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The Autoxidation of Selected Organic Solids in the Presence of Alumina

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A variety of organic solids have been autoxidized by passing air through a mixture of the powdered compound and ordinary or sodium methoxide-treated alumina. Methylene and hydroxymethylene groups adjacent to aromatic rings have been converted to carbonyl groups in the presence of both kinds of alumina (Table I) and several additional types of autoxidations have been carried out under the same conditions (Table II). The ability of base to promote many of these reactions is of special interest since it implies that these organic compounds react readily *via* ionic processes in the solid phase.

It has been repeatedly emphasized that the course of autoxidations is strongly influenced by the environment in which they are conducted[2,3] and that in typical liquid phase autoxidations low yields of a wide variety of products are obtained.[4] When an attempt was made in these laboratories to brominate anthracene in the presence of alumina the chief reaction was autoxidation of the anthracene to anthraquinone, a reaction which had previously been encountered in the course of a chromatographic procedure.[5] Since this environment contrasts so sharply with that obtaining in a liquid phase it was of interest to explore the scope and nature of autoxidation under these conditions.

The experiments of Tables I and II were carried out by passing air through a mixture of the powdered organic compound and ordinary or sodium methoxide-treated alumina. Since the standard conditions (*cf.* footnote *a*, Table I) were selected on the basis of studies on fluorene and fluorenol, they may be far from the optimum for the other compounds.

A number of alcohols with the hydroxymethylene groups adjacent to phenyl groups has been oxidized to ketones under the standard conditions, both with and without the sodium methoxide (Table I). These results gain interest from the fact that the literature contains very few examples of the autoxidation of alcohols to ketones and in fact there is good evidence that most alcohols are mild autoxidation inhibitors.[6,7]

Cyclohexanol has, however, been autoxidized to the hydroperoxide with 15% conversion; little if any ketone was formed directly but chemical reduction of the hydroperoxide to the ketone proceeded satisfactorily.[8] The conversion of cyclohexanol to cyclohexanone appears to have been involved to a major extent in the autoxidation of cyclohexane[9] and the autoxidation of phenylmethylcarbinol to acetophenone was an incidental parallel reaction in the formation of this ketone from ethylbenzene.[6]

TABLE I

AUTOXIDATIONS YIELDING KETONES[a]

	Without $NaOCH_3$		With $NaOCH_3$	
Compound	Recov.	Yld.,[b] %	Recov.	Yld.[b] %
Autoxidation of hydroxymethylene groups				
Xanthydrol	0.95	88	0.95	17
9-Hydroxy-9,10-dihydroanthracene	.77	60[c]	1.01	78[c]
Fluorenol	.80	39	0.93	81
p,p'-Dichlorobenzhydrol	.86	28	.99	48[d]
p,p'-Dimethoxybenzhydrol	.67	25	.98	60[e]
Benzhydrol	.79	19	.95	0
p-Bromophenylmethylcarbinol	.35	4	.94	7
Autoxidation of methylene groups				
Xanthene	1.05	92	1.08	94
Anthrone	0.77	63[f]	1.00	59
9,10-Dihydroanthracene	.79	59[g]	1.08	83[g]
2-Nitrofluorene	.87	39	1.15	23
Fluorene	.91	35	0.93	75
2-Bromofluorene	.78	23	1.02	71

[a] Std. conditions: Air was passed through a mixture of 0.01 mole of powdered organic compound and 50 g. of ordinary or sodium methoxide-treated alumina; a reaction time of 48 hr. and a temperature of 120° were employed with the untreated alumina while a time of 24 hr. and a temperature of 55° were used with the sodium methoxide-treated alumina. [b] Total weight of material eluted divided by weight of starting material. [c] Product was anthraquinone. [d] Heated 24 hr. at 89°; standard conditions gave 0% yield. [e] Heated 24 hr. at 120°; standard conditions gave 0% yield. [f] This reaction was previously encountered in the course of a chromatographic procedure (J. H. Pinckard, A. Chatterjee and L. Zechmeister, THIS JOURNAL, **74**, 1602 (1952)). [g] Yield of anthraquinone; anthracene was also isolated in 9% yield without the sodium methoxide and in 3% yield with the sodium methoxide.

