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RECEIVED for review August 20, 1964. Accepted March 28, 1966. This research supported in part by the National Science Foundation undergraduate research program.

Perhaloketones

Aromatic Derivatives of a Perchlorinated Caged Ketone

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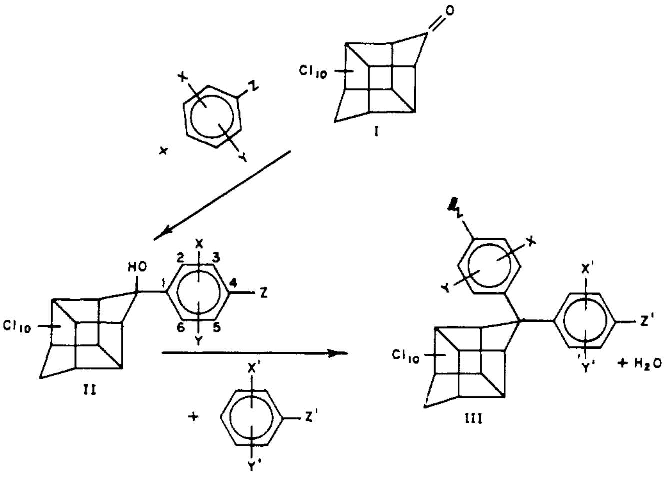
The perchlorinated cage ketone, decachloropentacyclo [5.3.0.0^{2,6}.0^{4,10}3.0^{5,9}] decan-3-one, (I) has been reacted with various aromatic compounds—mainly phenols and hydrocarbons—using several acid catalysts. Tertiary carbinols (II) were prepared from phenols, and "bis" compounds (III) were obtained from phenols and the other aromatic compounds. The carbonyl carbon atom in I is concluded to be less electropositive than that in the fluorinated acetones. A number of secondary derivatives were also prepared from the aromatic condensates of I.

THE electropositive nature of the carbonyl carbon atom in the perchlorinated caged ketone (I), decachlorooctahydro-1, 3, 4-metheno -2*H*-cyclobuta [cd] pentalen-2-one, also known as decachloropentacyclo [5.3.0.0^{2,6}.0^{4,10}.0^{5,9}] decan-3-one, or as Kepone, has already been demonstrated by its ability to form adducts with alcohols or amines, (*4*) and to undergo uncatalyzed condensation with aliphatic ketones and other compounds containing activated methylene groups (*3*). The purpose of this study was to determine the ease of reactivity of the carbonyl group of I with various aromatic nuclei, as follows:

The results obtained with three phenols and one phenolic ether are summarized in Table I. Several acid catalysts promote reaction on the nucleus, and good yields of either the 1 to 1 (Type II) or the 1 to 2 (Type III) molar ratio reaction products of I with phenols could be obtained. When toluenesulfonic acid is used as catalyst, temperature appears to be the major variable in determining the reaction ratio when the phenol is applied in large excess. With BF_3, on the other hand, only the Type III product was formed, even at room temperature or at 1 to 1 molar ratio. The Type II product was a mixture of the ortho and para isomers using either of two catalysts (toluenesulfonic acid or $AlCl_3$) at a 1 to 1 molar ratio of the reagents. (IIa and IIb were also prepared in pure form by an alternate unequivocal method comprised of



IIa: X = Y = H; Z = OH
IIb: X = H; Y = 2-OH; Z = H
IIc: X = Y = H; Z = OCH_3
IId: X = 3-CH_3; Y = 5-CH_3; Z = OH
IIIa: X = X' = Y = Y' = H; Z = Z' = OH
IIIb: X = X' = 3-CH_3; Y = Y' = H; Z = Z' = OH
IIIc: X = X' = Y = H; Y' = 5-CH_3; Z = Z' = OH
IIId: X = X' = Y = Y' = H; Z = Z' = OCH_3
IIIe: X = X' = 3-CH_3; Y = Y' = 5-CH_3; Z = Z' = OH
IIIf: X = X' = Y = Y' = Z = Z' = H
IIIg: X = X' = Y = Y' = H; Z = Z' = CH_3
IIIh: X = X' = H; Y = Y' = 3-CH_3; Z = Z' = CH_3
IIIi: X = X' = Y = Y' = H; Z = Z' = Cl
IIIj: X = X' = Y = Y' = H; Z = Z' = CH_3CONH

