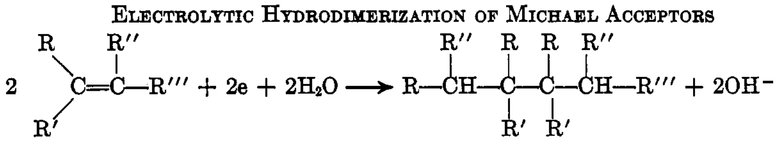
TABLE I

ELECTROLYTIC HYDRODIMERIZATION OF MICHAEL ACCEPTORS


$$2\ (R)(R')C{=}C(R'')\text{—}R''' + 2e + 2H_2O \longrightarrow R\text{—}CH(R'')\text{—}C(R)(R')\text{—}C(R)(R')\text{—}CH(R'')\text{—}R''' + 2OH^-$$

Catholyte												
Olefin					Salt,[a]	Water,	Cosolvent,	−Cathode,		Amp.-hr.	Temp.,	Product,
R	R′	R″	R‴	g.	g.	g.	g.	v.	Amp.	hr.	°C.	g.
C_6H_5	H	H	$COCH_3$	81.5	82.5	20.5	None	1.26–1.31	2.3	5.1	50–60	20.8[b]
CH_3	CH_3	H	$COCH_3$	70.0	56.2	14.1	CH_3CN (22.3)	1.59–1.79	2.3	9.3	25–28	28.4[c]
H	H	H	$\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2$	50	40.0	10.0	CH_3CN (40)	2.00–2.12	2.0	6.2	25–30	5.3[d]
H	H	H	$\overset{\overset{O}{\uparrow}}{P}(C_6H_5)_2$	30	50.0	32.5	CH_3CN (48)	2.19–2.20	1.0	3.3	30	2.0[e]
H	H	H	O_2SCH_3	50[f]	40.0	60.0	None	1.4–1.8	3.0	5.5	25	11.9[g]

[a] Tetraethylammonium *p*-toluenesulfonate. [b] Crude 4,5-diphenyl-2,7-octanedione, b.p. 188–190° (0.17–0.21 mm.). Crystallization from alcohol yielded white crystals, m.p. 163°. F. J. Dippy and R. H. Lewis [*Rec. trav. chim.*, **56**, 1000 (1937)] reported m.p. 161°. The dioxime melted at 232–234°. C. Harries and G. Eschenbach [*Ber.*, **29**, 380 (1896)] reported m.p. 235–237°. In addition, 27.5 g. of benzalacetone was recovered and a red-brown glassy residue was obtained as distillation residue. (By-products were probably due to self-condensation of the ketones under the alkaline conditions and relatively high temperatures used. At a lower temperature, as in the condensation of benzalacetone and acrylonitrile reported below, these glasses were not formed.) No benzylacetone was found (v.p.c.). [c] A mixture of hydrodimers and their transformation products[9] consisting of 12.4 g., b.p. 98–110° (20 mm.), n^{25}D 1.4669; 3.2 g., b.p. 110–122° (20 mm.), n^{25}D 1.4655; and 12.8 g., b.p. 123–132° (20 mm.), n^{25}D 1.4660. There was virtually no distillation residue. [d] Tetraethyl tetramethylenediphosphonate, b.p. 161–166° (0.3 mm.), n^{25}D 1.4445 [N. P. Bogonostseva [*Chem. Abstr.*, **51**, 6582*g* (1957)] reports b.p. 214–217° (7 mm.), n^{25}D 1.4460], shown by v.p.c. retention time and infrared spectrum to be identical with an authentic sample. [e] The 1,4-butylenebis(diphenylphosphine oxide) crystallized from a concentrated methylene chloride solution, m.p. 257–260°. A. Mondon [*Ann.*, **603**, 115 (1957)] reports m.p. 257°. Starting material was recovered from the filtrate. [f] The methyl vinyl sulfone,[16] after treatment of the precursor several times with triethylamine, boiled at 55–56° (0.3 mm.), n^{25}D 1.4622, and had 3.13% Cl. [g] Crude 1,2-bis(methylsulfonyl)ethane. After recrystallization from water, it melted at 190–191° and showed no depression in melting point when mixed with an authentic sample prepared from 1,2-ethanedithiol by an adaptation of Overberger and Schiller's procedures.[12] In addition 21.4 g. of chlorine-free methyl vinyl sulfone, b.p. 114–115° (18 mm.), n^{25}D 1.4602, was recovered.

the solvent, an additional 1.5 g. of II was obtained by filtration. The residue was dissolved in dilute ethanol and chilled. Crude hydrodimer of the amide separated as an oil. The material remaining in the ethanol-water was re-extracted into methylene chloride and distilled. Only the 3.5 g. (VI?) boiling at 200–214° (0.15 mm.) was collected. It did not crystallize on long standing.

