Analysis and Properties of Bis-(p-chlorophenyl)methylcarbinol

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Increasing use of bis-(p-chlorophenyl)methylcarbinol (DMC or Dimite) as a miticide has made it desirable to publish analytical procedures. The technical material may contain 4,4'-dichlorobenzophenone, the compound from which it is made, and 1,1bis-(p-chlorophenyl) ethylene, the dehydration product of bis-(p-chlorophenyl)methylcarbinol. For estimating the composition of mixtures with either one of these impurities, melting point-composition data are given. For mixtures which also contain the 2,4'-isomers, a quantitative dehydration to the ethylene derivatives and a quantitative oxidation to the dichlorobenzophenones allow the 4,4' content to be found approximately. Ultraviolet absorption curves for the three 4.4' compounds are useful for the analysis of both binary and ternary mixtures.

 $\label{eq:chlorophenyl} \begin{bmatrix} \text{NCREASING} & \text{use of bis-}(p\text{-chlorophenyl})\text{methylcarbinol} \\ [1,1\text{-bis-}(p\text{-chlorophenyl})\text{ethanol}] (7, 16, 17), (p\text{-ClC}_{6}H_{4})_{2^{-}} \end{bmatrix}$ C(OH)CH₃, as a miticide has made it desirable to publish the analytical procedures available for it. (A 25% emulsifiable solution is made by the Sherwin-Williams Co. under the name of Dimite.)

One synthetic route to this compound is the Grignard reaction of 4.4'-dichlorobenzophenone and a methylmagnesium halide (1, 8, 18). The ketone may be made by several Friedel-Crafts syntheses, such as that of carbon tetrachloride and chlorobenzene or p-chlorobenzotrichloride and chlorobenzene. These preparations yield varying amounts of 2,4'- and 2,2'-dichlorobenzophenone along with the desired 4,4' isomer. Methylation of these ketones yields the corresponding isomeric di-(chlorophenyl)methyl carbinols. Dehydration to an ethylene derivative, allows such

$$(ClC_6H_4)_2C(OH)CH_3 \longrightarrow (ClC_6H_4)_2C = CH_2 + H_2O \quad (1)$$

compounds to be present as impurities. Thus a technical grade made from the ketone may contain, in addition to bis-(pchlorophenyl)methylcarbinol:

Isomeric di-(chlorophenyl)methylcarbinols in which one or both

chlorine atoms are in the ortho position. 1,1-Bis-(*p*-chlorophenyl)ethylene (4,4'-DMC ethylene), and isomers in which one or both chlorine atoms are in the ortho position

4,4'-Dichlorobenzophenone and its isomers, 2,4'- and 2,2'-dichlorobenzophenone.

MELTING POINT-COMPOSITION DATA

The melting points of these various compounds are given in Table I.

In developing synthetic methods for bis-(p-chlorophenyl)methylcarbinol and the 4,4' ketone and in studying the behavior of bis-(p-chlorophenyl)methylcarbinol under various conditions, the melting point-composition data for bis-(p-chlorophenyl)methylcarbinol-4,4' ketone (Table II), for bis-(p-chlorophenyl)methylcarbinol-1.1-bis(p-chlorophenyl)ethylene (Table III), and the setting point-composition data for several mixtures (Table IV) were useful in analysis. Mixtures of the compounds were made with a mortar and pestle and the melting points were found in the usual apparatus with a calibrated thermometer and with particular attention for the first sign of melting. These Traces of bis-(p-chlorophenyl)methylcarbinol are measured by a colorimetric procedure based on nitration and reaction with sodium methylate, similar to the analysis of DDT; with 1.0-mg. samples the error is $\pm 2.0\%$. In addition to these procedures, properties of bis-(p-chlorophenyl)methylcarbinol reported include thermal stability, stability in the presence of acids and bases, volatility, and solubility and purification by crystallization. In the absence of acids and at room temperature bis-(p-chlorophenyl)methylcarbinol is stable. The methods of analysis and properties given are valuable in the manufacture of bis-(p-chlorophenyl)methylcarbinol from 4,4'-dichlorobenzophenone, and in its formulation, storage, and use as a miticide.

data are applicable only to mixtures which contain no 2,4' or 2,2'isomers.

Procedure for Setting Points. The setting point is taken in a 25×150 nm. test tube fitted with a calibrated thermometer graduated in 0.1° intervals, and a stirrer (Nichrome wire loop). The thermometer is inserted into the melt to the 70-mm. calibra-tion line through a two-hole stopper with the stirrer fitted through the second hole. The tube containing the sample is heated in an oil bath until the mixture is completely melted and it is then The melt is allowed to cool very slowly with stirring. Upon supercooling and subsequent crystallization the maximum temperature is read; the procedure is repeated as a check.

As the molecular weights of the ketone and ethylene are approximately the same-251 and 249, respectively-their effect on the setting point of bis-(p-chlorophenyl)methylcarbinol is the same: a depression of 5.7° for 10% of ketone or ethylene.

QUANTITATIVE DEHYDRATION

The dehydration of bis-(p-chlorophenyl)methylcarbinol to the ethylene derivative (Equation 1) should occur readily because bis-(p-chlorophenyl)methylcarbinol is a tertiary alcohol with

Table I. Melting Points of Bis-(p-chlorophenyl)methyl-carbinol and Related Compounds

