than are required for the reaction of hexachlorocyclopentadiene with some of the simpler conjugated dienophilic dicarboxylic acids or anhydrides (*2, 3*). At temperatures above 150° C. in inert solvents, *m*-xylene, mixed xylenes, *o*-dichlorobenzene, or with no solvent, a Diels-Alder reaction takes place to give two isolable products. One of these, compound II, has a melting point of 278° C. and is the predominant isomer produced under the conditions of the reaction. The other isomer, compound III, has a melting point of 256–257.5° C. and is isolated in 10 to 20% yield.

The total assignment of stereochemical configurations for compounds II and III has not been possible to date. Partial assignments and hence nonidentity of compounds II and III have been made using nuclear magnetic resonance. Compounds II and III were examined along with an authentic sample of the hexachlorocyclopentadiene-cyclohexene adduct (compound IV), m.p. 76–77° C. (*1*). NMR spectra were determined in pyridine and in carbon tetrachloride with 10 p.p.m. of tetramethylsilane as an internal reference. In compound IV, the group at 7.2 and 7.3 has a width at least 10 c.p.s. The breadth and shift indicate that this is the tertiary proton trans (180° C.) to the axial proton 8.7 and 9.0, whose spread and shift are consistent. Thus the cyclohexene ring has the boat conformation. Nothing can be surmised about the position of the CCl_2 bridge with respect to the ring in compounds II, III, or IV (Table II).

The anhydrides were converted by standard procedures into a series of esters; half-esters were easily prepared by reaction of the anhydrides with alcohols and no catalyst. The diesters of the high melting isomer (compound II) were prepared from methyl, ethyl, allyl, *n*-butyl, 2-ethylhexyl, and *n*-octyl alcohols. Isopropyl and methallyl alcohols could only be forced to the half-ester stage.

In preparations of the dimethyl esters of II and III, the synthesis of the dimethyl ester of the low melting anhydride, compound III, gave a solid product, m.p. 132° C. This ester, m.p. 132° C., may be compared with the solid ester, m.p. 102–103° C. prepared from the higher melting anhydride, compound II. The dialkyl esters of III prepared to date are uniformly lower melting than the comparable esters of II (Table I).

Table II. Tau Value Shifts

Compound IV in CCl_4	Compound IV in Pyridine	Compound II in Pyridine	Compound III in Pyridine
...	...	6.5	6.33[a]
7.20	7.28	7.4	6.97[b]
8.20	8.53	7.4	7.50
8.69	9.00	8.4	8.33[c]

[a] Hydrogens alpha to the carbonyl. [b] Tertiary hydrogens. [c] Prow or stern hydrogens.

INFRARED SPECTRA

Infrared spectra were recorded using a Beckman IR-9 spectrometer in the region 400 to 3800 cm.$^{-1}$. Solid state spectra were recorded using a mull technique, and the mulling agents used were Nujol (400 to 1333 cm.$^{-1}$) and Fluorolube (1330 to 3800 cm.$^{-1}$).

The compounds show a medium band in the 1599 to 1607 cm.$^{-1}$ region $\nu_{C=C}$ stretching. Apparently, the occurrence of $\nu_{C=C}$ at lower frequencies and increased intensity indicates substitution (chlorine) when compared with $\nu_{C=C}$ for cyclohexene, ~1650 cm.$^{-1}$. Carbon chlorine stretching consistently show up in the 675 to 875 cm.$^{-1}$ region in all of the compounds.

The carbonyl stretching frequency shows up at 1770 to 1780 cm.$^{-1}$, and the two carbonyl stretching frequencies show up at 1770 to 1780 cm.$^{-1}$ and 1700 to 1712 cm.$^{-1}$; the higher frequency band is weak, while the lower frequency band is strong. This is characteristic of the cyclic anhydride moiety.

In the esters, the $\nu_{C=O}$ at ~1750 cm.$^{-1}$ is clearly inappropriate for the anhydride or the compounds having a free carboxylic acid grouping and is correct for an ester of the $R—CO_2CH_3$ form where R— is not conjugated with the carbonyl.