Anal. Calcd. for $C_{16}H_{25}NO_3S$: C, 61.70; H, 8.09; N, 4.47; S, 10.29. Found: C, 64.46; H, 8.13; N, 4.75; S, 8.20.

Acknowledgment.—Instrumental analyses were performed by Donald R. Beasecker's group. The methyl vinyl sulfone was prepared by James D. Downing.

The Configuration of Chloroacrylic Acids, Amides, Esters, and Nitriles by Nuclear Magnetic Resonance Spectroscopy

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The configurations of pairs of geometric isomers of derivatives of 3-chloroacrylic and 2,3-dichloroacrylic acids are established by proton magnetic resonance spectroscopy. In the two-olefinic-proton series the structural assignments are based on coupling constants and the differential shielding effect of acidic functional groups, and the spectral assignments of the AB doublets are based on a relationship of structure to absorption frequency. In the one-olefinic-proton series the structural assignments are based on the differential shielding effect of acidic functional groups.

In a recent report,[1] the specific cotton defoliating activity of *cis*-3-chloroacrylic acid and certain structural analogs was disclosed. In view of the inactivity of *trans*-3-chloroacrylic acid and certain of its structural analogs, an investigation of the effects of structure and substitution on 3-chloroacrylic acid derivatives I and II was carried out and an unequivocal basis was sought for the assignment of configuration to pairs of geometric isomers in the two-olefinic-proton series I, and the one-olefinic-proton series II. The application of n.m.r. spectroscopy to the solution of this problem was expected to resolve the two-olefinic-proton case I, since numerous publications[2] attest to the discriminatory value of n.m.r. for *cis–trans* olefinic protons on the basis of the spin–spin coupling constant and doublet character of the peaks.

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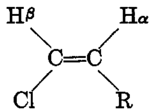
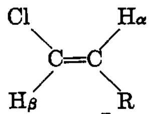
(1) R. A. Herrett and A. N. Kurtz, *Science*, **141**, 1192 (1963).

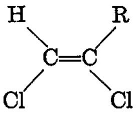
(2) (a) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 85; (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 193; (c) C. N. Banwell and N. Shepherd, *Mol. Phys.*, **3**, 351 (1960).



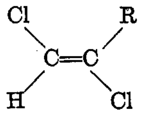
cis-I



trans-I



cis-II



trans-II

a, R = COOH
b, R = CO_2CH_3
c, R = $CONH_2$
d, R = CN
e, R = COCl

The structural assignment of isomer pairs containing a single olefinic proton (II) is made difficult by the absence of spin–spin splitting since this portion of their spectra consists of a single peak; accordingly, the assignment of structure must be based upon chemical shifts, *i.e.*, upon differential chemical shifts between *cis* and *trans* isomers. The chemical shifts will be a function of the shielding effects of the substituents on the resonance frequency of the olefinic proton. The fundamental correlations between structure and chemical shifts for trisubstituted olefins were devised by Jackman and Wiley,[3] who demonstrated that the relative positions of the resonance lines of the olefinic and allylic protons in the *cis* and *trans* isomers of α,β-unsaturated esters are characteristic of their stereochemistry. Their correlations provided, for the first time, a method for distinguishing between *cis* and *trans* trisubstituted olefins. In the many compounds which they investigated, the absorption occurred at a lower field when the olefinic proton or allylic methyl group was *cis* to the alkoxycarbonyl group.

The correlation of chemical shift with substituent type was also demonstrated by Jackman and Wiley[4] in a series of 2-substituted propenes, $CH_3C(R){=}CH_2$, in which the effect of the R substituent could be simultaneously observed on the *cis* and *trans* protons. The difference in chemicals shifts, $\delta_{cis} - \delta_{trans}$,[5] is a measure of the potential usefulness of the correlation in distinguishing between isomers. Substituents with large positive differentials are most useful: for example, the acid derivatives (COCl, CO_2Me, and $CONH_2$), aldehyde, ketone, and phenyl derivatives. Their data indicate that the nitrile group is not suited for isomer differentiation because the differential for this functional group is small and its sign is uncertain. On the basis of these correlations, it was anticipated that, with the possible exception of a nitrile substituent, the assignment of structure to *cis* and *trans* pairs in II could be successfully achieved in the presence of two chlorines (α and β). It was also anticipated that these correlations would corroborate our assignment of the olefinic proton signals in the spectra of *cis*- and *trans*-I. Our results justify these assumptions.