Compound	Structure	M.P., ° C.
4,4'-DMC 2,4'-DMC 2,2'-DMC	$(p-ClC_{\theta}H_4)_{\theta}C(OH)CH_3$ $(p-ClC_{\theta}H_4)(o-ClC_{\theta}H_4)C(OH)CH_3$ $(o-ClC_{\theta}H_4)_2C(OH)CH_3$	69.0-69.5 (8) Oila ?
4,4′-DMC ethylene 2,4′-DMC ethylene 2,2′-DMC ethylene	$\begin{array}{l} (p-\mathrm{ClC}_6\mathrm{H}_4)_2\mathrm{C} = \mathrm{CH}_2\\ (p-\mathrm{ClC}_6\mathrm{H}_4)(o-\mathrm{ClC}_6\mathrm{H}_4)\mathrm{C} = \mathrm{CH}_2\\ (o-\mathrm{ClC}_6\mathrm{H}_4)_2\mathrm{C} = \mathrm{CH}_2 \end{array}$	85-86 (1, 8) Oil ^b ?
4,4'-Dichlorobenzophe- none 2,4'-Dichlorobenzophe-	(p-ClC6H4)2CO	145-146 (14)
none 2.2'-Dichlorobenzophe-	$(p-ClC_6H_4)(o-ClC_6H_4)CO$	66-67 (15)
none	$(o-ClC_6H_4)_2CO$	45.4-46.1 (10

^a First prepared from 2,4'-dichlorobenzophenone (m.p. 59-62° C.) and methylmagnesium bromide in 88% yield by the same procedure used for 4,4'-DMC (8). It was a yellow viscous oil that could not be purified by crystallization or vacuum distillation; n^B 1.6042. Caled. for Ci₄H₁₅Cl₂O: Cl. 26.54; mol. wt. 267.2. Found: Cl. 24.85; mol. wt., 240. For analytical studies a more nearly pure sample was made from 2,4'-ketone melting at 64-66° C. 64-66° C. • Preparations and properties described in this article,

Table	п.	Melting	Point-Comp	osition	Data	for	Bis-
(p-c	hlor	ophenyl)m	ethylcarbino	l-4,4'-di	chloro	benze	0-
			_1				

	phenone	
4,4'-DMC, Wt. %	4,4' Ketone, Wt. %	M.P. (Corr.), °C.
100 95 90 87.5° 85 82.5 80 75 70 60 50	$\begin{array}{c} 0 \\ 5 \\ 10 \\ 12.5 \\ 15 \\ 17.5 \\ 20 \\ 25 \\ 30 \\ 40 \\ 50 \end{array}$	$\begin{array}{c} 69 & -69.5\\ 62.5-67\\ 58-65\\ 56-62.5\\ 55-62.5\\ 52-62\\ 53-62.5\\ 53-62.5\\ 53-62.5\\ 54-92\\ 71.5-104.5\\ 84.5-117\\ 97.5-124\end{array}$
40 30 20	60 70 80	108.5 - 131 118.5 - 135 128.5 - 140.5
ĩŏ	90 100	138.5 - 143.5 144.0 - 145.0

^a Minimum in diagram is at 82.5% DMC-17.5% ketone.

Melting Point-Composition Data on Bis-Table III. (p-chlorophenyl)methylcarbinol-1,1-Bis-(p-chlorophenyl)ethylene

	1	
4,4'-DMC, Wt. %	4,4'-Ethylene, Wt. %	M.P. (Corr.), ° C.
100	0	68.5-69.5
90	10	62.0-65.5
80	20	50.5-01.5 54 5 56 0
65	35	54 0-71 0
60	40	54.5-77.0
50	50	56.5-78.0
40	60	59.0-79.5
20	80	71.0-83.5
0	100	84,5-86.0

^a Minimum in diagram is at 70% DMC-30% ethylene, which melts over surprisingly narrow range of 54.5-56.0° C.

hydrogen on the alpha carbon atom. If the reaction were quantitative, an estimation of the water formed would be a measure of the bis-(chlorophenyl)methylcarbinol content of the sample. The Karl Fischer titration which has been so thoroughly developed by Mitchell and Smith (12, 13) was tried first. The preparation and standardization of the reagent and the titration were done in the usual way (12, 13).

The best dehydrating conditions Dehydration Procedure. found for the Fischer titration involved the use of purified dioxane as a solvent and p-toluenesulfonic acid as the catalyst. Duplicate samples of DMC (about 1.0 gram, weighed to four places) are added to dry 250-ml. glass-stoppered Erlenmeyer flasks, 25 ml. of the *p*-toluenesulfonic acid-dioxane solution (a 0.1 N solution of p-toluenesulfonic acid monohydrate in purified dioxane, 3) are added, and the mixture is heated under a reflux condenser for 4 hours on a steam bath. The reflux condenser is protected by a calcium chloride tube. Ten milliliters of the purified dioxane are used to wash down the condenser and joint of each flask after through the jackets. The glass joint is sealed with 2 to 3 drops of a light machine oil. Four blanks are run under identical condi-tions. Two blanks are cooled and titrated directly, while due tions. Two blanks are cooled and titrated directly, while du-plicate 1.0-gram samples of DMC are weighed into the remaining blanks and titrated at once, in order to estimate the water present in the sample.

Calculation.

% DMC =
$$F \frac{\frac{V_2 - V_s}{W_2} - \frac{V_1 - V_s}{W_1}}{0.6744}$$
 (2)

- where F = milligrams of water equivalent to 1 ml. of Fischer reagent
 - $V_1 = ml$. required to titrate blank containing sample
 - $V_2 =$ ml. required to titrate dehydrated mixture
 - $V_s = ml.$ required to titrate blank containing no sample

 - W_1 = sample weight in blank W_2 = sample weight If the sample is anhydrous, the formula reduces to:

% DMC =
$$\frac{F(V_2 - V_s)}{0.6744 W_2}$$
 (3)

Accuracy. Typical results on a sample of bis-(p-chlorophenyl)methylcarbinol of melting point 67.5-69.0°C. were 98.9 and 99.3%. The end point of the titration is reproducible to within 0.5 mg. of water, which leads to an error of $\pm 3\%$. With reasonable care in titrating and in excluding moisture during the whole procedure, the maximum error should not exceed $\pm 5\%$. Generally, the results were considerably better than this. The presence of ketone in the sample did not interfere.