A weak but definite band at 2850 cm.$^{-1}$ in the methyl ester series is characteristic of a methoxy group. A strong band at 1200 cm.$^{-1}$ is characteristic of esters of the RCO_2R' form where R— is again not conjugated with the carbonyl group.

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Improved Preparation of 2,3-Dihydro-*p*-dioxin(Dioxene)

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2,3-Dihydro-*p*-dioxin (dioxene) was prepared in 78% yield by a liquid-phase dehydrogenation-dehydration of diethylene glycol at 230° to 250° C.

THE COMPOUND 2,3-dihydro-*p*-dioxin (dioxene) has previously been prepared in low yield by the reaction of 2,3-dichloro-1,4-dioxane with Grignard reagents such as methyl, ethyl, or 1-butyl magnesium bromide (*4*) and by the reaction of 2,3-dichloro-1,4-dioxane with magnesium iodide (*5*). Also prepared in low yields by the catalytic vapor-phase dehydrogenation-dehydration of ethylene glycol (*3*), it is obtained in small amounts as a by-product from the copper chromite-catalyzed dehydrogenation of diethylene glycol; the major product is 2-*p*-dioxanone (*2*).

The authors were able to prepare dioxene in 78% yield by a liquid-phase dehydrogenation-dehydration of diethylene glycol at 230° to 250° C. Table I summarizes results obtained with various catalysts. Of the catalysts tested, the most effective was a copper chromite–potassium acid

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Table I. Effect of Catalysts and Additives on the Preparation of Dioxene

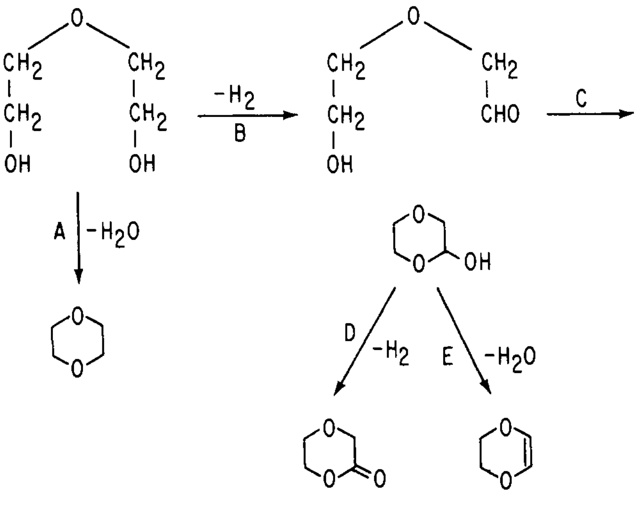
(10 mole reactions; catalyst used = 15 grams)

Catalyst	Additive, G.	Yields, %			
		Conversion	Dioxene	Dioxane	Dioxanone
Harshaw 1800P[a] copper chromite	None	100	2	0	73.5
Harshaw 1800P copper chromite	$KHSO_4$ (Baker fused powder), 10	36.5	86.5	2.5	0
Harshaw 0202P[b] copper chromite	$KHSO_4$, 10	44.5	87.0	3.4	0
Girdler T-1060[c] copper chromite	$KHSO_4$, 10	35.5	81.5	2.5	0
Harshaw 0202P	$KHSO_4$, 5	65.8	78.5	3.0	0
Girdler T-980[d] cobalt chrome	$KHSO_4$, 10	61.0	54.0	1.0	0
Copper metal (electrolytic dust)	$KHSO_4$, 10	~11	~24	0	0
Harshaw 1800P	$NaHSO_4$, 10	16.0	56.0	8.9	0
Harshaw 1800P	$K_2S_2O_7$, 10	40.5	77.5	2.8	0
Harshaw 1800P	2% Cr_2O_3 on silica gel	~25	~15	<5	85
Harshaw 1800P	Alumina	100	~8	0	71.0

[a] 40.8% Cu, 32.2% Cr. [b] 65.5% Cu, 11.6% Cr. [c] 35.8% Cu, 28.7% Cr. [d] 50.0% Co, 2.0% Cr.

sulfate combination. Normally, small amounts of 2-*p*-dioxanone and *p*-dioxane also formed. When the potassium acid sulfate was omitted from the reaction, the major product was 2-*p*-dioxanone.

