# Products Obtained by the Reaction of Trichlorotrimethylbenzenes with Fuming Nitric Acid. Side-chain Nitrooxylation *versus* Oxidation to Unsaturated Cyclic Ketones[1)]

Hitomi Suzuki, Shigeru Maruyama, and Terukiyo Hanafusa
*Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-sendamachi, Hiroshima 730*

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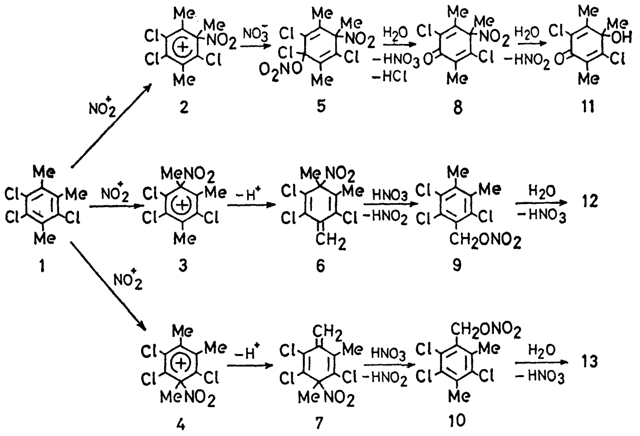
The reaction of trichlorotrimethylbenzenes with fuming nitric acid has been investigated. Trichloropseudocumene underwent both side-chain nitrooxylation and nuclear oxidation to give 2,5,6-trichloro-3,4-dimethylbenzyl nitrate, 3,5,6-trichloro-2,4-dimethylbenzyl nitrate, and 3,6-dichloro-4-nitro-2,4,5-trimethylcyclohexa-2,5-dienone. Trichloromesitylene yielded a mixture of several carbonyl compounds, from which 3,5-dichloro-4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone and two nitro-ketones, tentatively formulated as 2,4,6-trichloro-5-hydroxy-6-nitro-2,3,5-trimethylcyclohex-3-enone and 3,5-dichloro-2-hydroxy-6,6-dinitro-2,4,5-trimethylcyclohex-3-enone, were obtained as crystalline products by chromatography and fractional extraction. Trichlorohemimellitene behaved similarly towards the nitrating agent to give 2,6-dichloro-4-hydroxy-3,4,5-trimethylcyclohexa-2,5-dienone as the major product. The competitive modes of side-chain nitrooxylation and formation of cyclic ketones have been described.

In recent years attention has been paid to several new aspects of aromatic nitration, including various substitutions on alkyl side-chain of polyalkylbenzenes,[2)] acyloxylation,[3)] nitrative coupling,[4)] and oxidation to cyclic ketones.[5)] Although these reactions have so far been regarded as discrete and anomalous, they could be classified as branched-off processes of ordinary nitration. Nitronium ion attacks a polyalkylbenzene to form a nitrobenzenium ion, which could undergo four different types of reactions; loss of proton or some cationic species from the ring to give a nitrobenzene derivative (path *a*), proton release from the alkyl side-chain to yield a nitromethylenecyclohexadiene which could be transformed into benzylic compound (path *b*), capture of nucleophile to give an addition product which will collapse to form unsaturated cyclic ketone or acyloxylated product (path *c*), and attack on another aromatic ring to give a coupling product such as nitrobiaryl (path *d*). When the normal course *a* is suppressed, an unusual path *b*, *c*, or *d* will emerge. With highly alkylated benzene derivatives, the major nitrative processes are the side-chain nitrooxylation (path *b*) and the formation of unsaturated cyclic ketones (path *c*), the competitive modes of which are best illustrated by the behaviors of three isomeric trichlorotrimethylbenzenes towards fuming nitric acid.

