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β,β-Dichlorovinyl Ketones. I. Effect of Structure on Synthesis and Configuration[1]

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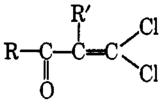
Spectral and other physical properties of methyl β,β-dichlorovinyl ketone (I), β,β-dichloroacrylophenone (II), methyl α-methyl-β,β-dichlorovinyl ketone (III), and α-methyl-β,β-dichloroacrylphenone (IV) indicated that I and II are coplanar (*s-trans* and *s-cis*, respectively) and highly conjugated, while the corresponding α-methyl-substituted compounds, III and IV, are noncoplanar and unconjugated. Synthesis of the latter two compounds, which are new, presented unusual difficulty, probably because of steric factors. A new and useful method was developed, involving synthesis and oxidation of the corresponding dichlorovinylcarbinol.

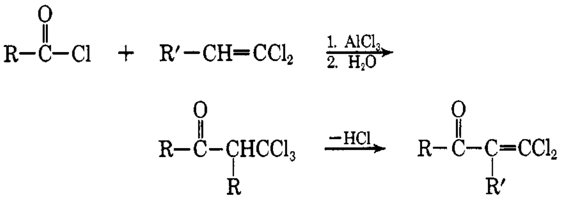
β,β-Dichlorovinyl ketones are compounds of considerable interest, because of their polyfunctionality and high degree of reactivity. Several compounds of this class have been prepared in the past by several workers, using several different methods, but there has been relatively little information on the reactions of such compounds. A program was therefore undertaken in these laboratories to investigate their chemistry further.

In this paper we describe the synthesis and structural properties of four β,β-dichlorovinyl ketones of varied structure: 4,4-dichloro-3-buten-2-one (I), 3,3-dichloroacrylophenone (II), 4,4-dichloro-3-methyl-3-buten-2-one (III), and 2-methyl-3,3-dichloroacrylophenone (IV).



I, R = CH_3; R′ = H
II, R = C_6H_5; R′ = H
III, R = CH_3; R′ = CH_3
IV, R = C_6H_5; R′ = CH_3

The synthesis of ketones I and II had been previously described, involving Darzens acylation of 1,1-dichloroethylene, followed by dehydrochlorination (sequences 1a and b).[3-7] The earlier procedures were improved, primarily by the use of carbon tetrachloride or methylene chloride as solvent during the reaction, and yields of 80–90% of theoretical were readily achieved for ketones I and II.



$$R-\overset{O}{\overset{\|}{C}}-Cl + R'-CH{=}CCl_2 \xrightarrow[2.\ H_2O]{1.\ AlCl_3} R-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}}HCCl_3 \xrightarrow{-HCl} R-\overset{O}{\overset{\|}{C}}-\underset{R'}{\underset{|}{C}}{=}CCl_2 \quad (1)$$

a, R = CH_3; R′ = H
b, R = C_6H_5; R′ = H
c, R = CH_3; R′ = CH_3

The corresponding α-methyl ketones (III and IV) proved to be difficult to prepare by this method. The reaction of 1,1-dichloropropene, with acetyl chloride (sequence 1a) gave III in a yield of only 17%. It was noted that dehydrochlorination of the intermediate trichloro ketone was unusually difficult in this case, requiring heating at 200° or treatment with base for a considerable time, rather than the very mild heating or steam distillation sufficient in other cases. With triethylamine in ligroin, however, the dehydrochlorination proceeded well, and the difficulty in the synthesis appeared to be due to side reactions during the condensation. Assignment of structure III to the product was supported by the elemental analysis, the infrared spectrum (discussed below), and the formation of several derivatives, including the 2,4-dinitrophenylhydrazone and various substitution products described elsewhere.[8,9]

Another synthetic approach to III investigated was free-radical-type addition of bromotrichlorometh-

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[1] Most of this material was taken from the Ph.D. thesis of R. A. Sanchez, Kansas State University, 1963, and was presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964.

[2] (a) Author to whom inquiries may be addressed: Department of Chemistry, University of Missouri, Columbia, Mo. (b) Deceased Feb 10, 1960.

[3] I. Heilbron, E. R. H. Jones, and M. Julia, *J. Chem. Soc.*, 1430 (1949).

[4] O. Wichterle and J. Vogel, *Chem. Listy*, **48**, 1225 (1954); *Chem. Abstr.*, **49**, 9326 (1955).

[5] M. Julia, *Ann. Chim.* (Paris), [12] **5**, 595 (1950).

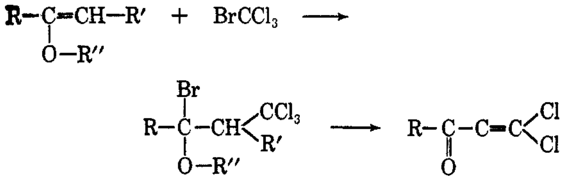
[6] L. I. Zakharkin, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 313 (1956); *Chem. Abstr.*, **50**, 15492 (1956).

[7] A. N. Nesmeyanov, O. A. Reutov, and A. S. Gudkove, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 260 (1961); *Chem. Abstr.*, **55**, 23335 (1961).