Results and Discussion

3-Chloroacrylic Acid Derivatives (I).—All of the olefinic protons in the 3-chloroacrylic acid derivatives (I) exhibited characteristic AB-type spectra consisting of two doublets of equal intensity. The integrated intensity for each olefinic proton was found to be 1 in those compounds having other protons, such as carboxyl or ester, which could be used for quantitative reference. Although the amide proton signals were broadened by quadrupole relaxation and they overlapped the olefinic signals, this did not interfere with the analysis of the spectra. The chemical shifts and coupling constants are assembled in Table I.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE OLEFINIC PROTONS IN 3-CHLOROACRYLIC ACID DERIVATIVES

Compound[a]	Solvent	Chemical shifts[b] for olefinic protons		
		β[c]	α[c]	*J*[d]
cis-3-Chloroacrylic acid	CCl_4	6.84	6.20	8.0
trans-3-Chloroacrylic acid	CCl_4	7.48	6.22	13.2
cis-3-Chloroacrylyl chloride	None	6.95	6.62	8.0
cis-3-Chloroacrylamide	Acetone	6.69	6.34	8.0
trans-3-Chloroacrylamide	Acetone	7.29	6.48	13.0
Methyl *cis*-3-chloroacrylate	None	6.86	6.26	8.0
Methyl *trans*-3-chloroacrylate	None	7.41	6.25	13.5
cis-3-Chloroacrylonitrile	CCl_4	7.11	5.95	7.8
trans-3-Chloroacrylonitrile	CCl_4	7.25	5.89	14.0

[a] *cis* and *trans* refer to the configurational relationship between the olefinic protons. [b] Centers of doublets in parts per million from TMS = 0 (δ). [c] α and β refer to the configurational relationship between the proton and the acid function. [d] Cycles per second.

The *cis*-Ia–e series show low-field doublets centered at δ 6.69 to 7.11 and high-field doublets centered at δ 5.95 to 6.62 with $J = 7.9 \pm 0.1$ c.p.s. The *trans*-Ia–d series show low-field doublets centered at δ 7.25 to 7.48 and high-field doublets centered at δ 5.89 to 6.48 with $J = 13.4 \pm 0.3$ c.p.s. The values of the coupling constants for *cis*-3-chloroacrylonitrile and *trans*-3-chloroacrylonitrile given by Scotti and Frazza[6] are 7.7 and 14.0 c.p.s., respectively, in good agreement with the values shown in Table I for the same compounds. The values of the coupling constants are thus fully consistent with those expected (*trans*-I > *cis*-I) without exception, although we are lacking n.m.r. data for *trans*-3-chloroacrylyl chloride. The low-field doublets are assigned to the β-proton and the high-field doublets to the α-proton for the following reasons. From Table II, it is clear that the variation in olefinic absorption frequency between *cis* and *trans* isomers of the same compound is much less for the high-field signal than for the low-field signal, averaging 0.02 p.p.m. for the former and 0.48 p.p.m. for the latter. There is a parallel relationship with the structure of the molecule. Structures *cis*-I and *trans*-I show that the geometric relationship of the α-proton to R differs very little in *cis* and *trans* isomers, whereas that of the β-proton differs considerably. Assuming that R, rather than chlorine, has the dominant influence on chemical shift, it seems reasonable to identify the low-field signal with the β-proton and the high-field signal with the α-proton. This assignment is reinforced in the *trans*-I isomers where the β-proton is *cis* to R, and by analogy with the trisubstituted olefins (as in *cis*-II) this should shift its resonance to lower field.

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(3) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958); *J. Chem. Soc.*, 2886 (1960).

(4) L. M. Jackman and R. H. Wiley, *ibid.*, 2881 (1960).

(5) δ in parts per million (tetramethylsilane = 0); *cis* and *trans* refer to the relationship of R to the olefinic proton.

(6) F. Scotti and E. Frazza [*J. Org. Chem.*, **29**, 1800 (1964)] prepared the nitriles *cis*-Id and *trans*-Id by the pyrolysis at 535° of α-acetoxy-β-chloropropionitrile.

TABLE II

SIGNAL SHIFTS[a] (OLEFINIC PROTONS) BETWEEN *cis* and *trans*[b] ISOMERS OF 3-CHLOROACRYLIC ACID DERIVATIVES

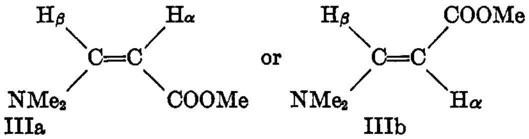
Compound	β-Proton (low field) $\delta_{trans\text{-I}} - \delta_{cis\text{-I}}$	α-Proton (high field) $\delta_{trans\text{-I}} - \delta_{cis\text{-I}}$
3-Chloroacrylic acid	0.64	0.02
3-Chloroacrylamide	0.60	0.14
Methyl 3-chloroacrylate	0.55	−0.01
3-Chloroacrylonitrile	0.14	−0.06
Av.	0.48	0.02

[a] Parts per million. [b] *cis* and *trans* refer to the configurational relationship between the olefinic protons.