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Table I. Phenolic Derivatives of I

Substrate	Catalyst[a]	Mole Ratio Catalyst:1	Mole Ratio Reagents	Reaction Conditions ° C.	Reaction Conditions Hours	Product(s)	Yield[b]	M.P.,[c] ° C.
Phenol	Anhyd. HCl	[d]	[e]	120	70	IIa	25	260–262[f]
Phenol	P	0.01	[e]	110	16	IIa	25	...
Phenol	T	0.15	[e]	132	9	IIa	80	...
Phenol	T	0.15	[e]	175	9	IIIa	81	306–308[g]
Phenol	T	0.01	[h]	135	22	IIa + IIb	29	...
Phenol	BF_3	10.0	[e]	25	24	IIIa	79	...
Phenol	$AlCl_3$	0.15	[h]	140	24	IIa + IIb	26	...
2-Cresol	BF_3	1.00	[h]	110	24	IIIb	95	251–255
2-Cresol	T	0.30	[e]	182	17	IIIb	...	...
2-Cresol(+IIa)	T	0.30	[e]	182	17	IIIc	100	264–268[j]
2,6-Dimethylphenol	T	0.03	[e]	170–180	7	IId + IIIe	...	...
2,6-Dimethylphenol	T	0.03	[e]	175–185	12	IIIe	...	310–315[k]
Anisole	BF_3	1.30	[l]	110	48	IIId	43	279–286[m]
Anisole	$AlCl_3$	0.38	[l]	135	3	IIc	15	198–200[n]

[a] P = Polyphosphoric acid; T = Toluenesulfonic acid monohydrate. [b] Crude yield based on I. [c] Uncorrected. [d] Bubbled through reaction mixture. [e] Excess phenolic compound used. [f] Analysis: Theor.: 32.9% C; 1.0% H; 2.9% OH; Found: 32.8; 1.0; 3.0. [g] Analysis: Theor.: 53.7% Cl; Found: 53.5. [h] Equimolar ratio used. [i] Analysis: Theor.: 41.8% C; 2.1% H; 51.5% Cl; Found: 41.8; 2.5; 50.9. [j] Analysis: Theor.: 40.8% C; 1.9% H; Found: 41.1; 1.7. [k] Analysis: Theor.: 43.5% C; 2.5% H; 49.5% Cl; Found: 43.9; 2.6; 49.5. [l] 1:2 molar ratio I: anisole used. [m] Demethylated to IIIa. [n] Demethylated to IIa; also proved identical with material made by the Grignard reaction.

reaction of I with Grignard reagents from 4- and 2-bromoanisoles, respectively, followed by demethylation in each case (*3*). N.M.R. spectral analysis of IIIa, however showed it to contain only material with para hydroxyl groups. IIIa was also prepared by demethylation of IIId, prepared directly from I and anisole.

That Type II compounds are intermediates for Type III compounds is strongly indicated by the fact that IIa (prepared via the Grignard reaction) gave IIIa upon treatment with BF_3 and phenol, and that IIa reacted with 2-cresol to form a hybrid Type III product (IIIc). Table I shows that Type II compounds are formed at a lower temperature than the Type III materials.

IIIa was converted to a tetrabromo derivative, aliphatic and aromatic esters, carbamates, and a polycarbonate. derived from bisphenols containing unhalogenated three-dimensional polycyclc bridges.