There appears to be some correlation between the yields of ketones obtained by the autoxidation of alcohols without the sodium methoxide (Table I) and the stability of the free radical obtained upon abstraction of a hydrogen atom from the carbinol carbon as might be expected on the basis of the mechanism which has been proposed.[9] In the autoxidation of alcohols promoted by bases a perketal, $R_2COH(OOH)$, may well be formed by a process analogous to that advanced for related base-catalyzed oxidations.[10,11] The perketal could decompose easily to give the ketone and hydrogen peroxide. The results (Table I) suggest that the ease of formation of the anion in the first step may

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[1] From the Ph.D. Thesis of Louis E. Trapasso, June, 1959.

[2] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946, p. 232.

[3] C. E. Frank, *Chem. Revs.*, **46**, 155 (1950).

[4] H. E. De La Mare and W. E. Vaughn, *J. Chem. Ed.*, **34**, 10, 64 (1957).

[5] Y. Matsumoto and E. Funkabo, *J. Chem. Soc.*, (*Japan*), **72**, 731 (1951).

[6] W. S. Emerson, J. W. Heyd, V. E. Lucas, W. B. Cook, W. I. Lyness and J. K. Stevenson, THIS JOURNAL, **70**, 3764 (1948).

[7] C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1957, p. 880.

[8] N. Brown, M. J. Hartig, M. J. Roedel, A. W. Anderson and C. E. Schweitzer, THIS JOURNAL, **77**, 1756 (1955).

[9] N. N. Semenov (Translated by M. Boudart), "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., Vol. I, 1958, pp. 126-127.

[10] Y. Sprinzak, THIS JOURNAL, **80**, 5449 (1958).

[11] N. Kornblum and H. E. De La Mare, *ibid.*, **73**, 880 (1951).

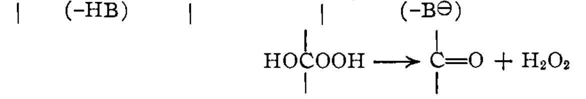
TABLE II

AUTOXIDATION OF ADDITIONAL COMPOUNDS[a]

Compound	Product	Without $NaOCH_3$ Recovery, %	Without $NaOCH_3$ Yld.	With $NaOCH_3$ Recovery, %	With $NaOCH_3$ Yld.
Anthracene	Anthraquinone	0.67	6[b]	1.05	18[c]
9-Methylanthracene	Anthraquinone	.71	20	1.05	0[d]
Acridane	Acridine	.86	50[e]	0.87	78
2-Naphthylamine	Dibenzo[*a,h*]-phenazine	.67	40	1.02	29[f]
2-Aminochrysene	Diphenanthro[1,2-*a*-1′,2′-*h*]phenazine	.66	9	0.97	0[g]
1-Bromo-2-aminonaphthalene	Dibenzo[*a,h*]phenazine	.60	0	.84	5
9-Chlorofluorene	Fluorenone	.82	42	.95	0
Diphenylacetonitrile	Benzophenone	.78	42	.92	80

[a] See footnote *a*, Table I, for standard conditions. [b] A 66% yield of starting material isolated. [c] A 75% yield of starting material isolated. [d] A 61% yield of starting material isolated. [e] A 4% yield of acridone isolated. [f] A 42% yield of starting material isolated. [g] A 68% yield of starting material was isolated.

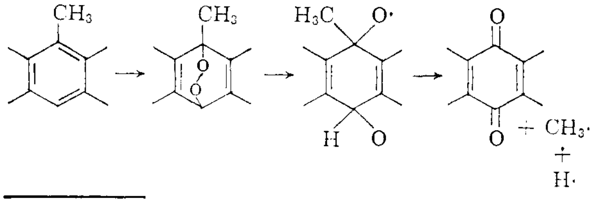
well be the chief factor which determines whether the reaction will proceed satisfactorily.



$$\mathrm{HO\overset{|}{\underset{|}{C}}H} \xrightarrow[(-\mathrm{HB})]{\mathrm{B}^{\ominus}} \mathrm{HO\overset{|}{\underset{|}{C}}^{\ominus}} \xrightarrow{\mathrm{O_2}} \mathrm{HO\overset{|}{\underset{|}{C}}OO^{\ominus}} \xrightarrow[(-\mathrm{B}^{\ominus})]{\mathrm{HB}} \mathrm{HO\overset{|}{\underset{|}{C}}OOH} \longrightarrow \mathrm{\overset{|}{\underset{|}{C}}{=}O} + \mathrm{H_2O_2}$$

In the second section of Table I results on the autoxidation of methylene groups flanked by two phenyl groups are listed. Ketones were obtained directly although hydroperoxides are the usual products of such autoxidations.[12] Suggestions concerning the role of surfaces in the early stages of these autoxidations[13] as well as in the decomposition of hydroperoxides to a ketone and water[14] have been advanced. In general, good yields were obtained and again the reactions are promoted by sodium methoxide. Autoxidation of fluorenes in alkaline solution has been reported previously and mechanisms for both the base-promoted and the base-free autoxidations of methylene groups have been proposed.[10,15,16] It is of interest that although 9,10-dihydroanthracene was readily converted to anthraquinone, starting material was recovered in good yield when diphenylmethane was subjected to the same conditions.