Unambiguous structural assignments can thus be made for the 3-chloroacrylic acids, amides, methyl esters, and nitriles (Ia–e). The differential $\delta_{trans\text{-I}} - \delta_{cis\text{-I}}$ shielding effect of the acid group on the β-proton decreases in the order $COOH > CONH_2 > COOCH_3 \gg CN$ (Table II), whereas the order given by Jackman and Wiley[4] for 2-substituted propenes is $COOCH_3 > CONH_2 \gg CN$. As has been observed above, these authors indicate that the nitrile group is not suited for *cis–trans* isomer differentiation in 2-substituted propenes because the differential shift for nitrile is small and its sign is uncertain. However, we find that the 3-chloroacrylonitriles *are* suited to *cis–trans* differentiation by the method of Jackman and Wiley; even though $\delta_{trans\text{-I}} - \delta_{cis\text{-I}}$ is relatively small (0.14 p.p.m.), the β-proton of the *trans*-I isomer is clearly downfield with respect to the β-proton of the *cis*-I isomer, as is shown by the larger coupling constant $J = 14$ c.p.s. (*vs.* $J = 7.8$ c.p.s.) for the *trans* isomer. Perhaps the chlorine β to the nitrile shifts the electrical center of gravity of the C≡N bond closer to the carbon atom thus producing a greater deshielding effect on a β-proton *cis* to the nitrile (*i.e.*, in *trans*-I, H_β is *cis* to R = CN) than is possible in the absence of chlorine on the β-carbon.

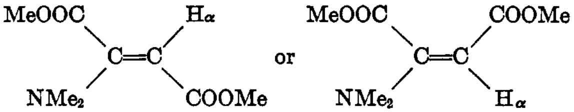
When only one isomer of an AB *cis–trans* pair of structure I is available, assignment of stereochemistry is hazardous. However, with the present collection of data we are now in a position to venture assignments in such cases. Consider, for example, the product of the addition of dimethylamine to methyl propiolate or to dimethyl acetylenedicarboxylate. Nucleophilic additions to acetylenic bonds supposedly take place by a *trans* mechanism; hence the expected products are

$Me_2NH + HC{\equiv}C{-}COOMe \longrightarrow$



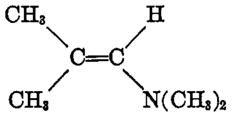
IIIa IIIb

$Me_2NH + MeOOC{-}C{\equiv}C{-}COOMe \longrightarrow$



IVa IVb

IIIa and IVa, respectively. We find that these additions go nearly quantitatively, and n.m.r. conclusively shows a single product since crude reaction product filtrates and recrystallization liquors show only those n.m.r. peaks identical with analytically pure products; hence, we are dealing with a stereospecific addition, or with one thermodynamically stable isomer. However, the n.m.r. spectra of both of these products lead us to believe that the addition products are IIIb and IVb (the *cis* addition products) rather than IIIa and IVa. The methyl propiolate addition product III has the expected AB-type spectrum with a doublet at δ 7.30 ($J = 13.0$ c.p.s.), a doublet at δ 4.38 ($J = 13.0$ c.p.s.), a singlet at δ 3.53, and a singlet at δ 2.88 (relative areas 1:1:3:6). The dimethyl acetylenedicarboxylate addition product IV has four singlets at δ 4.50, 3.58, 3.86, and 2.88 (relative areas 1:3:3:6). The appearance of the olefinic proton in IV at δ 4.50 allows us to assign δ 4.38 in III to H_α, and the near identity of these two shifts indicates the same structural relationship of the dimethylamino group to H_α in III and IV. Furthermore, H_β in III, by its appearance at δ 7.30, establishes a *cis* relationship of H_β to the carbomethoxy group; this now gives us structure IIIb in which the two olefinic protons are *trans*. A high coupling constant ($J = 13.0$ c.p.s.) lends additional support for the *trans*-IIIb structure although we readily admit to the pitfalls of assignments based on coupling constants. It is also of interest to cite the n.m.r. spectrum of N,N-dimethylisobutenylamine[7] (V) in which the olefinic proton appears at δ 5.17; this also supports the assignment of δ 7.30 in IIIb to H_β, the downfield shift being due to the expected deshielding effect of the carbomethoxy group on H_β. The upfield shifts of H_α in III and IV to δ 4.38 and 4.50 are due to a shielding effect of the dimethylamino group on H_α.