[8] R. L. Soulen, D. G. Kundiger, S. Searles, and R. A. Sanchez, *J. Org. Chem.*, **32**, 2661 (1967).

[9] R. A. Sanchez and S. Searles, paper in preparation.

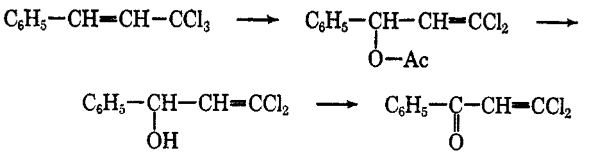
ane to 2-buten-2-yl acetate, followed by hydrolysis and dehydrochlorination (sequence 2b), which is analogous to a previous synthesis of I from bromotrichloromethane and isopropenyl acetate (sequence 2a).[10] Ketone III was obtained by this route in moderate yield, unusual difficulty being observed again in the dehydrochlorination step. The analogous reaction of propiophenone enol acetate (sequence 2c) gave none of the expected ketone IV, but the latter was obtained in about 6% yield from the similar addition of bromotrichloromethane to 1-ethoxy-1-phenylpropene, the adduct being decomposed thermally (sequence 2d). In each of these cases there was incomplete formation of the intermediate addition compound, even after long reaction times, and in the presence of free-radical catalysts or ultraviolet light.



(2)

a, R = CH_3; R′ = H; R″ = Ac
b, R = CH_3; R′ = CH_3; R″ = Ac
c, R = C_6H_5; R′ = CH_3; R″ = Ac
d, R = C_6H_5; R′ = CH_3; R″ = C_2H_5

A new synthetic approach was then developed, involving oxidation of the corresponding alcohol. For ketone II this was carried out by (1) the facile S_N2 displacement reaction of sodium acetate with 3,3,3-trichloro-1-phenylpropene in acetic acid,[11] forming 1,1-dichloro-3-phenyl-3-allyl acetate; (2) saponification at room temperature to the corresponding alcohol; and (3) oxidation with chromic anhydride or N-bromosuccinimide to the desired ketone (sequence 3). Although the over-all yield of only 26% makes this a less practical synthesis for ketone II than the Darzens method, it was a useful prototype for a very successful synthesis of ketone IV, which was carried out as follows: Wohl-Zielgler bromination of the readily available 1,1-dichloro-2-methyl-3-phenyl-1-propene (V) smoothly yielded the monobromide VI, which was hydrolyzed in a dilute base to the corresponding alcohol; oxidation by chromic anhydride in acetone then yielded the ketone IV in an over-all yield of 54% of theoretical (sequence 4).



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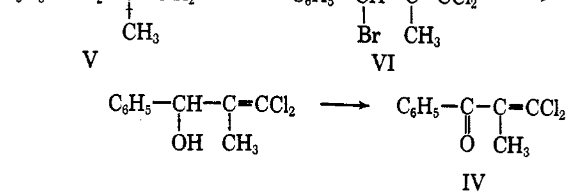

(4)

Attempted oxidation of V directly to IV by means of selenium dioxide, chromium trioxide, and buffered permanganate was not successful. These difficulties may be due to severe steric hindrance of the crowded methylene group in V toward these bulky reagents.

Properties and Configuration

The unusual difficulty of dehydrochlorination of the α-methyl-β,β,β-trichloro ketone intermediates may be attributed to decreased resonance stabilization of the resulting β-methyl ketones, as a result of steric inhibition to coplanarity. Stuart-Briegleb molecular models and van der Waals overlap diagrams (Figure 1) indicate considerable strain for coplanar configurations of both α-methyl ketones III and IV, and the spectral data also indicates noncoplanarity of these compounds.

This situation is in marked contrast to that for the ketones I and II, having no α-alkyl substituent, for which molecular models and van der Waals diagrams (Figure 1) show relatively little steric hindrance to coplanarity. The C=O and C=C frequencies in I and II both show relatively long wavelengths (Table I), as expected from the conjugation,[13] and the characteristic vinylic C—Cl stretching vibration is shifted toward shorter wavelength relative to its position at 13.05 μ in 1,1-dichloroethylene,[14] as expected for resonance delocalization involving canonical forms of the type $Cl^+{=}C{-}C{=}CO^-$.

TABLE I
INFRARED SPECTRA OF β,β-DICHLOROVINYL KETONES

Compd	Wavelength, μ $\nu_{C=O}$	$\nu_{C=C}$	ν_{CCl}[a]	$\nu_{=CH}$[b]
$Cl_2C{=}CHCOCH_3$ (I)	5.88	6.35	12.0	10.80
$Cl_2C{=}CHCOC_6H_5$ (II)	6.00	6.40	11.9	10.67
$Cl_2C{=}C(CH_3)COCH_3$ (III)	5.86	6.20	12.8	...
	5.95	6.30		
$Cl_2C{=}C(CH_3)COC_6H_5$ (IV)	5.97	6.19	12.5	...

[a] Assignment confirmed in I and II by absence of such a band in the spectra of the corresponding diamino and diphenoxy substitution products; to be described in succeeding papers. [b] Assignment confirmed by presence of similar band in the spectrum of each of such substitution products.