Additional types of autoxidations carried out according to the same standard procedures are listed in Table II. The evidence that base promotes the autoxidation of anthracene is of interest. The loss of a methyl group from 9-methylanthracene to give anthraquinone as shown by the results of mixture melting point determinations is also noteworthy. It is suggested, by extension of the route proposed for the conversion of methyl diphenylmethyl hydroperoxide to benzophenone,[17,18] that the methyl group is lost as shown



The loss of bromine from the 1-bromo-2-aminonaphthalene is also of interest but not without precedent.[19]

A halogen atom is also lost in the conversion of 9-chlorofluorene to fluorenone (Table II). Apparently this reaction proceeds by way of hydrolysis to fluorenol since *p*-chlorobenzyl and triphenylmethyl alcohols were isolated in 38 and 82% yields when the corresponding chlorides were subjected to the standard conditions without base.

It has recently been reported that diphenylacetonitrile is autoxidized to benzophenone in solution in the presence of bases, but not in their absence and an interpretation of the reaction was given.[20] Under the markedly different conditions of the present study good yields of benzophenone were obtained both with and without sodium methoxide. In the absence of base the fundamental reaction may be analogous to the autoxidation of a hydrocarbon to an alcohol.

$$(C_6H_5)_2CHCN \longrightarrow (C_6H_5)_2COHCN \longrightarrow (C_6H_5)_2C{=}O + HCN$$

It was found that no, or only momentary, external heating was required in certain cases if both base and copper salts[20] were used on the alumina to promote the reaction. In this way 35 and 75% yields of fluorenone were obtained from fluorene and fluorenol with a reaction time of about one hour during which the temperature rose spontaneously to about 120°. A 23% yield of the phenazine (Table II) was similarly obtained from 2-naphthylamine.

The alumina apparently serves some specific function in these autoxidations since attempts to use Ottawa sand or anhydrous sodium carbonate or sodium sulfate in place of the alumina for the autoxidation of fluorenol were unsuccessful; starting material was recovered almost quantitatively in each case.[21] It appears probable that much of the oxygen utilized is pre-adsorbed on the alumina, for quite extensive oxidation of both fluorenol and fluorene were found to occur even when no air was passed through the mixture of alumina and organic solid.

Autoxidations promoted by base or by both base and copper salts are considered to proceed by ionic

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(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 406, 409.

(13) P. George, *Trans. Faraday Soc.*, **42**, 210 (1946).

(14) A. D. Walsh, *ibid.*, **42**, 273 (1946).

(15) A. Wanscheidt, *Ber.*, **59B**, 2094 (1926).

(16) G. A. Russell, *J. Chem. Ed.*, **36**, 111 (1959).

(17) P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

(18) A. Willemart, *Bull. soc. chim.*, [5] **5**, 556 (1938).

(19) P. T. Cleve, *Ber.*, **20**, 1989 (1887).

(20) M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, **2**, 97 (1958).

(21) It is pertinent to note that a suspension of finely divided sodium carbonate, or certain other solid bases, in cumene promotes its conversion to the hydroperoxide (G. G. Joris, U. S. Patent 2,613,227, Oct. 7, 1952).

mechanisms and it is noteworthy that here such processes appear to proceed readily in the solid phase. The possibility that the reactions occur in a thin film of liquid on the alumina surface cannot be definitely eliminated, but the mixtures of reactants, products and alumina remain as a free flowing powder throughout the process. It appears probable that the reactions occurred in nonliquid adsorption complexes on the alumina surface. The implication that ionic reactions of organic compounds proceed rapidly under such conditions requires further investigation.

Acknowledgment.—It is a pleasure to acknowledge generous financial support by the National Science Foundation which greatly aided the progress of this work.