If large samples are available, the water of dehydration can be readily determined volumetrically after codistillation with benzene (2).

Apparatus. Distilling trap (Ace Glass 7705), 5 ml., calibrated in 0.1-ml. units. Flask, 500-ml., round-bottomed, 24/40 F joint.

Reflux condenser, 24/40 § joint. Glas-Col heating mantle, 500 ml. Calcium chloride drying tube for condenser. **Reagents.** A reagent grade of benzene is dried by distillation, using the distilling trap. Eastman Kodak *p*-toluenesulfonic acid monohydrate is used without purification. It is not necessary to use the anhydrous acid, as the specified amount of hydrate yields a negligible amount of water.

Procedure. A 45-gram sample of bis(p-chlorophenyl)methyl-carbinol is weighed to the nearest 0.1 gram and transferred to the500-ml. round-bottomed flask. After 250 ml. of dry benzene are added, the flask is connected to the distilling trap and condenser. The solution is refluxed until a constant water-level reading is obtained (1.5 to 2.0 hours). The condenser is washed down with three 10-ml. portions of dry benzene and the refluxing is continued another 15 minutes. The water-level reading is recorded to the another 15 minutes. The water-level reading is recorded to the nearest 0.05 ml and the amount of water is calculated by Equation 4. The trap is then drained of benzene and water.

The solution is cooled to at least 40° C., the flask is disconnected from the apparatus, and 0.2 to 0.3 gram of *p*-toluenesulfonic acid is added. The flask is quickly returned to the apparatus. The solution is again refluxed until a constant water volume is obtained, the condenser is washed down with dry benzene, and refluxing is continued for an additional 15 minutes. The waterlevel reading is recorded to the nearest 0.05 ml. A total reflux time of 2 hours is usually sufficient. The DMC content is calculated by Equation 5.

Calculations.

% H₂O = $\frac{\text{ml. of H}_2\text{O} \times 100}{\text{wt. of sample}}$ (4)

$$\% \text{ DMC} = \frac{\text{ml. of } H_2 O \times 1483}{\text{wt. of sample}}$$
(5)

Table IV. Bis-(p-chlorophenyl)methylcarbinol-4,4'-dichlorobenzophenone-1,1-Bis-(p-chlorophenyl)ethylene Setting Points

	0	
Compound(s)	M.P. (Uncorr.), °C.	Setting Point (Corr.), °C.
4,4'-DMC 4,4'-Dichlorobenzophenone 1,1-Bis-(p-chlorophenyl)ethylene DMC + 10% ketone DMC + 10% ethylene DMC + 5% ketone + 5% ethylene	$\begin{array}{c} 68.5-69.0^{a}\\ 143.5-145.5\\ 85.0-86.0\\ 60.5-66.0^{b}\\ 61.0-65.0^{b}\\ 59.0-67.0^{b} \end{array}$	$\begin{array}{c} 69.1 \\ 146.0 \\ 87.7 \\ 63.4 \\ 63.4 \\ 63.6 \end{array}$
a 36-14+ 67 5 60 08 - 64++'		. 1

^a Melts at 67.5-69.0° after setting point determination, showing that very little decomposition had occurred.
 ^b Taken after setting point determination.

When (p-chlorophenyl)(o-chlorophenyl)methylcarbinol (Table I, footnote) is analyzed by this procedure, the yield of water is 99 to 100%. Bis-(o-chlorophenyl)methylcarbinol was not made, but it is probable that it too would be quantitatively dehydrated. Thus this procedure probably measures the total content of bis-(chlorophenyl)methylcarbinol isomers, and, because the 4,4' isomer is most active (7), this analysis alone does not indicate accurately the miticidal value of the sample. For this reason the oxidation procedure was developed.

The 1-(p-chlorophenyl)-1-(o-chlorophenyl)ethylene was isolated from this dehydration as a colorless oil boiling at 142° to 155° at 3 mm.; n_D^{25} 1.6130. Calculated for $C_{14}H_{10}Cl_2$: Cl. 28.5%; found: Cl, 26.2%. It is considerably less absorbent in the ultraviolet than the 4,4' isomer (Figure 1).

Table V.	Setting Point-Composition Data for 4,4'- and	
	2,4'-Dichlorobenzophenones	

% 4,4' Ketone	Setting Point, ° C. (5)	Setting Point, ° C.ª
70	128.8	128.4
80	136.0	135.8
85	139.0	139.2
90	141.7	141.7
92.5	143.0	142.8
95	143.4	144.0
100	145.7	146.0

^a Data found by oxidizing carefully prepared mixtures of 4.4'- and 2.4'- DMC by procedure given below. Yields of mixed ketones were quantitative. Setting points of mixtures check closely with those of Forrest *et al.* (δ) given in middle column. Authors' figures were used in DMC work.

HYDROXYL DETERMINATIONS

Two methods for direct analysis by measuring the hydroxyl content of a sample were tried. The first used the well-known acetic anhydride-pyridine acetylation (θ), but bis-(p-chlorophen-yl)methylcarbinol was not acetylated under the conditions of this method, possibly because of the sterically hindered hydroxyl group and the ease of dehydration to the ethylene.

A number of experiments with the macro-Zerewitinoff determination of active hydrogen (20) were run with methylmagnesium iodide in *n*-butyl ether and various solvents for the sample. With *n*-butyl ether or benzene as the solvent the method gave only two thirds to three fourths of the theoretical hydrogen value. Some precipitation occurred in these experiments, which may account for the low values if bis-(*p*-chlorophenyl)methylcarbinol were removed in the form of an insoluble addition compound. With purified pyridine as the solvent (11) the results were erratic and usually high.