As shown in Table II, comparison of the ultraviolet spectra of I and II with those of 3-buten-2-one and 4-chloro-3-buten-2-one indicate that the β-vinylic chlo-

TABLE II
ULTRAVIOLET SPECTRA OF SOME VINYL KETONES[a]

Compd	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$
$CH_2{=}CHCOCH_3$[b]	210	7.0
$ClCH{=}CHCOCH_3$[b]	228	10.0
$Cl_2C{=}CHCOCH_3$ (I)	241	11.9
$Cl_2C{=}CHCOC_6H_5$ (II)	263	14.3
$Cl_2C{=}C(CH_3)COCH_3$ (III)	245	4.6
$Cl_2C{=}C(CH_3)COC_6H_5$ (IV)	253	13.4

[a] All spectra are in 95% ethanol solvent. [b] Reference 5.

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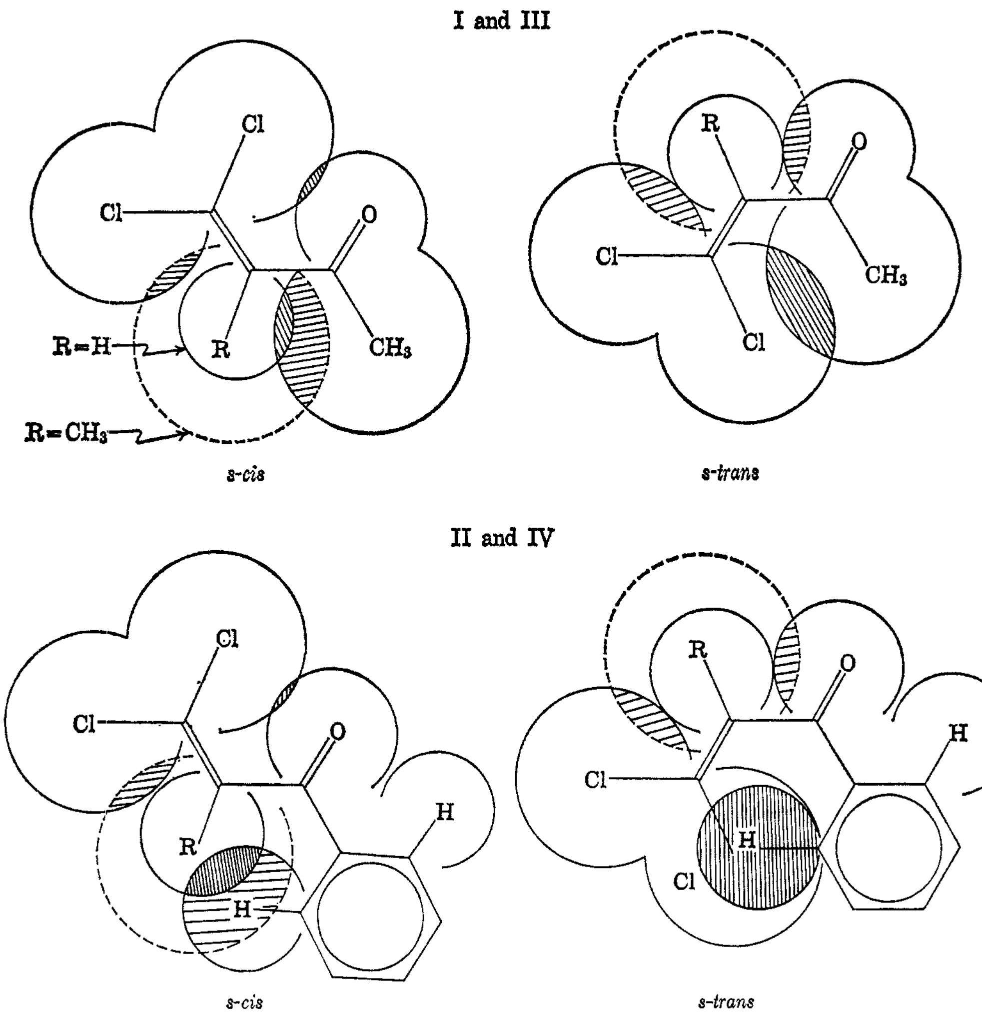
[10] M. S. Kharasch, E. Simon, and W. Nudenberg, *J. Org. Chem.*, **18**, 328 (1953).

[11] Related examples of this reaction with trichloroalkenes have been described.[12]

[12] A. N. Nesmeyanov, R. K. Freidlina, L. I. Zakharkin, and A. B. Beyavski, *Zh. Obshch. Khim.*, **26**, 1070 (1956); *Chem. Abstr.*, **50**, 16658 (1956).

[13] J. Dabrowski and J. Terpinski [*J. Org. Chem.*, **31**, 2159 (1966)] have recently reported very similar positions for these bands in 4-chloro-3-buten-2-one and deuterium derivatives.

[14] P. Joyner and G. Glockler, *J. Chem. Phys.*, **20**, 302 (1952).