As indicated in Table II, nonphenolic aromatic compounds could also be condensed with I using anhydrous $AlCl_3$ as catalyst to form Type III derivatives. Between 1.9 and 3.3 moles $AlCl_3$ were employed per mole I. No reaction occurred with *o*-xylene when 0.38 mole $AlCl_3$ was used, although anisole did react (at 1 to 1 molar ratio) with this quantity of catalyst (Table I). Paratoluenesulfonic acid and BF_3 were also ineffective in catalyzing interaction between I and *o*-xylene. No derivatives of Type II were isolated, although compounds of this type (as derived from benzene and chlorobenzene) have been prepared via the Grignard reaction(*3*).

Several of the compounds listed in Table II were converted to secondary derivatives. The methyl groups of IIIg were oxidized to carboxyl groups with chromic oxide, and the resulting dicarboxylic acid was converted to the methyl ester. Compound IIIj was hydrolyzed to the corresponding diamine, the amino groups of which could be diazotized in the normal manner.

EXPERIMENTAL

Purification of Crude I. Crude I hydrate, 100 grams, (obtained from Hooker Chemical Corp.) was dissolved in 450 ml. of 78% aqueous methanol at reflux, and the insolubles were then removed by hot filtration. The filtrate was refluxed for 10 minutes with charcoal (Darco G60; 3 wt. % based on I hydrate), filtered, and cooled at 10° C. to effect crystallization. The solid material was filtered, redissolved in 108 ml. of 78% aqueous methanol, heated to reflux, filtered hot, and the filtrate cooled to 10° C. The product was filtered, washed with 90 ml. of 78% aqueous methanol, and dried in an oven at 80% C. to constant weight. The yield of purified tri- to tetrahydrate was 63%. It was white and melted at about 349° (dec.). Such purification is not always essential (*3, 4*), but is recommended for best results in preparing derivatives of I.

I is soluble in the common organic solvents, expecially those containing oxygen, such as alcohols or ketones. It is insoluble in aqueous systems generally, but quite soluble in warm dilute aqueous sodium hydroxide. As stated below, anhydrous I can be prepared from the hydrate by azeotropic removal of water. However, anhydrous I absorbs moisture from the air to regenerate the stable hydrate.

Condensation of I with Phenolic Compounds. Purified I hydrate (12.2 grams, 0.024 mole) was mixed with phenol (22.6 grams, 0.24 mole), and the mixture heated to a melt at 80° C. Toluenesulfonic acid monohydrate (0.7 gram.) was added, and the mixture was heated with stirring for 9 hours at 170–175° C. If necessary, the water formed during reaction can be removed by distillation to permit main-

Table II. Reaction of I with Nonphenolic Aromatic Compounds[a]

Compound	Mole Ratio $AlCl_3$:I	Temp., ° C.	Time, Hours	Product	Yield	M.P., ° C.	Analysis C Calcd.	 C Found	 H Calcd.	 H Found	 Cl Calcd.	 Cl Found
Benzene	1.9	25–40	24	IIIf	60	279–282	42.0	41.7	1.6	1.8	56.4	56.1
Toluene	2.2	25–40	24	IIIg	57	228–230	43.9	44.5	2.1	2.1	54.1	53.9
o-Xylene	2.0	25–40	24	IIIh	88	262–264	45.6	45.7	2.6	2.6	51.8	51.1
Chlorobenzene	1.9	25–40	24	IIIi	73	285–286.5	37.8	38.0	1.2	1.4	61.1	60.4
Acetanilide[b]	3.3	48	60	IIIj	99	> 320	...[c]	...	...	...	...	...

[a] $AlCl_3$ used as catalyst; excess reagent used as solvent except as noted. [b] CS_2 used as solvent. [c] Identified by hydrolysis to the diamine.

tenance of this temperature range. The reaction mixture was poured into 350 ml. of hot water to precipitate the desired product, which was filtered. It was then boiled with 500 ml. of fresh water for 15 minutes and filtered to remove residual phenol. Final purification was effected by two recrystallizations from 90% aqueous methanol, followed by drying at 100° C. for 16 hours in vacuo. Yield: 81%.

This general type of procedure was employed for reacting I with 2-cresol and with 2,6-dimethylphenol, using the conditions summarized in Table I, and for condensing IIa with 2-cresol to form the hybrid derivative IIIc.