ANALYSIS BY OXIDATION TO DICHLOROBENZOPHENONES

Oxidation of bis-(*p*-chlorophenyl)methylcarbinol and its ethylene derivative by chromic acid in acetic acid yields 4,4'-dichlorobenzophenone (8):

$$(p-\mathrm{ClC}_{6}\mathrm{H}_{4})_{2}\mathrm{C(OH)}\mathrm{CH}_{3} + 4(\mathrm{O}) \xrightarrow{} (p-\mathrm{ClC}_{6}\mathrm{H}_{4})_{2}\mathrm{CO} + 2\mathrm{H}_{2}\mathrm{O} + \mathrm{CO}_{2} \quad (6)$$

$$(p-\text{ClC}_{6}\text{H}_{4})_{2}\text{C}=\text{CH}_{2} + 4(\text{O}) \longrightarrow (p-\text{ClC}_{6}\text{H}_{4})_{2}\text{CO} + \text{H}_{2}\text{O} + \text{CO}_{2} (7)$$

When this reaction is carried out in a large scale as described below, the yield of ketone is quantitative. The same procedure applied to (p-chlorophenyl)(o-chlorophenyl)methylcarbinol gives 2,4'-dichlorobenzophenone, melting point 63-66°C., in the theoretical yield. Similar oxidation of 1,1-bis-(p-chlorophenyl)-2,2-dichloroethylene derived from DDT has been used to establish the structure of DDT (9) and to analyze mixtures of isomeric DDT's (δ) .

Technical bis-(p-chlorophenyl)methylcarbinol contains mostly the 4,4' isomer, small amounts of the 2,4', and little or none of the 2,2'. Thus, oxidation gives a mixture of 4,4' and 2,4' ketones whose composition can be estimated from its setting point (Table V). This method does not differentiate between bis-(pchlorophenyl)methylcarbinol and its ethylene derivative but with the bis-(p-chlorophenyl)methylcarbinol content obtained by quantitative dehydration, one can calculate the minimum and maximum concentrations of bis-(p-chlorophenyl)methylcarbinol in the sample.

Procedure. In a 500-ml. **§** flask fitted with a reflux condenser place 35 grams of bis-(chlorophenyl)methylcarbinol weighed to the nearest 0.1 gram and 50 ml. of glacial acetic acid. Heat to boiling, remove the flame, and add a solution consisting of 50 grams of chromic acid, 50 ml. of water, and 50 ml. of glacial acetic acid dropwise through the condenser at a rate to maintain steady reflux. Continue refluxing for 2 hours, then add 200 ml. of hot water slowly through the condenser while boiling to provide mixing. Cool to room temperature. Suction filter and wash the cake twice with ammonium hydroxide solution (1 volume of concentrated ammonium hydroxide in 19 volumes of water), then with water. Dry in air or at 60° C. to constant weight. The theoretical yield from 35 grams of bis-(chlorophenyl)methylcarbinol is 32.8 grams of ketones. Note the per cent yield (actual yield \times 100/32.8) for use in calculations.

Dissolve the crude ketones in 150 ml. of chloroform, dry with 5 grams of anhydrous calcium chloride, and filter. Transfer to an evaporating dish and bring to dryness on a steam bath. Before each setting point is taken (see procedure above) hold the melt at 175° C. in an oil bath for 5 minutes to expel all chloroform.

This procedure has worked well on bis-(p-chlorophenyl)methylcarbinol prepared from the ketone. Other synthetic routes may give a product containing oxidizable impurities, so that this oxidation would be incomplete. This can be checked by reoxidizing the crude ketone and comparing the yield and setting point with the first oxidation. If these impurities gave final oxidation products which were not 4,4' or 2,4' ketone, the composition based on the setting point would be incorrect.

Calculations. The per cent of 4,4' ketone found by this procedure measures the total content of bis-(*p*-chlorophenyl)methylcarbinol, 1,1-bis-(*p*-chlorophenyl)ethyleæe, and 4,4' ketone in the sample. The maximum bis-(*p*-chlorophenyl)methylcarbinol content is equal to the smaller of the values found by quantitative dehydration and by this oxidation. The minimum bis-(*p*-chlorophenyl)methylcarbinol content is equal to the maximum bis-(*p*-chlorophenyl)methylcarbinol percentages minus the quantity [100 – the larger percentage of bis-(*p*-chlorophenyl)methylcarbinol found by quantitative dehydration and by this oxidation].



For example, assume a sample analyzes 90% bis-(chlorophenyl)methylcarbinols by dehydration and 80% 4,4' isomers by oxidation. The maximum bis-(p-chlorophenyl)methylcarbinol content is 80% and the minimum is 80 - (100 - 90) or 70%. If the purity was actually 80%, the remaining 20% must be 10% of (o-chlorophenyl)(p-chlorophenyl)methylcarbinol (to account for the 90% dehydration value) and 10% of 2,4'-ethylene and ketone. If the purity was only 70%, the remaining 30% must consist of 20% (o-chlorophenyl)(p-chlorophenyl)(p-chlorophenyl)methylcarbinol (to give the 90% dehydration analysis) and 10% 4,4'-ethylene and ketone to give the 80% oxidation analysis.

If the sample contained compounds other than 2,4'- and 4,4'bis-(chlorophenyl)methylcarbinols and the corresponding ethylenes and ketones, the per cent yield of ketones obtained by oxidation may be considerably below the theoretical yield and even less than the per cent bis-(chlorophenyl)methylcarbinol isomers found by dehydration or less than the per cent 4,4' isomer found by oxidation. In this case the maximum per cent bis-(*p*chlorophenyl)methylcarbinol is equal to the per cent yield of ketone. The minimum per cent bis-(*p*-chlorophenyl)methylcarbinol is found as usual.

The possibility of analyzing the mixture of ketones by the difference in ease of hydrolysis of the ortho and para chlorine atoms was tested. When 0.25-gram samples of each ketone were refluxed with 30 ml. of 1.0 N alcoholic potassium hydroxide solution for 4 hours and the chloride ion was determined in the filtrate, the 4,4' ketone gave 1.5 to 2.0% of the theoretical yield of chlorine and the 2,4' ketone gave 5.4 to 5.8%. Apparently the ortho chlorine atom is more rapidly hydrolyzed, but the difference did not appear to be great enough to serve as an analytical procedure.