V

2,3-Dichloroacrylic Acid Derivatives (II).—The literature is scanty on *cis–trans* isomers of 2,3-dichloroacrylic acid derivatives (II). Jura and Gaul[8] have discussed the differences in polarographic behavior of *cis*-IId and *trans*-IId (nitrile), but physical properties of these isomers were not disclosed. Tobey and West[9] have shown that the only 2,3-dichloroacrylic acid and methyl ester known have the *cis*-II configurations, the acid having a singlet olefinic proton resonance at δ 7.79 and the ester at δ 7.60. Similarly, only one amide, IIc, m.p. 134° (lit.[10] m.p. 134.6–135.0°), has been mentioned in the literature,[10] and the acid chloride IIe has been recorded[11] but with unspecified configuration.

We chose to prepare II derivatives starting with the pyrolysis of 2,2,3-trichloropropionitrile[12] which gives a mixture of *cis*-IId and *trans*-IId nitriles from which we hoped to obtain the amides and acids by hydrolysis. Jura and Gaul[8] mentioned the isolation of 94% pure *cis*-IId by fractional crystallization of the mixture of nitriles, but we preferred to study the hydrolysis of the mixtures

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(7) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961).

(8) W. H. Jura and R. J. Gaul, *J. Am. Chem. Soc.*, **80**, 5402 (1958).

(9) S. W. Tobey and R. West, *ibid.*, **86**, 56 (1964).

(10) (a) H. J. Prins, *J. prakt. Chem.*, [2] **89**, 420 (1914); (b) H. J. Prins and H. G. Haring, *Rec. trav. chim.*, **73**, 479 (1954).

(11) Wingfoot Corp., British Patent 563,047 (1944).

(12) J. G. Lichty, U. S. Patent 2,328,984 (1944).

since *cis-* and *trans-*IId could not be separated by distillation or vapor phase chromatography, even though isomerization to the thermodynamically stable isomers was expected under conditions of *acidic hydrolysis.*

The mixture of nitriles IId that we have obtained contained two singlets at δ 7.39 and 7.17 in the area ratio of 6:4. We assign the low-field, δ 7.39, signal to *cis*-IId and the high-field, δ 7.17, signal to *trans*-IId on the basis of a greater deshielding effect of the substituent R when it is *cis* to a β-proton as in *cis*-IId. Hydrolysis of this mixture with 80% H_2SO_4 at 80° gave mostly one amide, *cis*-IIc, m.p. 135.8–136.4°, showing a sharp singlet n.m.r. signal at δ 7.74. We were fortunate in being able to isolate from the mother liquors a small amount of the isomeric amide, *trans*-IIc, m.p. 118–119°, showing a sharp olefinic proton singlet at δ 6.82. Each of these amides was converted back to the original pure nitrile without isomerization.

Hydrolysis of the original mixture of nitriles with 80% H_2SO_4 at 140° gave only one acid, *cis*-IIa, m.p. 85.0–87.5°, showing a sharp olefinic proton singlet at δ 7.83. This acid, *cis*-IIa, was esterified with methanol to give pure *cis*-IIb (methyl ester), with the n.m.r. spectrum showing sharp singlets at δ 7.73 and 3.88 in the ratio 1:3. The n.m.r. spectra of *cis*-IIa and *cis*-IIb agree fully with the values reported by Tobey and West.[9]

An attempt was made to prepare *trans*-IIb by chlorination of methyl propiolate with and without illumination, but the same mixture of *cis*-IIb–*trans*-IIb (41:59) was obtained by either method judging from the two sharp singlet olefinic resonances at δ 7.71 and 7.01. The isomeric methyl esters were not resolvable by distillation or vapor phase chromatography but the identity of the low-field resonance with that of pure *cis*-IIb made from pure *cis*-IIa allows us to assign the high-field resonance to *trans*-IIb, thus completing the picture for this study except for *trans*-IIa. It is of interest that extended ultraviolet irradiation of carefully purified *cis*-IIc (amide) failed to decrease the ratio *cis*-IIc:*trans*-IIc below 90:10 which we believe is close to the thermodynamic equilibrium rather than to a photodynamic equilibrium; the presence of chlorine atoms[13] or other radicals is believed to be the cause of our inability to decrease this ratio. We are not certain that 90:10 *cis*-IIc–*trans*-IIc is the true equilibrium since irradiation of a 40:60 *cis*-IIc–*trans*-IIc mixture for 18 hr. gave a ratio of 50:50 *cis–trans* which at least is in the direction of the thermodynamically stable *cis*-IIc isomer. The n.m.r. data are summarized in Table III.