Experimental[22]

Experiments of Tables I and II.—In the standard procedure developed for these autoxidations, a six-bulb Allihn condenser (400 mm. jacket) mounted vertically was employed as the reaction vessel. An intimate mixture of 0.01 mole of the solid organic compound, well ground in a mortar, and 50.0 g. of Fisher adsorption alumina, 80 to 200 mesh, was supported on a glass wool plug at the bottom of the inner tube of the condenser which was approximately half filled by this amount of powder. All of the organic solids were recrystallized until their melting points agreed closely with the literature values. The lower water inlet of the condenser was replaced by a side arm 20 mm. in diameter and about 25 cm. long ending in a ground glass joint to which a 500-ml. flask was attached. The flask held a solvent of suitable boiling point which was heated by means of a hemispherical mantle. Thus the condenser jacket functioned as a reflux condenser to hold the powder at a constant temperature.

Dried air was passed upward through the powder by means of a vacuum pump at the rate of 2.7 l. per min. This caused "bubbling" of the powder and produced uniform exposure. In order to avoid sucking any fine powder into the pump a glass wool plug was placed in the top of the inner tube of the condenser and air leaving this tube passed through a foam trap[23] and a thin layer of oil before entering the pump. After the air flow was stopped at the end of the experiment the temperatures were read on a thermometer inserted into the powder through the top of the condenser.

In the experiments in which the sodium methoxide was used the alumina was freed of any moisture by heating it in an oil-bath at 200 ± 2° for 1 hr. at 15 to 20 mm. pressure. The 0.1 mole of powdered sodium methoxide (Fisher) was then added with vigorous shaking followed by 30 ml. of anhydrous methanol with further shaking. After the methanol was removed by heating the mixture at 200 ± 2° for 1 hr. under reduced pressure the resulting powder was allowed to cool, the pulverized organic compound was quickly and thoroughly mixed with it and the combined solids placed in the Allihn condenser and the autoxidation carried out as described above.

Upon completion of the heating the solid mixture was, unless otherwise noted, extracted in a Soxhlet for 14 hours with 210 ml. of 60° to 80° petroleum ether then for 5 hours with 180 ml. of chloroform and finally for 5 hours with 180 ml. of ethyl acetate. The desired products were ordinarily obtained from the petroleum ether and chloroform extracts by ordinary concentration and crystallization procedures. The ethyl acetate extract was usually merely evaporated to dryness and the residue weighed; this weight together with the weights of the desired product and other residues from the other extracts allowed the tabulated data on recovery to be calculated.

In the experiments in which the oxidation of primary amines to phenazines was studied (Table II) only two extraction solvents were employed, namely, tetrahydrofuran (210 ml. for 4 hr.) and ethyl acetate (180 ml. for 5 hr.). Repurified tetrahydrofuran was used and the possibility of peroxides forming in the tetrahydrofuran and causing further phenazine production was eliminated by the results of experiments in which equally good yields of product were obtained, although less conveniently, by using only ethyl acetate or chloroform as extraction solvents. Apparently the phenazine obtained from 2-aminochrysene is new. It was obtained as tan plates which melted at 424–428°. *Anal.*[24] Calcd. for $C_{36}H_{30}N_2$: C, 89.98; H, 4.19; N, 5.83. Found: C, 89.54; H, 4.31; N, 6.33.

The other tabulated yield data refer to crystalline material which, although frequently obtained in more than one crop, almost without exception melted within 4° of the highest value recorded for the compound. Since in numerous cases separation of solids by fractional crystallization was required, the yields represent minimum values and are of qualitative significance only.

Variation of Time, Temperature and Amounts in the Autoxidation of Fluorenol.—In these experiments, the fluorenol was, unless otherwise noted, adsorbed onto the alumina from a solvent rather than being merely mixed with it as in the above-described procedure. One and one-half grams of fluorenol was dissolved in 70 ml. of chloroform and 30 ml. of petroleum ether. The alumina (50 g.) was added and after swirling for 5 min. the slurry was filtered with suction and the filtrate poured over the filter cake three times. Suction was then continued until the filter cake appeared dry whereupon it was washed with 40 ml. of petroleum ether. In a group of four experiments it was found, by weighing the residues obtained upon evaporating the filtrates to dryness, that 1.40 ± 0.04 g. of fluorenol remained adsorbed. The remainder of the procedure was, unless otherwise noted, the same as previously described.

In a group of five experiments with a reaction time of 24 hr. the temperatures were 30, 89, 120, 148 and 189°: the corresponding yields of fluorenone were 0, 34, 54, 48 and 42%. It appears that at the higher temperatures by-products which are more tenaciously adsorbed are formed since the recovery, defined as for Table I, decreased rather consistently from 0.96 to 0.74 as the temperature was increased. The yields obtained in two additional experiments with reaction times of 12 and 48 hr. at 120° were 46 and 54%.