*Trichloropseudocumene (**1**)*: A solution of **1** and excess of fuming nitric acid ($d$=1.5) in dichloromethane was left standing at room temperature overnight. Quenching with water, followed by removal of the solvent *in vacuo* gave a syrupy substance, which was passed over alumina to give two trichlorodimethylbenzyl alcohols, mp 197—198 °C and 204—206 °C, and a carbonyl compound, mp 146—147 °C. Benzyl alcohols were identified as 2,5,6-trichloro-3,4-dimethylbenzyl alcohol (**12**) and 3,5,6-trichloro-2,4-dimethylbenzyl alcohol (**13**), respectively, by a comparison of their melting points, infrared spectra and $^1$H NMR spectra with those of the authentic specimens prepared from xylidines according to the sequences shown in Scheme 4. There was no indication of isomeric 3,4,6-trichloro-2,5-dimethylbenzyl alcohol (**14**) in the product.

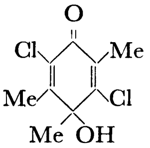
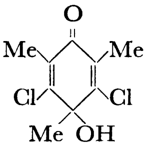
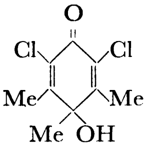
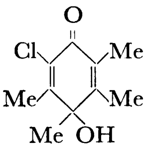
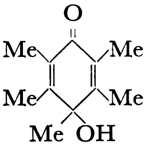


Scheme 1

A carbonyl compound with the molecular formula $C_9H_{10}O_2Cl_2$ showed mass peaks at $m/e$ 220 ($M^+$), 205 ($M^+$–$CH_3$), and 185 ($M^+$–Cl). Its infrared spectrum showed carbonyl absorption at 1666 cm$^{-1}$, carbon-carbon double bond absorption at 1621 cm$^{-1}$, and hydroxyl absorption at 3240—3400 cm$^{-1}$, suggesting a cross-conjugated hydroxy-ketone. Its ultraviolet spectrum exhibited absorption maxima at 246—247 (log $\varepsilon$=4.08) and 286—287 nm (log $\varepsilon$=3.34) characteristic of a 2,5-cyclohexadienone structure.[6)] Proton NMR spectrum showed three peaks due to methyls at 8.40, 7.96, and 7.73 $\tau$, and a broad peak due to hydroxyl at *ca.* 7.3 $\tau$. The dienone was thus presumed to be either 3,6-dichloro-4-hydroxy-2,4,5-trimethylcyclohexa-2,5-dienone (**11**) or 5,6-dichloro-4-hydroxy-2,3,4-trimethylcyclohexa-2,5-dienone, the former being favored upon an examination of the chemical shifts given in Table 1. Since the crude product mixture prior to chromatographic treatment showed intense infrared bands due to nitro and nitrooxy groups, products **11**, **12** and **13** no doubt were formed by the hydrolysis of the nitroketone **8** and benzyl nitrates **9** and **10**, respectively, during the elution.

Nitronium ion attacks **1** to form a mixture of benzenium ions, in which **2**—**4** would be important, since the electron-donating methyl group is bonded direct to the reaction site (Scheme 1). Proton release form

Table 1. Physical properties of some 4-hydroxycyclohexa-2,5-dienones

| Compound | Mp (°C) | $^1$H NMR spectra ($\tau$) | | IR spectra cm$^{-1}$ | UV spectra | |
|---|---|---|---|---|---|---|
| | | $CH_3$ | OH | | (nm) | log $\varepsilon$ |
|  | 146—147 | 8.40(Me; C-4)<br>7.96(Me; C-2)<br>7.73(Me; C-5) | *ca.* 7.3 | 764, 984, 1068,<br>1200, 1260, 1621,<br>1656, 3240—3400 | 246—247<br>286—287 | 4.08<br>3.34 |
|  | 96—98 | 8.31(Me; C-4)<br>7.99(2Me; C-2, C-6) | *ca.* 7.3 | 724, 987, 1073<br>1222, 1341, 1632,<br>1652, 3430—3400 | 245<br>284—286 | 4.03<br>3.29 |
|  | 204—205 | 8.51(Me; C-4)<br>7.74(2Me; C-3, C-5) | *ca.* 7.1 | 760, 1012, 1044,<br>1209, 1262, 1602,<br>1658, 3420 | 249<br>289 | 4.06<br>3.27 |
|  | 178—179[12] | 8.61(Me; C-4)<br>8.19(Me; C-3)<br>7.94(Me; C-2)<br>7.80(Me; C-5) | *ca.* 7.0 | 766, 902, 1073,<br>1221, 1270, 1612,<br>1636, 3400[b] | 246—247<br>286—287 | 4.08<br>3.34 |
|  | 138—140[13] | 8.63(Me; C-4)<br>8.16(2Me; C-3, C-5)<br>7.96(2Me; C-2, C-6)[a] | *ca.* 7.0 | 768, 919, 1001,<br>1028, 1084, 1276,<br>1613, 1662, 3390[b] | 242 | 4.20 |