Compound IIa was prepared similarly, except that the reaction was conducted at 132° C. for 9 hours. The reaction temperature must be kept below 140° C. to avoid formation of IIIa. IIa was recrystallized from 55% aqueous methanol, or from aqueous acetic acid.

The infrared spectrum of IIIa shows hydroxyl stretching at 2.93 μ and aromatic carbon-carbon double bond skeletal in-plane vibrations at 6.20, 6.25, and 6.62 μ. The N.M.R. spectrum was obtained from an acetone solution of IIIa, using tetramethylsilane as an external zero reference point. A typical AB patterm, indicating para substitution, was found in the aromatic region of the spectrum. Peak positions due to the protons ortho to the hydroxyl group were found at 6.20 and 6.35 p.p.m.; the protons meta to the hydroxyl group showed peaks at 6.83 and 6.98 p.p.m. The coupling constant was 9 c.p.s., which is consistant with the value normally found for two adjacent, nonequivalent aromatic protons. Some secondary splitting of the order of 1 to 2 c.p.s. was also observed in the AB pattern. This was attributed to coupling between meta protons. A sharp peak due to the hydroxyl proton was found at 8.11 p.p.m.

Esters of IIIa. IIIa (40 grams, 0.06 mole), pyridine (200 ml.), and acetic anhydride (50 ml.) were mixed and refluxed 1.5 hours. The diacetate (35 grams) separated upon cooling; drowning the filtrate in water gave an additional 9.0 grams. The total crude yield was, thus, 44 grams. (95%). Recrystallization from a mixture of carbon tetrachloride and chloroform gave m.p. 294.5–297°. Anal.: Theor.: 41.9% C, 1.9% H, 47.7% Cl; Found: 41.7, 1.9, 47.8. The dibenzoate and the dilaurate were prepared similarly.

Bromination of IIIa. To a solution of 10 grams (0.015 mole) IIIa in 500 ml. of absolute ethanol was added slowly with vigorous stirring a solution comprised of 10 grams of bromine and 15 grams of KBr in 100 ml. of water. More ethanol was added periodically to maintain homogeneity, to a final solution volume of 1200 ml. The product was precipitated by adding 250 ml. of water. After washing with water and drying, the yield was 13 grams (87%). After recrystallization from ethanol-water and ether-hexane, the product melted at 349–351° C. (decomp.). Anal.: Theor.: 27.0% C, 0.6% H, 55.2% total halogen as chlorine; Found: 27.3, 0.7, 54.0. The compound is concluded to be the bis(3,5-dibromo-4-hydroxyphenyl) derivative of I.

Carbamates of IIIa. A solution of 20 grams (0.03 mole) of IIIa, an isocyanate (0.1 to 0.2 mole), and triethylamine catalyst (5 drops) in 200 ml. of benzene was refluxed 17 hours, condensed to 100 ml., and cooled to effect crystallization. The solid was filtered, washed with cold benzene and recrystallized from benzene. Melting points were as follows: bis(*N*-*n*-octadecylcarbamate), 152–159° C.; (from *n*-octadecyl isocysnate), bis(*N*-ethylcarbamate), 229–231.5° C.; (from ethyl isocyanate) bis(*N*-phenylcarbamate), 227–235°. The infrared curves showed the presence of a carbamido group in each case.

Condensation of I with Anisole. Anhydrous I (49 grams, 0.1 mole), xylene (250 mo.), anisole (22 grams, 0.2 mole), and boron fluoride etherate (15 ml.) were mixed and heated at 110° C. with stirring for 48 hours. The reaction mixture was washed with water, concentrated by partial removal of the solvent, and crystallized to give 29 grams of solid IIId (43%). It was recrystallized from chloroform, m.p. 279–286° C.

Compound IIId was demethylated to IIIa as follows: IIId (0.5 grams) was refluxed for 17 hours with 50 ml. of HBr in glacial acetic acid. The solution was evaporated to dryness in vacuo, and the resulting oil was triturated with hexane to give a solid which was shown to be IIIa by comparison of the infrared spectra.