Compd	Overlap (A) cis	Overlap (A) trans
I	0.6	1.0
II	0.6	2.4
III	1.8	2.2
IV	2.3	3.6

Figure 1.—van der Waals diagrams and measured (radially within shaded areas) overlaps. Molecular dimensions and van der Waals radii were taken from L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 138, 224, and 260. Angles used were Cl—C=C, 123°; H—C=C, 122°; C—C=C, 125°; C—C=O, 120°.

rine atoms cause considerable bathochromic shift and increase in intensity in these compounds, again indicating essentially coplanar systems with a high degree of resonance.[15]

The question of which coplanar conformation (*s-trans* or *s-cis*) compounds I and II may be in was considered. The van der Waals diagrams (Figure 1) and molecular models for the phenyl ketone II indicated a clear preference for the *s-cis* conformation, which would be slightly twisted from coplanarity. In the *s-trans* conformation, on the other hand, an angle of about 60° between the planes of the phenyl and the dichloromethylene groups would be required.

For methyl ketone I, however, the models and van der Waals diagrams indicated that the *s-trans* form should be only slightly twisted from coplanarity, while the *s-cis* form would be coplanar and strainless. This situation for I, plus the possibility of direct-field attractive forces between the oxygen atom and a chlorine atom, due to resonance delocalization,[16] would tend to make the *s-trans* form less favored than is generally considered to be the case with α,β-unsaturated ketones.[16-18] A similar situation with 4-chloro-3-buten-2-one has been studied recently by Dabrowski and Terpinski, who concluded that both conformers were present, because of the double peaks observed for the C=O and C=Cl stretching vibrations.[13]

The spectrum of 4,4-dichloro-3-buten-2-one (I) also seems to contain a split carbonyl peak, the minor being at higher wavelength than the major band, in contrast to the situation with 4-chloro-3-buten-2-one. Since this minor band is at exactly one-half the wavelength of the very strong C—Cl stretching fundamental, it seems likely that it is the first overtone of the latter. No splitting was observed in the CCl ab-

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[15] K. Bowden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

[16] Direct field interaction between the oxygen atom and the α-carbon atom has been observed in the Raman spectra of simple α,β-unsaturated ketones having *s-cis* conformation, by K. Noak and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

[17] R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951).

[18] R. Mecke and K. Noak, *Chem. Ber.*, **93**, 210 (1960).

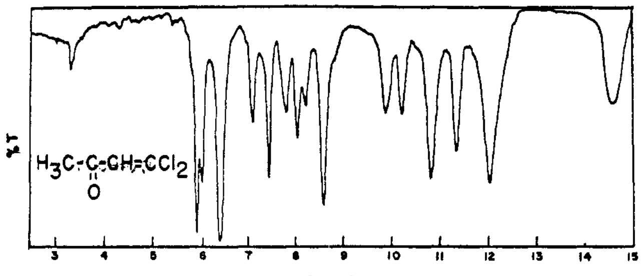

Figure 2.—Infrared spectrum of 4,4-dichloro-3-buten-2-one (thin film).

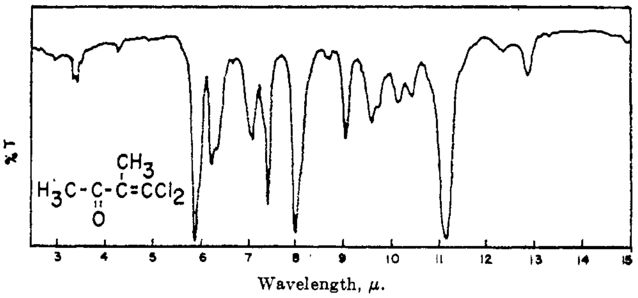

Figure 3.—Infrared spectrum of 4,4-dichloro-3-methyl-3-buten-2-one (thin film).

sorption, and the rest of the spectrum (Figure 2) seems too simple for a mixture of two species in at all similar proportions. The very narrow singlet nature of the methyl peak in the nmr spectrum is additional evidence for the conformational homogeneity of I.

The convenient correlation between conformation and relative positions and intensities of the C═C and C═O infrared absorptions deduced for alkyl-substituted α,β-unsaturated carbonyl compounds[18-21] cannot be applied here, since the β-chlorine atoms provide considerable additional conjugation, but the dipole moment offers a practical method of distinguishing between the *s-trans* conformation and the *s-cis* conformation.

The dipole moment of compound I was determined to be 2.4 D., a value which appears consistent only with the *s-trans* conformation. This value may be compared with the moment of 2.98 D. for methyl vinyl ketone, which is known to be *s-trans*.[22] The difference between this and the moment for the *s-trans* form of I, 0.6 D., would be approximately equal to the resultant vector of the two CCl moments opposing the carbonyl bond moment. This vector would be equal to the CCl moment itself on the assumption of 120° bond angles, and the resulting value of 0.6 D. for it seems not reasonable, in view of the decrease of the CCl moment with increasing π-orbital overlap, from 2.05 D. in ethyl chloride to 1.44 D. in vinyl chloride and 0.44 D. in chloroacetylene.[23] On the other hand, mesityl oxide, for which an *s-cis* configuration has been deduced,[24] shows a dipole moment of about 2.8 D., 0.4 D. higher than that for compound I; and substitution of chlorine atoms for the β-methyl groups would result in considerable further increase, since in this conformation the vector of the CCl moments would be additive with the carbonyl moments. Thus the observed moment for I is much too low to be explained in terms of the *s-cis* conformation. Apparently the enhanced resonance stabilization of the *trans* conformation compensates for the slight noncoplanarity that probably occurs, and electrostatic field interaction between the dipole extremities is too weak to have much influence on the conformational stability.