a) In carbon tetrachloride solution. b) With a KBr disc.

the most activated methyl groups of **3** and **4** would lead to the formation of nitromethylenecyclohexadienes **6** and **7**, which will pass over a benzylic intermediate—nitrite ion pair to give the corresponding benzyl nitrates **9** and **10**. Capture of the nitrate ion by **2** will give an unstable chloro-nitrate **5**, from which nitryl chloride is eliminated to yield ketone **8**. No change in the pseudocumene skeleton was observed in the products.

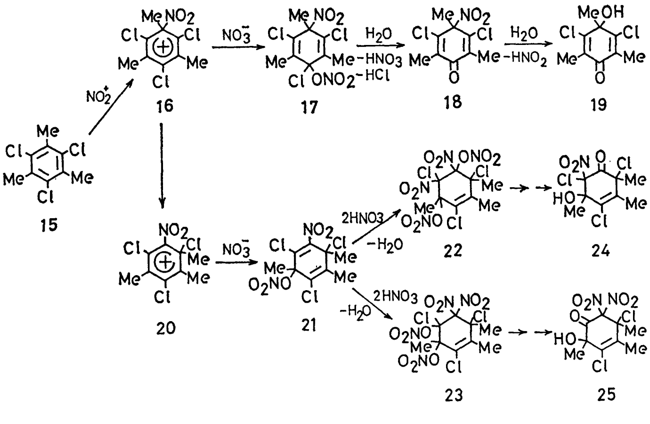
*Trichloromesitylene (**15**)*: A similar treatment of **15** with fuming nitric acid gave a mixture of several carbonyl compounds as a yellow pasty solid, which on chromatography over alumina gave a new carbonyl compound, mp 96—98 °C, from ether eluates. It had the molecular formula $C_9H_{10}O_2Cl_2$ and showed mass peaks at *m/e* 220 ($M^+$), 205 ($M^+$–$CH_3$), and 185 ($M^+$–Cl). Proton NMR spectrum showed peaks at 8.31, 7.99, and *ca.* 7.3 $\tau$ with an intensity ratio of 6 : 3 : 1. The infrared and ultraviolet data given in Table 1 are consistent with a cyclohexa-2,5-dienone structure. A lower shift of C=O frequency indicated the absence of chlorine atoms on both sides of the carbonyl group. These spectral evidences readily led to the formulation of 3,5-dichloro-4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone (**19**) for the carbonyl compound.