TABLE III

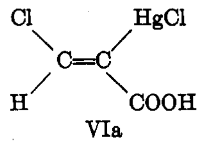
CHEMICAL SHIFTS FOR THE OLEFINIC PROTON IN 2,3-DICHLOROACRYLIC ACID DERIVATIVES

Compound[a]	Solvent	Chemical shifts[b]
cis-2,3-Dichloroacrylic acid	CCl_4	7.83
Methyl *cis*-2,3-dichloroacrylate	Neat	7.73
Methyl *trans*-2,3-dichloroacrylate	Neat	7.01
cis-2,3-Dichloroacrylonitrile	CCl_4	7.37
trans-2,3-Dichloroacrylonitrile	Neat	7.17
cis-2,3-Dichloroacrylamide	$CDCl_3$	7.74
trans-2,3-Dichloroacrylamide	$CDCl_3$	6.82

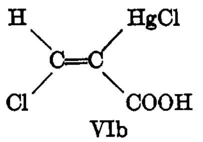
[a] *cis* and *trans* refer to the configurational relationship of the two chlorines. [b] Parts per million from TMS = 0 (δ).

Since all of the compounds in this group have only one olefinic proton, remote from any other protons, this signal in each case is a single sharp peak. When other suitable protons were present, the intensity of the peak was shown to be 1. Each pair of isomers produces two signals, one at higher field and the other at lower field. The identification of *cis* and *trans* forms depends, as was discussed above, on the differential deshielding effect of the substituent R. The *cis* and *trans* forms of the amide IIc and ester IIb are readily identified from the data of Jackman and Wiley.[5] The low-field proton must be *cis* to the deshielding group, and this places the chlorines *cis* to each other. The isomer with the high-field proton must, therefore, have *trans*-chlorines. The nitriles IId were not so readily distinguished, however. The small differential chemical shift reported by Jackman and Wiley, and the ambiguity in its sign, signified that the nitrile group could not be relied upon to follow the same shielding rules as the other acid derivatives. The difficulty was compounded by the reported[4] similarity in differential shielding effect of chlorine and nitrile. The problem was solved by converting amides of known configuration to nitriles. This can be done with retention of configuration by dehydration with phosphorus pentoxide. Surprisingly the nitrile group has a significant differential (0.20 p.p.m.) and its sign is the same as that of the acid derivatives. Thus, the ambiguity in the data of Jackman and Wiley regarding this substituent has been resolved. The resonance of a β-olefinic proton will be shifted to lower field if it occupies a position *cis* to a nitrile group in compounds of structures I and II.

We are now in a position to attempt the assignment of configuration to compounds of type VI where only one isomer is available. Thus, the addition of mercuric chloride to propiolic acid gives only one adduct resulting from either a *cis* or a *trans* addition. The n.m.r. spectrum of this adduct, 2-chloromercuri-3-chloroacrylic acid, shows a sharp olefinic proton singlet at δ 6.77, which is a reasonable value for a β-proton *trans* to a carboxyl, assuming that a chloromercuri group has little effect on the olefinic proton resonance. Accordingly, the configuration of the adduct is VIb, resulting from a *trans* addition to the triple bond which is the expected mode of electrophilic addition.

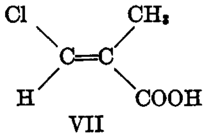


VIa



VIb

Another example is *trans*-3-chloro-2-methylacrylic acid[14] (VII) which shows an olefinic proton resonance at δ 7.48. The low-field position of this proton clearly establishes the configuration as VII with the olefinic proton *cis* to the carboxyl



VII

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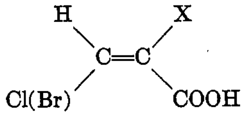
[13] Ultraviolet irradiation in the presence of halogen gives the thermodynamic equilibrium: C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 302.

[14] A. F. Ferris and I. G. Marks, *J. Org. Chem.*, **19**, 1971 (1954).