A reaction path which could account for the formation of dioxene, 2-*p*-dioxanone, and *p*-dioxane is as follows



A similar reaction sequence has been proposed by Summerbell, Jerina, and Grula (*6*) to explain the formation of substituted dioxenes in the copper chromite–catalyzed dehydrogenation-dehydration of dialkylene glycols.

The authors have shown that 2-hydroxydioxane is dehydrated in refluxing diethylene glycol to yield dioxene. This observation lends support to the proposed path. Potassium acid sulfate in functioning as a mild dehydrating agent may be a selective catalyst poison for dehydrogenation reaction D. Good dehydrating agents such as H_2SO_4 favor direct dehydration of diethylene glycol to *p*-dioxane, path A. Hemiacetal formation, C, is favored by acidic conditions.

Experiments were also run with copper chromite in combination with other additives. Of these, the following resulted in the formation of large amounts of polymeric material: CaF_2, K_2SO_4, Li_3PO_4, $CsHSO_4$, $KF \cdot 2H_2O$, Na_2HPO_4, and H^+ Dowex 50 × 8 resin. In the presence of other additives [$AlCl_3$, $Al_2(SO_4)_3$, $SnSO_4$, $Fe_2(SO_4)_3$, $ThCl_4$, $LiHSO_4$, and $CuSO_4 \cdot 5H_2O$], the principal product was *p*-dioxane. With other additives, the reaction proceeded much as it did when only copper chromite was present—i.e., *p*-dioxanone predominated. This latter class included alumina, $MgSO_4$, CO, $(CH_3)_2S$, and B_2O_3.

EXPERIMENTAL

Dioxene. A 1-liter flask equipped with a stirrer and a thermocouple was connected to a 3¾-foot vacuum-jacketed Vigreux column, which in turn was attached to a fraction cutter and a receiver. The receiver was vented to a wet-test meter to permit measurement of the hydrogen evolved during the reaction. The column head was connected to a recorder-controller which controlled the heat input to the reactor mantle. Diethylene glycol (1060 grams, 10 moles) was mixed with 15 grams of Harshaw 1800P copper chromite and 5 grams of potassium acid sulfate. After the entire system had been purged with nitrogen, the stirred mixture was heated. A reflux ratio of 3 to 1 was used, and the head temperature was controlled at 125° C. At about 230° C. reactor temperature, evolution of hydrogen started, and at about 235° C., products began to distill. After 15 hours of distillation, the reaction was finished—i.e., hydrogen evolution ceased and less than 4 ml. per hour of product was being collected. A total of 123 liters (STP) or 5.5 moles of hydrogen was evolved during the reaction.

The product layers were separated to give 345.6 grams of lower layer, which analyzed as 96.0% dioxene and 2.3% dioxane, and 169.5 grams of upper layer, which analyzed as 6.0% dioxene, 0.9% *p*-dioxane, 84.5% H_2O, 1.5% 2-*p*-dioxanone and 7.1% diethylene glycol. Analyses were by vapor phase chromatography except the water analysis which was done by the ASTM azeotropic method (*1*). The vapor phase chromatographic analyses were run on a column packed with 10% dichloromethyl diphenyl oxide–diethylene glycol adduct on Chromosorb WAW, 60 to 80 mesh support using an F and M Model 300 gas chromatograph. The reaction residue was filtered, and 415.0 grams of diethylene glycol (b.p. 105–7°/1.1 mm.) were recovered by distillation. The conversion was 57.5% with a 79.2% yield of dioxene of 96% purity.

The dioxene was purified as follows: It was washed twice with 10% of its volume of 30% NaOH and then distilled on a 6-foot × 1-inch column packed with ⅛ inch 0.095 gage stainless steel helices using a 10 to 1 reflux ratio. Distillation gave a small amount of low-boiling material (8.8% of the charge) followed by distillation of dioxene (b.p. 93-5° C.). A 67.5% yield of dioxene of 99% purity was obtained.

Samples of dioxene were checked for peroxide content by a polarographic method over a 3-year storage period. There was no evidence of peroxide in any of the samples.