When the product was subjected to fractional extractions with a mixture of light petroleum and dichloromethane, another ketone was obtained with the composition $C_9H_{10}NO_4Cl_3$, mp 153—154 °C with decomposition. Its mass spectrum showed fragment ion peaks derived from non-detectable molecular ion at *m/e* 220 ($M^+$–$NO_2$–Cl), 185 ($M^+$–$NO_2$–2Cl), 177 ($M^+$–$NO_2$–Cl–CO–$CH_3$), and 142 ($M^+$–$NO_2$–2Cl–CO–$CH_3$). The lower mass spectrum consisted of the prominent peak clusters centered at *m/e* 107 ($C_7H_6OH^+$), 91 ($C_7H_7^+$), and 77 ($C_6H_5^+$) in accord with a structure related to the benzenoid compound. Its ultraviolet spectrum showed no maximum above 220 nm, suggesting a cyclohex-3-enone structure. Proton NMR spectrum contained three methyl singlets at 8.21, 7.76, and 7.73 $\tau$ and one hydroxyl peak at *ca.* 5.5 $\tau$ (broad, exchangeable with $D_2O$). Its infrared spectrum showed absorption due to an aliphatic nitro group at 1572, 1560, 1359, and 1342 cm$^{-1}$; a carbonyl group at 1715 cm$^{-1}$; a carbon-carbon double bond at 1650 cm$^{-1}$; and a hydroxy group at 3440 cm$^{-1}$. The asymmetric vibration bands of nitro group are shifted towards a high-frequency region, while the symmetric frequency is lowered. This may reflect the presence of a geminal chloro-nitro grouping,[7] which can be attached to C-2, C-5, or C-6 of the cyclohex-3-enone skeleton. Chlorine atoms do not undergo intramolecular migration under the nitrating conditions. The nitro group on the activated allylic carbon atom usually undergoes a facile solvolytic replacement during aqueous work-up. This makes it possible for three chlorine atoms to be placed on C-2, C-4, and C-6, respectively, and favors the chloro-nitro grouping to be placed on the less activated C–6. Thus the hydroxy group must be located on C–5, and three methyl groups on the remaining C–2, C–3, and C–5. The product may be represented by the formula 2,4,6-trichloro-5-hydroxy-6-nitro-2,3,5-trimethylcyclohex-3-enone (**24**).

When the reaction mixture was flash-evaporated *in vacuo* and the resulting pasty substance was immediately chromatographed over silica gel, a third carbonyl compound melting at 131—135 °C under the liberation of a brown fume was eluted from benzene. It had the formula $C_9H_{10}N_2O_6Cl_2$ and showed mass peaks at *m/e* 249 ($M^+$–$NO_2$–OH), 220 ($M^+$–$2NO_2$), 185 ($M^+$–$2NO_2$–Cl), 177 ($M^+$–$2NO_2$–CO–$CH_3$), and 142 ($M^+$–$2NO_2$–Cl–CO–$CH_3$). Prominent peak clusters centered at *m/e* 107, 91, and 77 are typical of a structure closely related to the benzenoid compound. The absence of ultraviolet maximum above 220 nm suggests a cyclohex-3-enone structure. Its proton NMR spectrum displayed three methyl peaks at 8.39, 7.88, and 7.76 $\tau$ and one hydroxyl absorption at *ca.* 7.7 $\tau$ (broad, exchangeable with $D_2O$). Its infrared spectrum indicates the presence of geminal nitro groups (1582, 1572, 1333, and 850 $cm^{-1}$), a carbonyl group (1750 $cm^{-1}$), a carbon-carbon double bond (1628 $cm^{-1}$), and a hydroxy group (3495 $cm^{-1}$). It is unlikely that chlorine atoms underwent the intramolecular migration or replacement by nitro group during the course of reaction.[8] Two chlorine atoms could reasonably be assigned to C–3 and C–5 of the cyclohex-3-enone. The unusually higher shift of the C=O stretching vibration at 1750 $cm^{-1}$ is attributed to the presence of a *gem*-dinitro grouping adjacent to the carbonyl group. We lean toward the location of this grouping at the non-allylic C–6 position because of its stability toward solvolytic replacement. Placing the hydroxy group on C-2 and three methyl groups on C-2, C-4, and C-5, respectively, we can formulate the product as 3,5-dichloro-2-hydroxy-6,6-dinitro-2,4,5-trimethylcyclohex-3-enone (**25**).