As shown in Tables I and II, the presence of an α-methyl substituent in the β,β-dichlorovinyl group was found to cause significant changes in the infrared and ultraviolet spectra, indicating noncoplanarity of the C═C—C═O system. The positions of the CCl vibration in III and IV approached that found in unconjugated 1,1-dichlorovinyl compounds, and the intensities of the C═C vibrations were very much less than those of the C═O vibrations. The carbonyl absorption band in III (Figure 3) shows a low-frequency shoulder at 5.95 μ, which cannot be ascribed to an overtone or to Fermi resonance, since there is no significant absorption in the 12-μ region. This, together with the doublet nature of the C═C absorption, suggests that the material is not conformationally homogenous, consisting of a mixture of the twisted quasi-*trans* and quasi-*cis* forms. As expected from this situation, both of the methyl peaks in the nmr spectrum appear as doublets.

In the ultraviolet spectrum, the bathochromic effect of α-methyl substitution was observed to be 4 mμ for III and −10 for IV, in contrast to the value of 10 mμ predicted by Woodward's rules.[24] The effect of the α-vinylic methyl group to cause a decreased extinction coefficient and a lower than normal bathochromic (or even hypsochromic) effect for a methyl group is clearly indicative of noncoplanarity.[25,26] It was further noted that the nmr chemical shift for the carbonyl methyl group in III was 0.07 ppm further downfield than for I, as might be anticipated from the decreased conjugation in III.

The semiempirical equation (5) of Braude, Sondheimer, and Forbes[27] relates the degree of noncoplanar-

$$\cos^2\theta = \frac{\epsilon}{\epsilon_0} \qquad (5)$$

ity of a conjugated system to the extinction coefficients of the nonplanar compound (ϵ) and a corresponding coplanar structure (ϵ_0). Insertion of the spectral data for I and III (Table I) gives a value for θ of 52°, the distortion of III from a coplanar (and presumably *s-trans*) conformation. This is similar in magnitude to that observed in the 2,6-disubstituted acetophenones, to which the Braude relationship (5) has been applied with apparent success.[27]

The Braude equation (5) cannot be readily applied to the case of compound IV, because of the undoubted coplanarity of the carbonyl and phenyl groups and the possibility of a different interaction between the latter two when the dichlorovinyl–carbonyl interac-

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(19) K. Noak and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

(20) R. Mecke and K. Noak, *Spectrochim. Acta*, **12**, 391 (1958).

(21) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(22) G. K. Estok and J. S. Denn, *J. Am. Chem. Soc.*, **77**, 4769 (1955).

(23) C. P. Smyth and K. B. McAlpine, *ibid.*, **56**, 1967 (1934).

(24) R. B. Woodward, *ibid.*, **64**, 76 (1947).

(25) E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Vol. I, Academic Press Inc., New York, N. Y., 1955, pp 131-193.

(26) An analogous situation exists with β-1-methylionone, which has been discussed by E. A. Braude and E. R. H. Jones, *J. Am. Chem. Soc.*, **72**, 1041 (1950).

(27) E. A. Braude, F. Sondheimer, and W. F. Forbes, *Nature*, **173**, 117 (1954).

tion varies. The ultraviolet spectrum of IV is shifted toward that of acetophenone [λ_{max} 241 mμ (EtOH), (ϵ_{max} 13,300)],[28] and it thus appears that the α-methyl substitution here disrupts the cross-conjugation which may occur in compound II, by isolating the dichlorovinyl function from the remaining system. The infrared spectrum of IV is entirely consistent with this interpretation, and Briegleb models and van der Waals diagrams indicate much prohibitive strain for either coplanar form of this compound.

In summary, the evidence indicates that there is a wide variation of configuration among these four β,β-dichlorovinyl ketones, I being *s-trans* and coplanar, II being *s-cis* and coplanar, III being a mixture of quasi-*trans* and quasi-*cis*, and IV being definitely noncoplanar with respect to the vinyl and carbonyl groups, although undoubtedly coplanar with respect to the phenyl and carbonyl groups.

These differences of configuration may be expected to be of some importance with regard to chemical reactions. Thus, the failure of the intermediate trichloro ketone of sequence 1c to undergo the facile and exothermic dehydrochlorinations typical of sequences 1a and 1b may be explained in terms of the lower resonance stabilization of ketone III relative to I and II. These differences cannot be adequately explained simply on the basis of the added moderate steric hindrance of the methyl group. Furthermore, one might anticipate that compounds III and IV would be less susceptible to Michael-type additions. Subsequent papers will elucidate this point.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. Infrared spectra were obtained with a Model 137 or 237 Perkin-Elmer spectrophotometer, and ultraviolet spectra were obtained on a Cary Model 11 spectrophotometer. A Varian Model A-60 spectrophotometer was used for nmr spectra, and molecular weights were determined with a Mechrolab model 301A osmometer. Elemental analyses were performed by Weiler and Straus, Oxford, England, and by Galbraith Laboratories, Knoxville, Tenn.