It was found that good yields of fluorenone could be obtained in less time by first using a low and then a high temperature. Thus when the alumina and fluorenol mixture was first heated for 2 hr. at 89° and then for 3 hr. at 148° the yield was 47% while heating for 2 hr. at 89° and then for 3 hr. at 189° gave a 72% yield.

In a group of four experiments 0.200, 0.450, 1.50 and 4.00 g. of fluorenol was dissolved in the chloroform and petroleum ether and the alumina added as before; the amounts of fluorenol adsorbed were 0.200, 0.450, 1.43 and 3.13 g. With a reaction time of 24 hr. and a temperature of 120° the corresponding yields of fluorenone were 32, 42, 54 and 63%. The recovery was 0.86 ± 0.02 in all cases. A satisfactory explanation of the increasing yields cannot be given at present.

The effect of varying the amount of sodium methoxide was determined using the standard procedure for the experiments of Tables I and II. With 0.025 and 0.050 mole of sodium methoxide the yields of fluorenone were 23 and 49%. Starting material was recovered to the extent of 60 and 25% in the two cases.

Variation in Time, Temperature and Amounts in the Autoxidation of Fluorene.—Here, too, the fluorene was adsorbed from a solvent onto the alumina. Two grams of fluorene was dissolved in 70 ml. of petroleum ether with warming before adding the 50.0 g. of alumina. The remainder of the procedure was like that described in the preceding section for the adsorption and reaction of fluorenol.

In a series of four experiments in which the temperatures were 89, 120, 148 and 189° and the reaction time was 24 hr. the yields of fluorenone were 0, 8, 13 and 32%, respectively. With a reaction time of 48 hr. and the same temperatures the corresponding yields were 29, 30, 29 and 23%. In all eight experiments the weights of fluorene adsorbed was 1.01 ± 0.07 g. and in both series of experiments the re-

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[22] All melting points are corrected.

[23] Ace Glass Inc., Vineland, N. J., Cat. No. 5230.

[24] We wish to thank Professor Kathryn Gerdeman and Miss Jane Swan for the microanalyses.

covery, defined as for Table I, tended to decrease from about 0.88 to about 0.72 as the reaction temperature increased.

To determine the effect of varying the amount of fluorene, 1.00, 2.00 and 4.00 g. of fluorene were mixed with the 50.0 g. of alumina in a group of three experiments. The remainder of the procedure followed that given above for the experiments of Tables I and II. The resultant yields of fluorenone were 31, 34 and 40%. Comparison of the 31% yield obtained in the first experiment of this group with the 30% yield obtained in the second experiment of the preceding series indicates that it makes no significant difference whether the fluorene is adsorbed onto the alumina or merely mixed with it.

Study of Free Radical Promotors.—The spontaneous reactions using both a base and a copper salt were carried out: Fifty grams of alumina was added to 0.001 mole of cupric chloride dihydrate in absolute methanol, the slurry was swirled and filtered and the filter cake was added to a solution prepared from 120 ml. of anhydrous methanol and 12 g. of sodium. The mixture was swirled intermittently for 5 min., filtered with suction and the filtrate poured over the filter cake four times. The filter cake was then heated in an oil-bath at 200 ± 2° at 15 mm. pressure for 30 min. with occasional shaking. After the cooled powder was rapidly and thoroughly mixed with 0.01 mole of the pulverized organic compound to be oxidized the mixture was placed in the modified Allihn condenser and dried air was passed through in the standard fashion.

With fluorene a spontaneous reaction occurred after the air was passed through for 25 min. with no external heating; after 8 min. more the temperature rose to 119°. The temperature soon dropped and the air stream was stopped after a total of about 70 min. A 35% yield of fluorene was isolated and from the mother liquors a 5% yield of di(biphenylene)-ethylene which melted at 187.5–189° (lit. m.p. 189–190°) was obtained. *Anal.* Calcd. for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.02; H, 5.19. The isolation of this symmetrical product strongly indicates fluorenyl free radicals were formed.

With fluorenol little heat was apparent after air was passed through for 30 min. The base of the condenser was therefore heated for 30 sec. with a microburner whereupon reaction began as evidenced by heat evolution which continued for 20 min.; after 8 min. the temperature was 122°. Air was passed through a total of 80 min. and the yield of fluorenone was 75%.

