovering a relationship between Hammett σ constants and proton NMR chemical shifts, which, in contrast to most of those that have been published would be significant by conforming to eq 1 with a correlation coefficient >0.95 and a variation factor (b) > 1.00.

In this study, the measurable quantity chosen for correlation with the Hammett σ constant was the chemical shift of the hydroxyl proton of the triarylcarbinol (**1**) (Chart I) dissolved in deuterated dimethyl sulfoxide. The selection of this particular chemical shift was prompted by the paper of Ouellette, Marks, and Miller[5] upon the conformational and substituent dependence of the hydroxyl proton chemical shift of arylcarbinols. Ouelette and his co-workers reported that the chemical shifts of the hydroxyl protons in each of five series of dimethyl sulfoxide solutions of arylcarbinols (**2**) were linearly correlated with

(1) Chapman, N. B., Shorter, J., Eds. "Advances in Linear Free Energy Relationships"; Plenum Press: New York, 1972.

(2) Chapman, N. B., Shorter, J., Eds. "Correlation Analysis in Chemistry"; Plenum Press: New York, 1978.

(3) Tribble, M. T.; Traynham, J. G. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972; 165–172.

(4) Ewing, D. F. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; 363.

(5) Ouellette, R. J.; Marks, D. L.; Miller, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 913.

0022-3263/83/1948-1368$01.50/0