4,4-Dichloro-3-buten-2-one (I).—The method of Heilbron, Jones, and Julia,[3] with the modifications of using carbon tetrachloride as solvent (200 ml to suspend 3.0 moles of aluminum chloride before addition of acetyl chloride and subsequently vinylidene chloride), efficient stirring, and maintenance of temperature at 25° or less throughout the reaction, gave I in 87% yield: bp 64° (22 mm); $n^{20}\text{D}$ 1.4940; 2,4-dinitrophenylhydrazone mp 196–197° [lit.[3] bp 58° (15 mm); $n^{20}\text{D}$ 1.4940; 2,4-dinitrophenylhydrazone mp 195°]; nmr (25% solution in CCl_4) δ 2.29 (singlet, area 3), 6.61 (singlet, area I). The infrared spectrum is given in Figure 3.

1,1-Dichloro-3-acetoxy-3-phenylpropene.—The procedure used was similar to that of Nesmeyanov and co-workers for related reactions.[11] A solution of 16.9 g of 3,3,3-trichloropropenylbenzene,[29] 9.7 g of anhydrous sodium acetate, 0.7 g of potassium iodide, 5 ml of acetic anhydride, and 45 ml of acetic acid was heated under reflux for 1.5 hr and was then poured into ice-water and extracted with methylene chloride. The extract was dried over sodium sulfate and distilled, to yield 15.2 g (81%) of the title compound, bp 81–86° (0.02 mm), with a pure, redistilled sample having bp 86° (0.02 mm), $n^{19}\text{D}$ 1.5378. This material was identical in infrared spectrum, boiling point, and refractive index with an authentic, analytically pure sample of 1,1-dichloro-3-acetoxy-3-phenylpropene prepared by acetylation of 3,3-dichloro-1-phenyl-2-propenol.[12]

3,3-Dichloro-1-phenyl-2-propenol.—A solution of 15.2 g of the above acetate ester and 4.1 g of potassium hydroxide in 70 ml of ethanol was allowed to stand at room temperature for 15 hr and was then poured into ice–water. The precipitated solid was recrystallized from ligroin (bp 60–70°) yielding 10.2 g (81%) of fine, white needles, mp 57–59° (lit.[30] mp 57–58°).

3,3-Dichloroacrylophenone (II). A.—The method of Julia[5] was followed, with the modification of using methylene chloride as a diluent during the reaction. The yield on a 0.8-mole scale experiment was 79%: bp 140–150° (14 mm); $n^{20}\text{D}$ 1.5941; 2,4-dinitrophenylhydrazone mp 168–169° [lit.[5] bp 82° (0.2 mm); $n^{19}\text{D}$ 1.5936; 2,4-dinitrophenylhydrazone mp 170–171°]; nmr (25% solution in CCl_4) δ 7.16 (singlet, area 1), 7.33–7.57 (multiplet, area 3), 7.75–7.95 (multiplet, area 2).

B.—A solution of 2.45 g of 3,3-dichloro-1-phenyl-2-propanol, 1.22 g of chromic anhydride, 5 ml of water, and 0.05 ml of sulfuric acid in 20 ml of acetic acid was heated at 50–60° for 15 min, poured into ice–water, and after recrystallization with sodium carbonate, extracted with chloroform. The dried extract was distilled to give 0.95 g (39%) of slightly impure II: bp 79–82° (0.01 mm), $n^{19}\text{D}$ 1.5743.

C.—A solution of 5.35 g of 3,3-dichloro-1-phenyl-2-propanol, 4.70 g of N-bromosuccinimide, and 0.3 g of benzoyl peroxide in 100 ml of carbon tetrachloride was heated at the boiling point for 0.5 hr and then processed in the usual manner to give 2.13 g (40%) of II: bp 76–78° (0.01 mm), $n^{19}\text{D}$ 1.5923.

4,4-Dichloro-3-methyl-3-buten-2-one (III). A.—A solution of 121 g of 2-acetoxy-2-butene (prepared by the method of Hauser and collaborators[31]) and 1000 g of bromotrichloromethane was irradiated for 60 hr under a nitrogen atmosphere with a Sperti ultraviolet lamp. After removing the acetyl bromide formed by distillation, the residue was steam distilled and the aqueous layer of the distillate was separated and extracted with chloroform, with the extracts added to the organic layer, which was then dried over sodium sulfate, filtered, and distilled, to give 80.1 g (42%) of 4,4,4-trichloro-3-methyl-2-butanone: bp 84–87° (16 mm), d^{27}_4 1.323, $n^{20}\text{D}$ 1.4790, MR = 39.8 (calculated 39.4), infrared 5.80 μ (strong), as expected for a saturated ketone.