Condensation of I with Aromatic Hydrocarbons. Anhydrous I was prepared by refluxing I hydrate with 3 or 4 weights of toluene or xylene for the removal of water by azeotropic distillation over about 1 hour. Anhydrous I crystallized on cooling and was filtered. (It forms hydrates fairly rapidly on exposure to air and should, therefore, be used immediately after preparation or stored under anhydrous conditions.)

Anhydrous I (48 grams, 0.096 mole) was dissolved in 450 ml. of dry benzene in a three-necked laboratory reaction flask equipped with a mechanical stirrer. Anhydrous aluminum chloride (25 grams, 0.19 mole) was added all at once to the solution at room temperature with stirring, but without external cooling. The reaction mixture turned dark. and heat was evolved, taking the temperature of the solution to 40° C. The reaction mixture was stirred overnight at room temperature and was then mixed with dilute HCl to remove the $AlCl_3$. Methylene chloride was added to assist layer separation. The organic layer was dried over anhydrous magnesium sulfate, and the solvent removed to give 38 grams of tan solid product, IIIf, m.p. 272–278° C. Treatment with decolorizing carbon in boiling benzene gave a white product, m.p. 279–282° C. The other compounds listed in Table II were prepared similarly, except that carbon disulfide was employed as reaction solvent for the preparation of IIIj since both reagents are solids, and the reaction mixture was refluxed for 60 hours.

Oxidation of IIIg. IIIg (80 grams, 0.12 mole), glacial acetic acid (1200 ml.), and concentrated H_2SO_4 (150 ml.) were mixed in a laboratory reaction flask with stirring and cooling. Chromic oxide (100 grams) was added at 25–30° C. with stirring and external cooling. The reaction appeared to be complete in about an hour. The mixture was stirred overnight, poured into water, and the solid product separated by filtration. The yield of crude dicarboxylic acid was 87 grams (100%). It was purified by recrystallization from a mixture of methanol and chloroform, m.p. 360° C. Anal.: Theor.: 40.4% C, 1.4% H, 49.6% Cl; Found: 40.8, 1.9, 49.4.

The acid was converted to the dimethyl ester by refluxing overnight with excess methanol with a small quantity of concentrated H_2SO_4 added as catalyst. After recrystallization from benzene-hexane, it melted at 288–291° C. Anal.: Theor.: 47.6% Cl; Found: 47.5%.

Deacetylation of IIIj. Compound IIIj (37 grams, 0.05 mole), glacial acetic acid (500 ml.), and concentrated HCl (500 ml.) were mixed and refluxed overnight. The dihydrochloride so obtained was filtered, washed, and dried. The yield was 29 grams (80%). It was converted to the free base by stirring for 2 hours with 10% NaOH and purified by recrystallization from 50% aqueous methanol, m.p. >310° C. (decomp.). Anal.: Calcd.: 4.3% N; Found: 4.4%.

DISCUSSION

The results obtained in the present study can be instructively compared with those noted previously from similar studies involving hexafluoroacetone, and related perhaloketones also containing an electron-deficient carbonyl carbon atom (*1, 2*). The perhalo acetones, like I, react with phenols (*1*) to form Type II carbinols using some of the same catalysts ($AlCl_3$, toluenesulfonic acid). The acetones, on the other hand, also gave Type II carbinols with BF_3, while I only gave Type III derivatives with this catalyst. (BF_3 did give Type III compounds from the acetones with longer times of reaction). Likewise, Type III materials could be prepared from I using toluenesulfonic acid, but such were not observed using this catalyst with the acetone compounds. These results indicate that the carbonyl carbon atom of I is less electropositive than that in the fluorochloroacetones, resulting in a weaker carbon-oxygen bond in Type II compounds derived from I, with consequent easier formation of Type III derivatives from I. This situation results from the higher electronegativity of the fluorine atom compared with that of chlorine. Similarly, I easily forms Type III derivatives from hydrocarbons with $AlCl_3$ as catalyst, while the acetone compounds have been observed to form only Type II derivatives (*1*) from hydrocarbons.