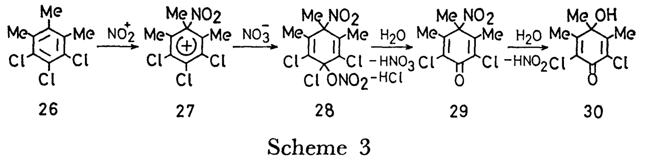
The infrared and proton NMR spectra of the crude product from **15** indicated the presence of some additional carbonyl compounds which, however, could not be isolated as crystalline solid. Formation of the side-chain substitution products could not be observed.

Scheme 2 outlines one possible pathway from **15** to these carbonyl compounds. Nitrobenzenium ion **16**[9] derived from **15** has neither a good leaving group nor a methyl group favorably situated for proton release. Thus it will take up the nitrate ion to give **18** *via* **17**, or undergo isomerization to **20** followed by the anion capture to give **21**, from which **24** and **25** could be derived through an addition-elimination sequence and subsequent hydrolysis.



Scheme 2

*Trichlorohemimellitene (26)*: A similar treatment of **26** with fuming nitric acid followed by ordinary work-up gave a carbonyl compound, mp 204—205 °C, as the major product. Its formula, as established by mass spectrometric molecular weight determination and elemental analysis, was $C_9H_{10}O_2Cl_2$. On the basis of the spectroscopic data (Table 1), it was readily identified as 2,6-dichloro-4-hydroxy-3,4,5-trimethylcyclohexa-2,5-dienone (**30**). Formation of **30** from **26** can be rationalized by Scheme 3; preferential attack of nitronium ion will occur at C-2 of **26** to give ion **27**. Capture of the nitrate ion by **27** followed by elimination of nitryl chloride from unstable chloro-nitrate **28** would give a nitro-ketone **29**, which undergoes a facile hydrolysis during aqueous work-up to yield **30** as the final product.



Scheme 3

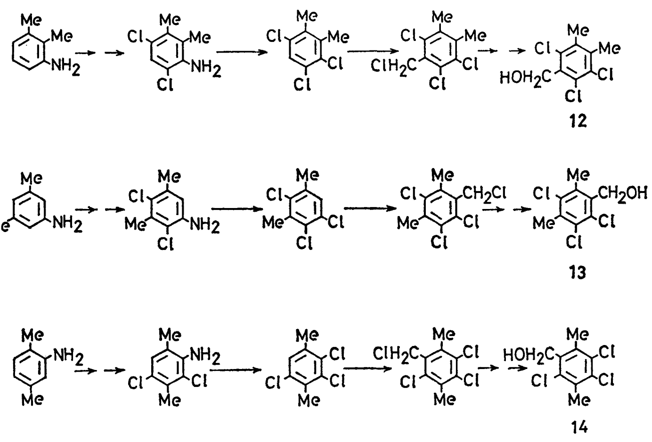
The presence of a pair of methyl groups in position *para* to each other seems critical for the facile formation of benzyl nitrates. A pair of *para* methyl groups at C-1 and C-4 in **1** undergo side-chain nitrooxylation to form two benzyl nitrates **9** and **10**, whereas the unpaired methyl group at C-2 remains intact during the course of reaction. In contrast to **1**, **15** and **26** both bearing no paired methyl groups in *para* positions undergo only addition-elimination sequences to give unsaturated cyclic carbonyl compounds **19**, **24**, **25**. and **30**. No side-chain substitution was observed with these compounds.