Thirty grams of 4,4,4-trichloro-3-methyl-2-butanone was heated with saturated aqueous potassium carbonate solution at about 60° for 5 hr, followed by separation of the layers and extraction of the aqueous layer with chloroform. The chloroform extracts and the organic layers were combined, dried, and distilled to give 8.2 g (33% yield, 52% conversion) of III: bp 64–69° (15 mm), d^{27}_4 1.253, $n^{20}\text{D}$ 14822, MR = 34.4 (calculated for III, 32.4), nmr (25% in CCl_4) two equal-intensity doublets (J = 1 cps) at δ 1.98 and 2.35.

Anal. Calcd for $C_5H_6Cl_2O$: C, 39.28; H, 3.93; Cl, 46.37. Found: C, 39.70; H, 4.11; Cl, 46.19.

The 2,4-dinitrophenylhydrazone of III was prepared and recrystallized from ethanol–chloroform: mp 198–198.5° (with 2,4-dinitrophenylhydrazine mp 172–174°).

Anal. Calcd for $C_{11}H_{10}Cl_2N_4O_4$: C, 39.70; H, 3.02; N, 16.85. Found: C, 39.89; H, 3.03; N, 17.08.

Further distillation of the product from the potassium carbonate treatment gave 6.2 g of an intermediate fraction, bp 69–75° (15 mm), $n^{20}\text{D}$ 1.4820, and 10.4 g (35%) of recovered 4,4,4-trichloro-3-methyl-2-butanone, bp 75–84° (15 mm), $n^{20}\text{D}$ 1.4790.

B. To a cooled, well-stirred solution of 19.6 g of acetyl chloride in 200 ml of methylene chloride was added 33.3 g of anhydrous aluminum chloride, followed by dropwise addition of 33.3 g of 1,1-dichloropropene. After being stirred at 0° for 1 hr, the reaction mixture was allowed to warm to room temperature during 3 hr and finally heated under reflux for 15 min. It was poured on ice, and the lower layer was separated and combined with methylene chloride extracts (two of 50 ml) of the upper aqueous solution. The combined, nonaqueous liquid was dried over sodium sulfate, filtered, and distilled to give 8.0 g (17%) of crude 4,4,4-trichloro-3-methyl-2-butanone: bp 93–117° (18 mm), $n^{20}\text{D}$ 1.484–1.487.

Heating the above product at 200° for 30 min caused a rigorous evolution of hydrogen chloride. The black residue was distilled under reduced pressure to give 3.5 g (9% over-all yield) of III: bp 66–69° (16 mm), $n^{20}\text{D}$ 1.4822. Use of a high temperature for dehydrohalogenation resulted in a lower yield of III.

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When the aluminum chloride condensation of acetyl chloride and 1,1-dichloropropene in methylene chloride was carried out entirely at 0–5° during 15 hr, and the trichloro ketone product was dissolved in a solution of 2 molecular equiv of triethylamine in ligroin and allowed to stand at room temperature for 15 hr, 5.8 g (17% over-all) of III was obtained: bp 65–66° (15 mm).

1-Ethoxy-1-phenylpropene.—To a solution of 30.0 g of anhydrous hydrogen chloride in 150 ml of absolute ethanol, cooled in an ice bath, 220 g of ethyl orthoformate was added, followed at once by 153 g of propiophenone. After the initial exothermic reaction, which was controlled by the ice bath, had subsided, the solution was allowed to warm to room temperature. After standing for 3 days, during which a deep purple color developed, it was distilled to give 137 g (81%) of 1-ethoxy-1-phenylpropene: bp 96–99° (15 mm), $n^{19}\mathrm{D}$ 1.5237 [lit.[32] bp 100–101° (16 mm), $n^{25}\mathrm{D}$ 1.5207–1.5210].

1-Methoxy-1-phenylpropene was prepared in an analogous manner: bp 88–92° (14 mm) [lit.[33] bp 96–98° (19 mm)].

1,1-Dichloro-2-methyl-3-phenyl-1-propene (V) was prepared by the aluminum chloride catalyzed condensation of 1,1,3-trichloro-2-methyl-3-phenyl-1-propene with benzene, according to the general procedure of Kundiger and Pledger:[34] bp 53–58° (0.03 mm), $n^{20}\mathrm{D}$ 1.5510 [lit.[35] bp 67–68.5° (0.25 mm), $n^{20}\mathrm{D}$ 1.5467].

1,1-Dichloro-2-methyl-3-bromo-3-phenylpropene (VI).—A mixture of 68.5 g of V, 62.3 g of N-bromosuccinimide, and 2 g of benzoyl peroxide in 600 ml of carbon tetrachloride was heated under reflux for 2 hr and then at 40° for 15 hr. After cooling, the mixture was filtered, and the filtrate distilled to yield 71.4 g (75%) of VI: b 93–111° (0.01 mm), $n^{19}\mathrm{D}$ 1.584–1.594, infrared strong bonds at 6.25 and 10.8–11.0 μ, characteristic of $C{=}CCl_2$. The compound was used for the following reaction without any further purification.