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Chlorination of Butanone

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The chlorination of butanone was investigated. Mono- and dichloro isomers are separated by vapor-phase chromatography and identified by NMR spectroscopy. The infrared spectra of the chlorobutanones in the C-Cl stretching frequency region (670 to 800 cm.$^{-1}$) is presented as a convenient method of identifying specific isomers.

A USEFUL intermediate in the preparation of a variety of heterocycles (*5, 11*) is 3-chloro-2-butanone. However, an attempt to prepare 4,5-dimethyl-2-aminothiazole from this ketone by standard procedures (*1, 3*) resulted in an intractable mixture of isomers, from which the desired heterocycle was obtained in low yield. Apparently the starting ketone was impure. The chemical literature contains numerous references to the preparation of 3-chlorobutanone by the direct chlorination of butanone (*2, 6, 8-10, 12, 13*). In these methods, purification and separation of the mono- and dichloro isomers is achieved by fractional and steam (*4*) distillation, and identification is often based on the preparation of known derivatives from individual fractions (*2, 13*).

The authors have reinvestigated a number of the methods previously described for the preparation of pure 3-chloro-2-butanone and made several modifications. Vapor-phase chromatography showed that some methods gave mixtures of up to five products and that these, in our hands, could not be satisfactorily separated by fractional distillation (*15*). All the mono- and dichloro products were separated by condensing the fractions from the VPC column. Each fraction was checked for homogeneity by rechromatographing through a second column of different polarity. Subsequent identification of the products was made on the basis of analysis and NMR spectroscopy.

The mono- and dichlorobutanones had distinguishable infrared adsorption spectra (liquid film) in the C-Cl stretching frequency region (670 to 800 cm.$^{-1}$, see Figure 1). Once all the products had been identified, this proved the most rapid and convenient method of classifying the VPC fractions.

The NMR spectra of the chlorobutanones were simple, and generally all features were readily identified. In the case of 3,3-dichlorobutanone (*14*) some uncertainty exists over the assignment of the C_4-proton signal, but this did not prevent the identification of each isomer. An unexpected anomaly was found in the spectrum of 1,3-dichlorobutanone. The methylene protons on C_1 appear as two distinct signals ($\tau = 5.64$; 5.70), each integrating for one proton. The steric hindrance to free rotation about the C_1-C_2 bond observed in molecular models suggests that the two signals may arise from rotational conformations present in the 1,3-dichlorobutanone but not in the 1,4-isomer. Alternatively, the effect may be caused by the nearness of the asymmetric C_3 atom. Compounds containing a methylene group adjacent to an asymmetric center exhibit nonequivalent protons, and in this case only a carbonyl function intervenes.

Table I. Chloro Derivatives of Butanone

Product	Method[a] and Yield[b]						NMR[c] Signals from Protons at:			Ultraviolet[d]	
	A	B	C	D	E	F	C-1	C-3	C-4	$\lambda_{max.}$	mμ(log ε)
1-Chloro-	28	10		9	6	5	6.05	7.39q (7)	8.90t (7)	283	(1.60)
3-Chloro-	49	27	36	88	81	90	7.72	5.80q (6)	8.45d (6)	291	(1.55)
1,1-Dichloro-			3				4.24	7.13q (7)	8.87t (7)	290	(1.10)
1,3-Dichloro-	20	63	10		2	4	5.64 5.70	5.34q (7)	8.35d (7)	289	(1.51)
1,4-Dichloro-	2						6.00	6.29t (6)	6.92t (6)	275	(1.58)
3,3-Dichloro-			51				7.47[e]		7.85[e]	292	(1.64)
Unidentified	1			3	11	1					

[a] See experimental section for description of methods A to F. [b] Yields are not percentage of theory, but represent the proportion of product isolated. [c] Proton magnetic resonance spectra were measured in carbon tetrachloride using a Varian A-60 spectrometer operating at 60 mc./sec. Chemical shifts are recorded on the τ scale relative to an internal tetramethylsilane reference. Unless otherwise indicated, values refer to singlet absorptions; for multiple signals the following abbreviations have been used; d = doublet; t = triplet; q = quartet; spin-spin coupling values (J) are in parenthesis; values are in cycles per sec. (500 c.p.s. scale). [d] Spectra measured in 95% ethanol using a Cary Model 14 recording spectrometer. [e] Assignment uncertain.