The process of the side-chain nitrooxylation could be explained by the intermediacy of 1-methyl-1-nitro-4-methylenecyclohexa-2,5-dienes **6** and **7**, which would undergo the heterolytic scission of the carbon-nitrogen bond to give a benzyl cationic species—nitrite ion pair; recombination at benzyl carbon atom followed by oxidation affords side-chain nitrooxylation products **9** and **10**. The required disposition of methyl groups in position *para* one another might be taken to indicate that the transition state of the conversion of nitromethylene-cyclohexadiene to benzyl nitrite is closer to the benzylic structure and stabilized more effectively by the electron-donating methyl group at *para* position. **1** bearing a pair of methyl groups reacts with the nitrating agent more readily than **15** and **26** which lack such structural advantage, indicating the high propensity of the nitrobenzenium ions **3** and **4** to form nitromethylenecyclohexadienes **6** and **7** rather than to take up anion or undergo isomerization. Oxidation to unsaturated cyclic ketone (path *c*) could effectively compete with side-chain nitrooxylation (path *b*) only under the conditions in which the formation of 1-nitro-4-methylenecyclohexa-2,5-diene intermediate is structurally disfavored. Thus, on dissolution in excess fuming nitric acid ($d$=1.5) at room temperature, tetrachloro-*p*-xylene gave 2,3,5,6-tetrachloro-4-methylbenzyl nitrate (mp 80—82 °C) in 88% yield,[10] while a similar treatment of tetrachloro-*o*-xylene and tetrachloro-*m*-xylene led to the formation of a mixture of carbonyl compounds. Addition of sulfuric acid to the reaction system was found to facilitate the proton removal from the side-chain in favor of path *b* over path *c*. This is best exemplified by the nitration of 5,6-dinitroprehnitene; treatment with fuming nitric acid afforded 4,5-dinitro-2,3,6,6-tetramethylcyclohexa-2,4-dienone and 2,3,4,5-tetranitro-2,3,6,6-tetramethylcyclohex-3-enone, whereas the action of the mixed acid gave 5,6-dinitro-2,3,4-trimethylbenzyl nitrate as the major product.[11]

## Experimental

Melting points are uncorrected. IR spectra were determined in mulls on a Jasco 402G spectrophotometer. Proton NMR spectra were obtained in deuteriochloroform on a Hitachi Perkin-Elmer spectrometer using TMS as internal standard. Ultraviolet spectra were measured in methanol with a Shimadzu QV-50 spectrophotometer. Mass spectra were recorded on a Hitachi RMU-6E instrument.

Trichloropseudocumene, trichloromesitylene, and trichlorohemimellitene were prepared by the chlorination of the corresponding hydrocarbons and purified through chromatography on alumina. 2,5,6-Trichloro-3,4-dimethylbenzyl alcohol, 3,5,6-trichloro-2,4-dimethylbenzyl alcohol, and 3,4,6-trichloro-2,5-dimethylbenzyl alcohol were obtained from the corresponding chlorides *via* hydrolysis of acetates, which in turn were prepared from 3-*o*-xylidine, 5-*m*-xylidine, and *p*-xylidine, respectively, following the sequences shown in Scheme 4. Physical properties of trichlorodimethylbenzyl compounds obtained in context with the present work are summarized in Table 2. All new compounds gave satisfactory analytical results.



Scheme 4

*Nitration of Trichlorotrimethylbenzenes*: The general procedure is illustrated below, taking an example from the reaction of trichloropseudocumene **1**.

To a stirred solution of **1** (7.5 g; 0.034 mol) in dichloromethane (38 ml) maintained at 0—5 °C, fuming nitric acid ($d$=1.5; 17.4 g; 0.375 mole) was added dropwise over a period of 30 min. After standing at room temperature overnight, the reaction mixture was poured into a large excess of