3,3-Dichloro-2-methyl-1-phenyl-2-propenol.—An emulsion of 50.9 g of VI in 500 ml of 5% sodium hydroxide containing about 5 g of Tide detergent to effect emulsification, was stirred rapidly for 2 days at room temperature and was then extracted with methylene chloride. The dried extracts were distilled to yield 29.6 g (75%) of the desired alcohol, bp 104–108° (0.05 mm), $n^{20}\mathrm{D}$ 1.5743, plus 2.6 g (6.6%) of a somewhat less pure fraction, bp 108–124° (0.05 mm), $n^{20}\mathrm{D}$ 1.5783. The infrared spectrum showed strong bands at 3.0 (OH) and at 6.25 and 10.8–11.2 μ ($C{=}CCl_2$).

3,3-Dichloro-2-methylacrylophenone (IV). **A.**—A solution of 77.6 g of 1-ethoxy-1-phenylpropene, 0.6 g of benzoyl peroxide, and 309 g of bromotrichloromethane was allowed to stand at room temperature for 20 hr, followed by heating on a steam bath for 4 hr. Distillation yielded 6.0 g (6%) of IV: bp 78–79° (0.05 mm); $n^{20}\mathrm{D}$ 1.5677; nmr (25% in CCl_4) a poorly resolved doublet (half-height width 2 cps) at δ 2.10 and a complex multiplet at 7.15–8.05, relative areas about 1:2.

Anal. Calcd for $C_{10}H_8Cl_2O$: C, 55.90; H, 3.76; Cl, 32.95; mol wt, 215. Found: C, 55.95; H, 3.75; Cl, 31.76; mol wt (osmometric in CCl_4), 213.

Similar irradiation of a solution of 1-methoxy-1-phenylpropene in carbon tetrachloride gave no appreciable reaction, although carbon tetrachloride had been used in reactions of this type,[10] and it was thought that the addition process might be more facile with it than with bromotrichloromethane because of decreased steric hindrance.

The general method of Kharasch and co-workers,[10] involving addition of trichloromethyl radical to an enol acetate, was unsuccessful. Propiophenone enol acetate, prepared by the method of Bedoukian[36] did not react appreciably with bromotrichloromethane upon heating at 100° for 3 days in the presence of benzoyl peroxide or 2,2′-azobis(isobutyronitrile).

B.—A modification of the oxidation procedure of Djerassi, Engle, and Bowers[37] was used on 3,3-dichloro-2-methyl-1-phenylpropenol. To a stirred solution of 16.5 g of this alcohol in 400 ml of acetone, maintained at 5–10°, a solution of 7.61 g of chromic anhydride in 30 ml of 25% aqueous sulfuric acid was added dropwise. Stirring was continued for 2 hr, as the temperature was allowed to rise slowly to 25°. Ice–water was added and the mixture extracted with methylene chloride. The extracts were washed successively with water, 10% sodium bicarbonate, and water and then were dried over sodium sulfate and filtered. Distillation of the filtrate gave 7.6 g (46%) of IV: bp 77–80° (0.04 mm), $n^{20}\mathrm{D}$ 1.5695. Its infrared spectrum was identical with that of the product described under A. Further distillation gave an additional 7.0 g (43%) of the product in somewhat less pure state: bp 80–89° (0.04 mm), $n^{20}\mathrm{D}$ 1.577–1.584.

Measurement of Dipole Movement of I.—The general method described by Smyth[38] was followed. Dielectric constants were measured on a Sargent chemical oscillometer, operating at 5 Mc, which was calibrated with 12 pure solvents (ε 2–80). Densities were determined on a Westphal balance. Solutions were prepared volumetrically in redistilled benzene. The sample of I used was redistilled through a fractionating column immediately before the determinations and had the following physical constants: bp 56–58° (14 mm), $n^{25}\mathrm{D}$ 1.4908, d^{25}_4 1.302.

The data obtained are given in Table III, where X_2 = mole fraction of solute in benzene, d = density, $\epsilon_{1,2}$ = dielectric constant, and $P_{1,2}$ = polarization of the solution indicated. The polarization of the solute in solution, $P_2 = (P_{1,2} - XP_1°)/X_2$, was extrapolated to zero concentration to give $P_2° = 149$. $P_1°$, the polarization of pure benzene, had the value 26.6. The dipole moment was calculated by the usual equation, $\mu = 0.0128\,(P_2° - \mathrm{MR_D})T$, where T = the absolute temperature and $\mathrm{MR_D}$ being 31, and had the value 2.41 D.

TABLE III

DIPOLE MOMENT DATA FOR I AT 25°

X_2	d, g/ml	$\epsilon_{1,2}$	$P_{1,2}$	P_2
0.5560	1.133	8.90	7.135	107.0
0.3195	1.031	5.78	58.15	125.5
0.1870	0.969	4.26	48.13	141.7
0.1020	0.924	3.20	38.60	145.0
0.5365	0.900	2.68	32.45	136.0
0.2747	0.888	2.47	29.55	134.7

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Registry No.—I, 5780-61-0; II, 10562-42-2; III, 10562-44-4; 2,4-dinitrophenylhydrazone of III, 10562-46-6; IV, 10562-47-7; VI, 10562-49-9; 4,4,4-trichloro-3-methyl-2-butanone, 10562-50-2; 3,3-dichloro-2-methyl-1-phenyl-2-propenol, 10562-51-3.

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