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.

ACKNOWLEDGMENT

The authors express their appreciation to Floyd L. Beman, who developed the vapor phase chromatographic analytical procedure and the purification method.

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RECEIVED for review December 22, 1966. Accepted April 7, 1967.

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 (τ = 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

	Method[a] and Yield[b]						NMR[c] Signals from Protons at:			Ultraviolet[d]	
Product	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.

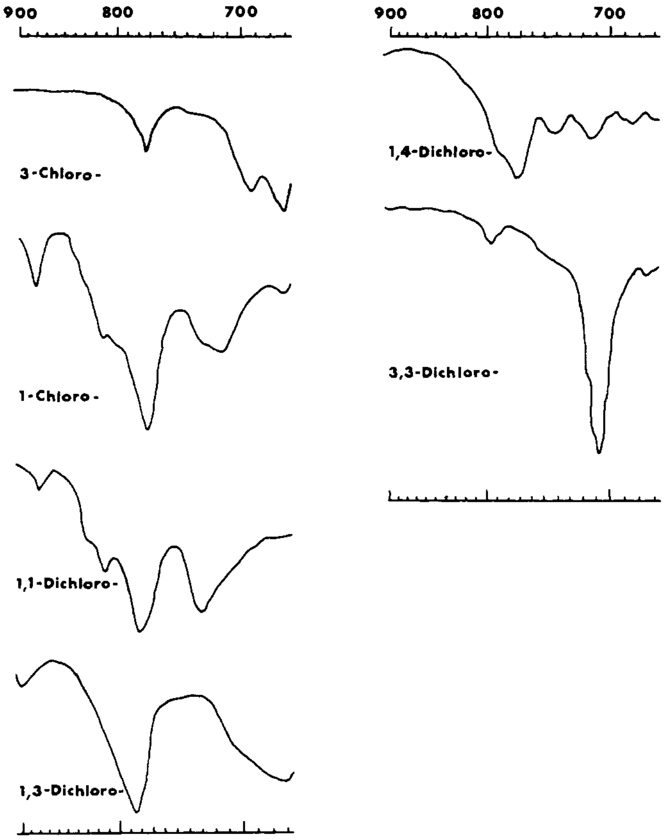

Figure 1. Infrared spectra (liquid film) of mono- and dichlorobutanones
Perkin-Elmer Model 137 spectrophotometer

EXPERIMENTAL

Chlorinations were carried out by the methods and variations listed below. In working up the reaction products, the water-insoluble part was washed with water and sodium carbonate solution until neutral to Congo red, dried ($MgSO_4$), and distilled once at atmospheric pressure without fractionation. The mono- and dichlorobutanones were separated by vapor-phase chromatography using an F. and M. Model 500 programmed temperature gas chromatograph and a 6-foot Carbowax column, temperature-programmed when advantageous. The yield of each product was estimated by measuring the area under the VPC signal.

Chlorinations in Aqueous Solution. The method of Kling (*9*) was used with the following variations: (A) The reaction temperature was not allowed to exceed 40° C., and (B) the maximum reaction temperature was 60° C.

Chlorinations with Sulfuryl Chloride. These were based on earlier methods employed for the chlorination of 2-pentanone (*1, 3, 14*). The following variations were introduced: (C) sulfuryl chloride (2 equiv.) added to butanone (1 equiv.) at 0° to 5° C.; (D) sulfuryl chloride (1 equiv.) added to butanone (10 equiv.) at reflux temperature; (E) sulfuryl chloride (1 equiv.) added to butanone (1 equiv.) in *n*-pentane solvent (5 volume dilution) at 25° C.; (F) as for E, but at 0° C. For our purposes, method D or F was convenient for the preparation of pure 3-chlorobutanone in 75 to 80% yields, using a preparative gas chromatograph. The percentage distribution of products by the various methods, and spectral characteristics of the six different products obtained, are summarized in Table I.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation via its Undergraduate Research Participation Program.

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RECEIVED for review December 23, 1966. Accepted February 19, 1967

Synthesis and Characterization of Several Schiff Bases

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The reaction of a substituted aniline with an aldehyde has been used to prepare several new compounds. Yields, melting points, and elemental analyses are given.

COMPOUNDS of the structure R—CH=N—R′ have been prepared by reacting *p*-(acetoxymercuri) aniline, 2,4,5-trichloroaniline, 3-methylthioaniline, and *p*-iodoaniline with various aldehydes in benzene as described by a published procedure (*1*). Table I summarizes the yield, melting point, and elemental analysis of the compounds prepared. The infrared spectra were consistent in each instance with the desired structure. All starting materials were used as obtained from commercial sources.

EXPERIMENTAL

A benzene solution of aldehyde (0.2 mole) and substituted aniline (0.2 mole) were refluxed until as close to the theoreti-