ULTRAVIOLET ABSORPTION SPECTRA

The ultraviolet absorption curves (Figure 1) for pure bis-(*p*-chlorophenyl)methylcarbinol and pure 1,1-bis-(*p*-chlorophenyl) ethylene in the range of 220 to 260 m μ show a great difference at 240 m μ . The ethylene has an absorption maximum at this point (due to the ethylene double bond conjugated with the rings) while bis-(*p*-chlorophenyl)methylcarbinol does not. Synthetic mixtures were prepared from the pure compounds and examined in the Beckman Model DU ultraviolet spectrophotometer. The plot of per cent bis-(*p*-chlorophenyl)methylcarbinol *rs*. specific extinction at 240 is a straight line. The equation for this straight line was found and thus the per cent bis-(*p*-chlorophenyl)methylcarbinol in a sample consisting only of bis-(*p*-chlorophenyl)methylcarbinol and its ethylene is calculated from the value of the extinction at 240 m μ :

$$\% 4,4' - DMC = \frac{103.6 - \text{specific extinction}_{240}}{0.928}$$
(8)

A determination can be run in 1 hour or less on 0.1-gram samples with a maximum error of $\pm 2\%$.

From the absorption curve of the pure 4,4' ketone (Figure 1) and mixtures with bis-(*p*-chlorophenyl)methylcarbinol, it was found that binary mixtures could be analyzed by measuring the specific extinction at 260 m μ :

$$\% 4,4'-\text{ketone} = \frac{\text{specific extinction}_{260} - 2.9}{0.96}$$
(9)

$$\% 4,4'$$
-DMC = 100 - $\%$ ketone (10)

From a study of synthetic mixtures of ethylene and ketone, the following equations were derived, by which measurements at 240 and 260 m μ will allow these binary mixtures to be analyzed:

$$\% 4,4'-\text{ethylene} = \frac{\text{specific extinction}_{240} - 34.8}{0.687}$$
(11)

$$\% 4,4'-\text{ethylene} = \frac{105 - \text{specific extinction}_{250}}{0.45}$$
(12)

Both wave lengths should be checked, but the measurement at 260 m μ gives a more accurate analysis because of the greater difference in absorption at that point.

The final step in this development was the analysis of ternary mixtures of the 4,4' isomers of bis-(chlorophenyl)methylcarbinol-ethylene-ketone. To avoid the inherent error of obtaining the bis-(p-chlorophenyl)methylcarbinol content by difference, the method involves a dehydration step so that the increase in the ethylene content measures the bis-(p-chlorophenyl)methylcarbinol. The following procedure was carefully checked against known mixtures.

Procedure. A 0.1- to 0.15-gram is weighed to the third place in a 100-ml. glass-stoppered volumetric flask. After diluting to the mark with spectroscopically pure iso-octane and dissolving, 1.0 ml. of solution is removed with a graduated 1.0-ml. pipet and diluted to 100 ml. The optical density $(\log I_0/I)$ of this solution is measured at the wave lengths 240 m μ and 260 m μ in 1-cm. quartz cells. From these values the % ethylene is calculated:

$$\%$$
 1,1-bis-(p-chlorophenyl) ethylene =

$$\frac{(1.27)(\log_{290} I_0/I - 0.108) - (2.98)(\log_{260} I_0/I - 0.029)}{\text{concentration, grams per liter}}$$
(13)

Another sample weighing 0.1 to 0.15 gram is weighed to the third place and transferred to a 125-ml. round-bottomed flask having an air condenser attached through a ground-glass joint. The sample is dissolved in 10 ml. of Skellysolve B and 0.3 ml. of purified thionyl chloride (4) is added. The thionyl chloride effects the dehydration. The flask is heated for 1 hour in an oil bath maintained at 90° to 100° C. After cooling, the condenser and ground-glass joint are washed down with 10 ml. of Skellysolve B are added, and the solution is again taken down to near dryness. This step is repeated two more times and finally the residue is heated on the bath for 10 minutes. This operation expels the excess thionyl chloride and the Skellysolve B. "Near dryness' is emphasized because side reactions occur if concentrated thionyl chloride is heated with the residue. The residue is then dissolved in 30 to 40 ml. of iso-octane and the solution and washings are transferred to a 100-ml. volumetric flask. After following the same dilution procedure described for the first sample, the optical density is measured at 260 m μ . From this and the previous value at 260 m μ the following equation:

Specific extinction
$$=$$
 (14)

 $\frac{\log I_0/I}{(\text{concn., grams per liter})(\text{length of light path through cell, cm.})}$

Then, with E and E' as the specific extinction before and after dehydration,

$$\% 4,4' - DMC = 2.02 (E'_{260} - E_{260})$$
 (15)

% 4,4'-ketone = 100 - (% 4,4'-DMC + % 1,1-bis-(p-chlorophenyl)ethylene) (16)

Typical results from this ultraviolet absorption analysis are shown in Table VI. Up to 90% bis-(*p*-chlorophenyl)methylcarbinol the accuracy is satisfactory but as the total concentration of 4,4'-ketone plus 1,1-bis-(*p*-chlorophenyl) ethylene falls below 10%, the accuracy decreases.