Cotton Defoliation Activity.—In the original article disclosing the cotton defoliation activity[1] of *cis*-3-chloroacrylic acid we obtained an excellent correlation of activity with structural specificity with one exception. In general, one can conclude that cotton defoliation activity will occur with compounds having structure VIII, where X = H or CH_3 but not where X is larger than methyl. Since Cl is of the same order of size as methyl,[15] one would expect X = Cl to lead to a defoliant; therefore, we were surprised to find that the 2,3-dichloroacrylic acid which we tested and which was thought to have structure *trans*-IIa actually has the two chlorines *cis* as shown by our n.m.r. data and as confirmed by the work of Tobey and West.[9] Assuming that an electronegative atom in position X is not important for cotton defoliation but rather that the size of the group X is of importance, we can now understand why the tested *cis*-2,3-dichloroacrylic acid (*cis*-IIa) was inactive since it belonged to the *inactive* series where a β-proton is *cis* to a carboxyl, such as in *trans*-Ia and *trans*-3-chloro-2-methylacrylic acid (VII).


VIII

Experimental

N.m.r. spectra were measured on a Varian A-60 spectrometer with tetramethylsilane (TMS) as internal standard. δ values are given in parts per million with respect to TMS = 0, taken neat or in solvent as indicated. All melting points were determined on a Fisher-Johns melting point apparatus and are corrected. Infrared spectra were taken with a Beckman IR-5 or IR-4 spectrophotometer in CS_2 from 2.0 to 7.5 μ and in CCl_4 from 7.5 to 15 μ unless KBr disks are indicated.

cis-**3-Chloroacrylic Acid** (*cis*-**Ia**).—The addition of hydrogen chloride to propiolic acid is catalyzed by cuprous chloride,[16a] allowing the reaction to take place at temperatures below that where isomerization to *trans*-3-chloroacrylic acid becomes significant. In a typical preparation, 35.5 g. (0.484 mole) of propiolic acid[16d] of 95.4% purity was added over 25 min. to a stirred solution of 3.00 g. of cuprous chloride in 81 ml. of concentrated hydrochloric acid; a temperature of 8–12° was maintained by cooling. After storage at 0° overnight, the reaction mixture was extracted several times with chloroform, the chloroform was evaporated, and the residue was recrystallized from hexane giving 42.3 g. (82%) of *cis*-3-chloroacrylic acid, m.p. 60–62°. Recrystallization from 19:1 aqueous hydrochloric acid gave analytically pure material of m.p. 60.8–61.4° (lit.[16b] m.p. 63–64°). Principal peaks in the infrared spectrum appeared at 1709, 1623, 1418, 1244, 1190, 918, 813, 773, and 713 cm.$^{-1}$.

trans-**3-Chloroacrylic acid** (*trans*-**Ia**) was prepared by the method of Backer and Beute[17] in 52% yield, m.p. 84.7–85.1° (lit.[17] m.p. 85.5–86.0°). *trans*-3-Chloroacrylic acid was also obtained in 62% yield by heating a mixture of 300 g. of *cis*-3-chloroacrylic acid and 720 ml. of 6 *N* hydrochloric acid on a steam bath for 4 hr. followed by extraction and recrystallization. Principal infrared peaks appeared at 1706, 1616, 1422, 1307, 1266, 1178, 935, 917 (sh), 862, and 683 cm.$^{-1}$.

Methyl *cis*-**3-Chloroacrylate** (*cis*-**Ib**).—Esterification of *cis*-3-chloroacrylic acid with methanol and a catalytic amount of sulfuric acid gave a 79% yield of the ester. The ester boiled at 79–83° (78 mm.): $n^{20}D$ 1.4570; infrared bands at 1739 (C═O), 1626 (C═C), 1353, 1002, 808, and 704 cm.$^{-1}$; it was 98% pure by vapor phase chromatography.

Methyl *trans*-**3-Chloroacrylate** (*trans*-**Ib**).—This ester was prepared in 85% yield in a manner analogous to the *cis* methyl ester Ib. The product boiled at 74–75° (131 mm.): $n^{20}D$ 1.4510; infrared bands at 1727 (C═O), 1613 (C═C), 833, and 706 cm.$^{-1}$; it showed one peak by vapor phase chromatography.

cis-**3-Chloroacrylyl Chloride** (*cis*-**Ie**).—A mixture of 106.5 g. (1.00 mole) of *cis*-3-chloroacrylic acid and 137.4 g. (1.00 mole) of phosphorus trichloride was heated at 65° for 30 min., then at 98° for 5 hr. Distillation through a 12-in. Vigreux column gave 66.0 g. (53%) of *cis*-3-chloroacrylyl chloride, b.p. 99–103° (260 mm.), $n^{20}D$ 1.4941. Principal infrared bands appeared at 1757, 1600, 1335, 997, 855 (broad), and 757 cm.$^{-1}$. A precut boiling at 87–95° (260 mm.) was contaminated with *trans*-3-chloroacrylyl chloride.