The procedure followed with 2-naphthylamine was essentially the same as for fluorenol and the temperature reached was also about the same. A 23% yield of dibenzo-[*ah*]phenazine was obtained.

In two experiments to determine whether benzoyl peroxide had any effect the 50 g. of alumina containing 1.06 ± 0.02 g. of adsorbed fluorene was well mixed with 0.002 mole of benzoyl peroxide. With a reaction time of 24 hr. a 30% yield of fluorenone was obtained at a temperature of 120° while a 24% yield was obtained at a temperature of 148°. The corresponding yields obtained without benzoyl peroxide, as described above, were 8 and 13%.

Supplementary Experiments.—In an experiment to determine how much oxidation ocurred if air was not passed through the system 1.40 g. of fluorenol adsorbed onto the 50 g. of alumina was employed. The reaction time was 48 hr. and the temperature 120°. Except that no air was passed through the system the procedure was exactly like that described above for the time and temperature studies. The yield of fluorenone was 20% as compared to the 54% yield obtained when an air stream was used.

Fluorene was used in place of fluorenol in a similar experiment carried out according to the standard procedure for the experiments of Tables I and II (without sodium methoxide) except that no air was passed through the heated mixture of alumina and fluorene. The yield of fluorenone was 17% as compared to the tabulated value of 35% produced when an air stream was used.

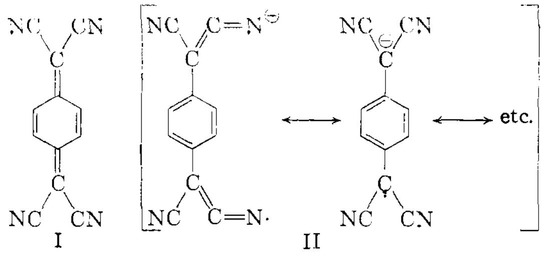
COMMUNICATIONS TO THE EDITOR

7,7,8,8-TETRACYANOQUINODIMETHANE AND ITS ELECTRICALLY CONDUCTING ANION-RADICAL DERIVATIVES

Sir:

7,7,8,8-Tetracyanoquinodimethane (TCNQ) has been synthesized and found to yield a series of stable anion-radical derivatives. Certain of these derivatives have the lowest electrical resistivities yet reported for organic compounds. This report describes the synthesis of TCNQ and its anion-radical derivatives.

TCNQ (I) is a strong pi-acid[1] and forms two series of salt-like crystalline complexes, each involving complete transfer of an electron to TCNQ with the formation of the anion-radical TCNQ$^{\overline{\cdot}}$ (II). The first series is represented by the formula $M^+TCNQ^{\overline{\cdot}}$ and is generally characterized by relatively high electrical resistivity (10^4–10^{12} ohm cm.). The second series, represented by the formula $M^+(TCNQ^{\overline{\cdot}})(TCNQ)$, contains a molecule of formally neutral TCNQ in addition to TCNQ$^{\overline{\cdot}}$ and is characterized by exceptionally low electrical resistivity (0.01–100 ohm cm.).[2,3] In addition, the electrical resistivity is highly anisotropic along the three principal crystal axes.



I II

TCNQ, m.p. 293.5–296°, was synthesized in high yield by the bromine–pyridine dehydrogenation of 1,4-bis-(dicyanomethylene)-cyclohexane obtained by condensation of malononitrile with 1,4-cyclohexanedione.[4] *Anal.* Calcd. for $C_{12}H_4N_4$:

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[1] The equilibrium constant for π-complex formation between TCNQ and pyrene is 78.4 as compared to 29.5 for the complex between tetracyanoethylene and pyrene; see R. E. Merrifield and W. D. Phillips, This Journal, **80**, 2278 (1958).

[2] For comparison, the resistivity of hyperpure silicon is about 1000 ohm cm., graphite about 10^{-3} ohm cm., and most organic compounds, 10^{10}–10^{14} ohm cm. The lowest resistivity previously reported for an organic compound appears to be 8 ohm cm. for the metastable iodine/perylene complex (J. Kommandeur and F. R. Hall, *Bull. Am. Phys. Soc.*, Series II, **4**, 421 (1959).

[3] Detailed physical study of the anion-radical derivatives has been carried out. Data on electrical and magnetic properties (R. G. Kepler, P. E. Bierstedt, and R. E. Merrifield, *Phys. Rev. Letters*, in press) and on EPR studies (D. B. Chesnut, H. Foster, and W. D. Phillips, *J. Chem. Phys.*, in press) will appear shortly.