Table VI.	Ultraviolet	Analysis	of Ternary	Mixtures
			0%	4.4'-DMC

Mix-	x- % 4,4'-DMC		% 4,4' Ketone		Ethylene	
ture	Theoret.	Found	Theoret.	Found	Theoret.	Found
$ \frac{1}{2} 7 8 $	80 70 90 95	79.670.889.493.4	$\begin{smallmatrix}10\\20\\5\\2.5\end{smallmatrix}$	$ \begin{array}{r} 10.1 \\ 19.9 \\ 6.7 \\ 3.9 \end{array} $	$\begin{array}{c}10\\10\\5\\2.5\end{array}$	$ \begin{array}{c} 10.3 \\ 9.3 \\ 2.9 \\ 2 \\ 8 \end{array} $

The derivation of Equation 15 depends on the fact that the dehydration with thionyl chloride is not quantitative. Many dehydration experiments under various conditions showed that the most reproducible degree of dehydration, as measured by the increase in absorption at 260 m μ , was 88%. Thus, the quantity 0.88 \times 60, where 60 is the specific extinction of the pure 1,1-bis-(*p*-chlorophenyl)ethylene, is used. Also considered is the molecular weight change of bis-(*p*-chlorophenyl)methylcarbinol \rightarrow ethylene, which gives the ratio of 1.068. Thus Equation 15 originated from:

$$\% 4,4'-\text{DMC} = \frac{(E'_{260} - E_{260}) \times 1.068 \times 100}{0.88 \times 60}$$
(15a)

COLORIMETRIC ANALYSIS OF SMALL QUANTITIES

By modifying the method of determining DDT (19) which involves nitration of the sample, reaction with sodium methylate, and a colorimetric measurement of the product, a satisfactory procedure for bis-(p-chlorophenyl)methylcarbinol in quantities of 0.12 to 3.3 mg. has been developed. Figure 2 shows the absorption spectra in the visible for the colored products derived from bis-(p-chlorophenyl)methylcar, binol and 1,1-bis-(p-chlorophenyl)ethylene and (o-chlorophenyl)-(p-chlorophenyl)methylcarbinol. The analysis is based on the peaks at 418 or 530 m μ . The longer wave length is preferred because the greater absorption allows better accuracy. It is seen that the ethylene reacts almost identically with bis-(p-chlorophenyl)methylcarbinol and is therefore estimated with it. Very probably the bis-(p-chlorophenyl)methylcarbinol is immediately dehydrated to the ethylene on reaction with nitric acid and it is the ethylene which is nitrated. The (o-chlorophenyl)(p-chlorophenyl)methylcarbinol product is much less absorbing. If the sample contained an appreciable amount of this isomer, the colorimetric analysis would give an erroneously low result for the total bis-(c-chlorophenyl)methylcarbinols present.



A. Nitrated 4,4'-DMC
 B. Nitrated 1,1-Bis(p-chlorophenyl)ethylene
 C. Nitrated 2,4'-DMC

Reagents. The following reagents were prepared as described earlier (19): nitrating acid, 2% sodium hydroxide solution, sodium chloride solution, cotton, and 10% sodium methylate solution. If the sodium methylate is to be used over an extended period of time, it is probably better to make up a second more concentrated solution and to adjust the concentration of the first solution for each analysis by the addition of small amounts of the second solution as determined by the acidimetric titration (19). In addition, reagent benzene is dried by refluxing with a distilling trap until no more water appears in the trap and is then distilled. Ether is freed of peroxides by shaking with small portions of a 1 to 1 mixture of ferrous sulfate pentahydrate and sodium bisulfate until a brown color is no longer developed and then distilled.

Procedure. A benzene solution of the bis-(p-chlorophenyl)methylearbinol sample is concentrated to a few milliliters on a steam bath and transferred quantitatively to a large test tube $(20 \times 175 \text{ mm.})$. A boiling chip is added and the test tube is heated by immersing it to one third of its length in a steam bath. When evaporation appears to be complete, 10 ml. of absolute alcohol are added and the contents are taken down to dryness. This step is repeated and then the last traces of vapor are removed by inserting a glass tube attached to the vacuum line one third of the way into the test tube. The test tube is cooled in an ice bath and 2 to 5 ml. of the nitrating mixture are cautiously added. After any initial violent reaction has subsided, the test tube is transferred to the steam bath and heated for 1 hour. Then 25 ml. of ice-cold distilled water are added to the test tube to halt the nitration. The contents are then transferred to a 125-ml. separatory funnel by means of a small funnel and 25 ml. of wash water and 50 ml. of ether in small portions. The funnel is tightly stoppered and shaken for 1 minute. Sufficient time must be allowed for drainage before opening stopcocks or removing stoppers, so that ether solution is not lost by being sprayed from the funnel.

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After drawing off and discarding the lower layer, the ether solu-tion is shaken with 10 ml. of 2% sodium hydroxide solution. This operation is repeated until the lower aqueous layer is alkaline to litmus The ether layer is then washed with two 10-ml. portions of saturated sodium chloride solution. After the second washing, the lower layer is drawn off as completely as possible and the bore of the funnel is dried with a rolled piece of filter paper. A small long-stemmed funnel is packed with a 0.5-inch plug of cotton. The cotton plug is moistened with ether and the ether solution in the separatory funnel is slowly filtered through the cotton into a The separatory funnel is washed with 250-ml. Erlenmever flask, 50 ml of ether in four portions, which are also filtered through the cotton plug and added to the main solution. The ether is removed by heating on the steam bath and when evaporation is complete, a glass tube attached to the vacuum line is inserted in the flask as before. The residue is then dissolved in 25 ml. of dry benzene. Five milliliters of this solution are pipetted into a 125ml. Erlenmeyer flask containing 10 ml. of clear $10 \pm 0.1\%$ sodium methylate solution. Fifteen minutes after mixing the solutions, the optical density at 530 m μ , (log $I_0/I)_{550}$, is measured with a Beckman Model DU spectrophotometer, whose sensitivity knob is set at three turns from the clockwise limit in order to ensure maximum accuracy. The blank solvent for comparison is pre-pared by mixing one volume of benzene with two volumes of sodium methylate solution.