TABLE 2. PHYSICAL PROPERTIES OF SOME TRICHLORODIMETHYLBENZYL COMPOUNDS

| Compound | Mp (°C) | $^1$H NMR spectra ($\tau$) | | | IR spectra cm$^{-1}$ |
|---|---|---|---|---|---|
| | | CH$_3$ | CH$_2$ | OH | |
| 2,5,6-Trichloro-3,4-dimethylbenzyl series | | | | | |
| Chloride | 73—74 | 7.60<br>7.57 | 5.07 | | 687, 756, 893, 1009, 1149, 1170, 1274 |
| Nitrate | 54—56 | 7.59<br>7.52 | 4.19 | | 847, 981, 1170, 1276 1643 |
| Alcohol | 197—198 | 7.60<br>7.56 | 5.01 | 7.92 | 692, 1037, 1166, 1255 3260—3300 |
| 3,5,6-Trichloro-2,4-dimethylbenzyl series | | | | | |
| Chloride | 96—97 | 7.50<br>7.46 | 5.20 | | 685, 747, 878, 932, 997, 1145, 1170, 1261 |
| Nitrate | 102—103 | 7.52<br>7.43 | 4.28 | | 887, 976, 1170, 1276, 1298, 1614, 1646 |
| Alcohol | 204—206 | 7.48<br>7.45 | 5.11 | 8.22 | 690, 973, 1003, 1030, 1161, 3240 |
| 3,4,6-Trichloro-2,5-dimethylbenzyl series | | | | | |
| Chloride | 96—98 | 7.45<br>7.45 | 5.20 | | 709, 756, 892, 934 993, 1144, 1184, 1273 |
| Nitrate | 98—99 | 7.48<br>7.46 | 4.28 | | 887, 976, 1170, 1276, 1298, 1614, 1646 |
| Alcohol | 204—205 | 7.47<br>7.47 | 5.11 | 8.30 | 631, 980, 1007, 1034, 1164, 3240 |

water, and the organic layer was separated, thoroughly washed with water and aqueous sodium hydrogen carbonate, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a reddish brown syrupy substance, a part (4.0 g) of which was chromatographed on silica gel with light petroleum as eluant to give a mixture of benzyl nitrates **9** and **10** (0.24 g), and with light petroleum-benzene a bisbenzyl ether (0.05 g); mp 213—215 °C; $^1$H NMR, 7.57 (2 Me), 7.48 (2 Me), and 5.20 $\tau$ (2 $CH_2$); IR, 1170, 1070, and 966 cm$^{-1}$; MS, *m/e* 458 ($M^+$); Found: C, 46.97; H, 3.21%. Calcd for $C_{18}H_{16}OCl_6$: C, 46.85; H, 3.47%. Elution with benzene furnished some noncrystallizable gummy substance (0.02 g). Further elution with benzene-ether afforded two benzyl alcohols **13** (0.51 g) and **12** (0.22 g) in this order, and finally ketone **11** (0.59 g) was obtained from ether eluates.

*3,5,6-Trichloro-2,4-dimethylbenzyl Alcohol (**13**)*: Found: C, 45.13; H, 3.67%. Calcd for $C_9H_9OCl_3$: C, 45.09; H, 3.76%.

*2,5,6-Trichloro-3,4-dimethylbenzyl Alcohol (**12**)*: Found: 45.19; H, 3.73%. Calcd for $C_9H_9OCl_3$: C, 45.09; H, 3.76%.

*3,6-Dichloro-4-hydroxy-2,4,5-trimethylcyclohexa-2,5-dienone (**11**)*: Found: C, 48.85; H, 4.50%. Calcd for $C_9H_{10}O_2Cl_2$: C, 48.87; H, 4.50%.

*3,5-Dichloro-4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone (**19**)*: Found: C, 49.00; H, 4.62%. Calcd for $C_9H_{10}O_2Cl_2$: C, 48.87; H, 4.50%.

*2,4,6-Trichloro-5-hydroxy-6-nitro-2,3,5-trimethylcyclohex-3-enone (**24**)*: Found: C, 35.09; H, 3.73%. Calcd for $C_9H_{10}NO_4Cl_3$: C, 35.72; H, 3.34%.

*3,5-Dichloro-2-hydroxy-6,6-dinitro-2,4,5-trimethylcyclohex-3-enone (**25**)*: Found: C, 34.86; H, 3.33; N, 8.89; O, 30.87; Cl, 22.56%. Calcd for $C_9H_{10}N_2O_6Cl_2$: C, 34.53; H, 3.23; N, 8.94; O, 30.66; Cl, 22.64%.

*2,6-Dichloro-4-hydroxy-3,4,5-trimethylcyclohexa-2,5-dienone (**30**)*: Found: C, 48.97; H, 4.53%. Calcd for $C_9H_{10}O_2Cl_2$: C, 48.87; H, 4.50%.

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