Ketones with a relatively electronegative carbonyl carbon atom, on the other hand, apparently form only Type III derivatives from phenols under the conditions employed to date (*6*, *7*).

ACKNOWLEDGMENT

We are indebted to J. P. Sibilia for the N.M.R. study of IIIa.

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RECEIVED for review September 9, 1965. Accepted February 1, 1966.

Nuclear Magnetic Resonance Spectra of 1,2-Dithiole-3-thiones

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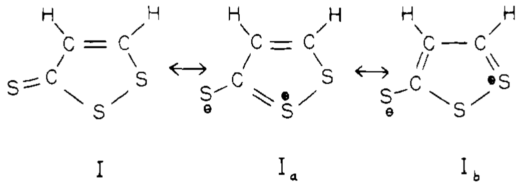
Nuclear magnetic resonance spectra are recorded for various aryl- and alkyl-substituted 1,2-dithiole-3-thiones and their carbonyl analogs. By examining the spectra of known compounds, resonance field positions have been assigned for hydrogen or methyl groups attached at either the 4- or 5- position in the 1,2-dithiole-3-thione ring system. Protons in the 4- position give a resonance at 2.6 to 2.8τ while protons in the 5-position show a resonance at 1.6 to 1.7τ.

THE 1,2-dithiole-3-thione ring system is recognized as pseudoaromatic (*4*). This is the result of the contributions of the sulfur electrons, which coupled with the carbon-carbon double bond electrons provide six electrons to satisfy the Huckel rule for aromaticity. While crystallographic studies have provided some details on the resonance contributions of structures I, Ia, and Ib (*2*), there has been little work on the use of nuclear magnetic resonance as a tool to evaluate the nature of protons attached to the dithiole ring and to substantiate structural assignments.

In the course of synthetic work on dithioles, the NMR spectra of a number of 1,2-dithiole-3-thiones substituted in the 4- and 5- positions by alkyl and aryl groups were measured and tabulated. Generalizations with possible analytical value are drawn from the data and some suggestions are made regarding the observed chemical shifts and spin coupling constants.



I $\quad$ I_a $\quad$ I_b

EXPERIMENTAL

Nuclear magnetic resonance spectra were taken on 10 weight % solutions of the organic compound in carbon tetrachloride using a Varian A-60 instrument. Concentrations greater than 10% showed appreciable shifts to higher fields for the individual proton resonances, but lower concentrations had negligible effects. All measurements were made using tetramethylsilane as an external reference.

5-Phenyl-1,2-dithiole-3-thione (m.p. 122° C.) (*1*), 5-phenyl-1,2-dithiole-3-one (m.p. 117–18° C.) (*1*), and 4-phenyl-1,2-dithiole-3-thione (m.p. 122–23° C.) (*3*), were prepared by previously reported procedures. 4-Neopentyl-5-*tert*-butyl-1,2-dithiole-3-thione (b.p. 152° C. at 1 mm.) was obtained from the reaction of triisobutylene with sulfur (*5*). 4-Methyl-1,2-dithiole-3-thione (m.p. 40–41° C.) 4-methyl-5-*tert*-butyl-1,2-dithiole-3-thione (m.p. 79–80° C.), and 4-neopentyl-1,2-dithiole-3-thione (m.p. 85–86° C.), were obtained by the method of Spindt, Stevens, and Baldwin (*7*). 1,2-Dithiole-3-thione was prepared by the method of Mayer and Kubasch (*6*).

4-Phenyl-1,2-dithiole-3-one. Six grams (0.028 mole) of 4-phenyl-1,2-dithiole-3-thione was dissolved in 150 ml. of acetone and to the stirred solution a solution of 9.6 grams of $KMnO_4$ in 150 ml. of acetone was added in 1 hour. When the solution was concentrated to 50-ml. volume and