Table VII. Colorimetric Determination of Small Amounts of Bis-(p-chlorophenyl)methylcarbinol

No	DMC Taken,	DMC Caled. from	m Readings, Mg.
140.	141 8.	+10 mµ	550 mµ
1	0.12	0.08	0.09
2	0.24	0.23	0.23
3	0.47	0.46	0.47
4	0.71	0.68	0.70
5	1.01	1.12	1.09
6	1.23	1.27	1.26
7	1.60	1.62	1.59
8	2.52	2.47	2.48
9	3.28	3.22	3,29

Calculations.

Weight of DMC, mg. = $(1.80)(\log I_0/I)_{530}$ (17)

If the final concentration resulting from the above procedure is too low or too high for spectrophotometric measurements, the pipet used in removing the 5-ml. aliquot is rinsed with benzene into the remaining 20 ml of benzene solution, which represents four fifths of the original sample. The benzene is removed by adding a boiling chip and heating on the steam bath. The residue is dissolved in a suitable volume of benzene, and aliquot is drawn and again mixed with twice its volume of 10% sodium methylate reagent and the optical density is again measured at 530 m μ . The amount of bis-(p-chlorophenyl)methylcarbinol is calculated with the following formula:

Weight of DMC, mg. = $(1.80)(5/4)(V/25)(\log I_0/I)_{530}$ (18)

where V is the new volume of benzene solution from which an aliquot is taken.

Table VIII. Thermal Stability of Bis-(p-chlorophenyl)methylcarbinol

(M.p. 67-69° C. Results in % DMC)

Time.		Temperature		
Hours	45° C.	65° C.	85° C.	105° C.
$\begin{array}{c}2\\4\\24\\42\end{array}$	· · · · ·	97 	97 93 48 24	82 77 39 30
Days				
27	••	94 94	••	• •
12		90 71	••	
27	 	58	• •	
48 104	94 93	•••		
194	90	••		

Accuracy. The figures of Table VII show that the accuracy of the determination made at 530 m μ increased with increasing sample size—the error at 0.1 mg. may be as high as 25% and at

Table IX.	Stab	ility of l	Bis-(<i>p</i> -chlorophenyl)met	hyl-
carbing	ol in	Mixtures	s at Room Temperature	
				·

(M.p. 07-09 ° C.	Results In 70 DAIO)	
Sample	69 Days ⁴	194 Days
4.4'-DMC 4.4'-DMC + 0.5% EtaN 4.4'-DMC + 0.5% pyridine 4.4'-DMC + 0.1% p-TolSOaH 1/1 by wt 44'-DMC-CaCOa	100 100 100 100 100	$100 \\ 100 \\ 100 \\ 94 \\ 100$
 A Measurements taken at about r 	nonthly intervals.	100

Table X.	Stability of Bis-(p-chlorophenyl)methylca	r-
	binol in Mixtures at 45° C.	

(M.p. 67-69° C.	Results in % DMC)	
Sample	7 Days	14 Days
4,4'-DMC 4,4'-DMC + 0.5% Na ₂ CO ₃ 4,4'-DMC + 0.1% p-TolSO ₃ H 1/1 by wt., 4,4'-DMC-CaCO ₃	98.8 99.1 72.0 99.1	98.799.126.299.1

3 mg. as low as 0.4%. It is estimated that the average error at about 1.0 mg, would be $\pm 2.0\%$ and that the precision at that sample weight might also be $\pm 2.0\%$.

PROPERTIES OF BIS-(p-CHLOROPHENYL)METHYLCARBINOL

Stability. To determine the thermal stability of bis-(p-chlorophenyl)methylcarbinol samples were observed in air at room temperature and at elevated temperatures up to 105° C. for as long as 6 months. It was assumed that the only reaction which would occur was that of dehydration to the ethylene (Equation 1) and that the ultraviolet absorption spectra would therefore provide a suitable analytical method. At room temperature in 6 months there was no change in the bis-(p-chlorophenyl)methylcarbinol content. In 6.5 months at 45° C, the sample has deteriorated by only 10% (Table VIII). At higher temperatures the rate increased rapidly.

Table XI.	Stability of Bis-(<i>p</i> -chlorophenyl)methylcar- binol in SD-1 Ethanol
Table Al.	binol in SD-1 Ethanol

(M.p. 67-69° C. Results in % DMC)

Time	At	0.1 N	0.1 N H ₂ SO ₄		0.1 N KOH	
Hours	reflux	Rm. T.	At reflux	Rm. T.	At reflux	
1			77	9 8	98	
2			57			
3			41			
4	98	96	33	98	98	
5			21			
24	98	98		98	98	
96		98		98		

As bis-(*p*-chlorophenyl)methylcarbinol may be formulated either in dry mixtures or in solution for spraying purposes, its stability under both conditions, as affected by acids and bases, was tested. At room temperature dry mixtures containing *p*toluenesulfonic acid, triethylamine, pyridine, or calcium carbonate are mostly unchanged for about 6 months (Table IX), although the sample containing 0.1% *p*-toluenesulfonic acid had started to deteriorate.

At 45° the samples containing bases were unchanged at the end of 2 weeks, but the presence of 0.1% of the acid caused rapid deterioration (Table X). Thus, the powerful catalytic action of strong acids in the dehydration of alcohols to olefins is occurring here in the solid state. Obviously bis-(*p*-chlorophenyl)methylcarbinol must not contain even the slightest traces of acids.

The behavior of bis-(p-chlorophenyl)methylcarbinol in solution was tested with ethanol (SD-1) as the solvent in the presence of sulfuric acid (0.1 N) and potassium hydroxide (0.1 N), both at

room temperature and at reflux (Table XI). In the absence of acid there is no deterioration even at reflux at the end of 96 hours. Again the acid strongly accelerated dehydration; at 5 hours' reflux about 80% of the bis-(*p*-chlorophenyl)methylcarbinol had been consumed. The effect of heat alone is less marked in the case of the solution than for the solid; from Table IX bis-(*p*-chlorophenyl)methylcarbinol heated at 65° for about 24 hours had dropped to about 60% purity but in ethanol solution at reflux (78° C.) there was no change in this time. This may be due to reduced exposure to the oxygen of the air for the bis-(*p*-chlorophenyl)methylcarbinol in solution.

Volatility. Bis-(*p*-chlorophenyl)methylcarbinol cannot be vacuum-distilled at 1 mm. or vacuum-sublimed without some dehydration to the ethylene derivative.

Table XII.	Volatility of Bis-(p-chlorophenyl)methylcar-
binol,	DDT (Technical), DDT (Pure) at 25° C.

Time, Days	${}^{\rm DMC}_{(1.0219 \text{ G.}),}_{\%}$	DDT (Tech.) (1.0132 G.), %	DDT (Pure) (1.0092 G.), %
$ \begin{array}{c} 1 \\ 2 \\ 4 \\ 6 \\ 11 \\ 15 \\ 27 \\ 36 \\ $	$\begin{array}{c} 0.39^{a} \\ 0.53 \\ 0.81 \\ 0.90 \\ 1.00 \\ 1.14 \\ 1.49 \\ 1.67 \\ 1.67 \end{array}$	$\begin{array}{c} 0.12^{a} \\ 0.18 \\ 0.20 \\ 0.22 \\ 0.25 \\ 0.27 \\ 0.37 \\ 0.37 \\ 0.37 \end{array}$	$\begin{array}{c} 0.11^{a} \\ 0.12 \\ 0.17 \\ 0.17 \\ 0.22 \\ 0.22 \\ 0.26 \\ 0.26 \\ 0.26 \end{array}$
42 As par cont.	1.72 of original waight lo	0.37	0.26

^a As per cent of original weight lost.

Carbon tetrachloride solutions each containing about 1.0 gram of bis-(p-chlorophenyl)methylcarbinol (m.p. $67-69^{\circ}$ C.), technical DDT, and pure DDT (melting point $105-107^{\circ}$ C.) were allowed to evaporate on watch glasses and the loss in weight of the solid was observed on standing at room temperature. The data of Table XII show that bis-(p-chlorophenyl)methylcarbinol is four to eight times more volatile than DDT but is still relatively nonvolatile.

	(M.p. 58-60° C.	Grams per 100 ml.)	
		Temperature		
Solvent	60° C.	45° C.	25-30° C.	
Toluene D.C. naphtha n-Butyl ether Skellysolve B Ether SD-1 ethanol Tetrahydrofura	440 490 	311 32 	$125 \\ 7 \\ 82 \\ 3.7 \\ 110 \\ 175-200 \\ 215 \\ 215 \\ 125$	

Solubility. The approximate solubility of two samples of bis-(*p*-chlorophenyl)methylcarbinol differing in purity was found in various solvents by noting the quantity of solvent required to dissolve a weighed sample at the temperature indicated.

Table XIV. Approximate Solubilities of Bis-(p-chlorophenyl)methylcarbinol

(M.p. 65-69° C.	Grams per 100 ml.)
Solvent	At 25–30° C.
Toluene D.C. naphtha n-Butyl ether Skellysolve B Ether SD-1 ethanol Tetrahydrofuran	110 7 85.0 4.3 152 125-150 243

The following solvents were tried in a series of crystallization experiments: Skellysolve B, chloroform, carbon tetrachloride, toluene, acetic acid, methanol, 95% ethanol, and 80% ethanol. The last two solvents were made from SD-1 alcohol. By the amount of bis-(p-chlorophenyl)methylcarbinol recovered and its purity, Skellysolve B is best. Two milliliters per gram are heated to boiling, filtered, cooled to 0° C., and filtered, and the solid is washed with a little cold Skellysolve B. Mixtures that contain only 50% or less of bis-(p-chlorophenyl)methylcarbinol along with ketone and/or ethylene are difficult to purify.

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RECEIVED for review September 29, 1951. Accepted December 5, 1951.

Method for Continuous Extraction with a Chelating Agent

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A continuous method has been developed for safely extracting gram amounts of thorium as the nitrate salt from the actinium and radium isotopes present in tracer quantities after cyclotron bombardment of the thorium. The method uses a benzene solution of thenoyl trifluoroacetone as the chelating agent and leaves the tracer activities carrier-free in the raffinate accompanied by a minimum of foreign salts. One gram of thorium can be extracted from a highly radioactive solution in about 3 hours in the apparatus described. The extractor is especially useful for work with very radioactive materials, as a minimum of shielding is required and most operations are automatic. The method is readily adaptable to other types of extraction problems and the equipment can be scaled to fit requirements.

THE use of chelating agents in a variety of extraction methods developed over the past few years has greatly increased the number of possibilities of separating many of the elements (2). In the field of nuclear chemical separations, especially, "chelating extractions" have made possible very clean-cut separations of many elements in widely varying concentrations—from macro amounts to tracer amounts (1, 4).

In the field of solvent extraction many different systems for continuous extraction have been devised (10). Separations using chelating agents have not in general, however, been adaptable to continuous systems. The work reported here arose from the problem of safely separating macro amounts (1 to 5 grams) of thorium from the highly radioactive fission and spallation products (7, 9) present in tracer quantities after high-energy bombardment of the thorium target material in the Berkeley 184-inch cyclotron. It was especially important that the radium and actinium isotopes be completely recovered from the thorium for this work. In precipitation reactions the bulky precipitate formed carried down large percentages of the radioactive tracer material even with "holdback carriers" present (δ). Although

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several solution and reprecipitation cycles allowed recovery of the desired materials, the operator was exposed to large amounts of radiation in the process. Solvent extraction with "pentaether" (dibutoxy tetraethylene glycol, obtainable from Carbide and



Figure 1. Extraction Apparatus