trans-**3-Chloroacrylyl chloride** (*trans*-**Ie**) was prepared in 61% yield in a manner analogous to the *cis* isomer; the product boiled at 111–115°, $n^{20}D$ 1.4913. Principal infrared bands appeared at 1754, 1600, 1220, 1100, 1032, 928, 867, and 715 cm.$^{-1}$.

cis-**3-Chloroacrylamide** (*cis*-**Ic**).—Gaseous ammonia was passed into a cooled, stirred solution of 33.0 g. of *cis*-3-chloroacrylyl chloride (containing about 10% *trans* isomer) in 175 ml. of ethyl ether. Soxhlet extraction of the solid products with ether for several days gave 24.0 g. (85%) of crude *cis*-3-chloroacrylamide, m.p. 90–105°. Recrystallization twice from a mixture of isopropyl ether and isopropyl alcohol gave 17.3 g. of *cis*-3-chloroacrylamide, m.p. 107–112° (containing about 10% of the *trans* isomer) (lit.[6] m.p. 111–112°). Infrared bands appeared at 1681, 1616, 1408, 1312, 1218, 807, 758, and 703 cm.$^{-1}$.

trans-**3-Chloroacrylamide** (*trans*-**Ic**) was prepared in 76% yield from ammonia and *trans*-3-chloroacrylyl chloride; the product melted at 145–147° without recrystallization (lit.[18] m.p. 143.5–145°). Infrared bands were at 1667, 1600, 1408, 1129, 938, 930, 854, 804, and 709 (broad) cm.$^{-1}$.

cis-**3-Chloroacrylonitrile** (*cis*-**Id**).—Dehydration of *cis*-3-chloroacrylamide (*cis*-Ic, containing about 10% of the *trans* isomer) with P_2O_5 at 130–200° gave a mixture of 60% *trans*-3-chloroacrylonitrile and 40% *cis*-3-chloroacrylonitrile judging from a vapor phase chromatograph. The retention times were 8.0 and 18.0 min., respectively, on a 13-ft. column of silicone 550 and Carbowax 4000 (3:2) on Chromosorb W at 130°. The n.m.r. spectrum was also consistent with a 60:40 *trans–cis* mixture. Eventually, a sample containing 90% *cis*-3-chloroacrylonitrile was prepared (see below).

trans-**3-Chloroacrylonitrile** (*trans*-**Id**) was prepared by the P_2O_5 dehydration of *trans*-3-chloroacrylamide (*trans*-Ic); a 70% yield of *trans*-3-chloroacrylonitrile, m.p. 42–44°, was obtained (lit.[18] m.p. 45–46°). The product showed only one peak by vapor phase chromatography: infrared bands at 2217 (C≡N), 1609 (C═C), 1163, 917 (vs), and 868 (vs) cm.$^{-1}$.

cis- (*cis*-**Id**) **and** *trans*-**3-Chloroacrylonitrile** (*trans*-**Id**). **Pyrolysis Method.**—The pyrolysis of 2,3-dichloropropionitrile at 450–600°[19] produces mixtures of *cis*- and *trans*-3-chloroacrylonitrile and 2-chloroacrylonitrile. In our hands, pyrolysis at 550° of 22.0 g. of 2,3-dichloropropionitrile[20] in a Pyrex tube packed with 3-mm. Pyrex helices for a contact time of 10 sec. gave 19.9 g. of pyrolysate and a conversion of 92%. The composition of the neutral, dried product by vapor phase chromatography was 23.8% *cis*-3-chloroacrylonitrile, 25.9% *trans*-3-chloroacrylonitrile, 33.2% 2-chloroacrylonitrile, and 7.8% 2,3-dichloropropionitrile (area %). The addition of toluene to the pyrolysis feed remarkably suppressed the yield of both of the 3-chloroacrylonitriles without affecting the yield of the 2-chloro isomer. The addition of 20 mole % of toluene at 500° with a contact time of 9.0 sec. gave an 0.8% yield of 3-chloro isomers and an 11.2% yield of 2-chloroacrylonitrile. The addition of 50 mole % of toluene at 465° with a contact time of 20 sec. gave no 3-chloro isomers and a 45% yield of 2-chloroacrylonitrile at 47% conversion of the 2,3-dichloropropionitrile. We attribute this result to inhibition of dehydrohalogenation by toluene by a radical process; *i.e.*, elimination of a 3-H and a 2-Cl is a radical process, whereas elimination of a 2-H and a 3-Cl is a nonradical process. Further support for this hypothesis is that 2,3-dichloropropioni-

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(15) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.

(16) (a) Union Carbide Corp., Belgian Patent 631,355(1963); (b) F. Straus and W. Voss, *Ber.*, **B59**, 1681 (1926); (c) A. D. Macallum, U. S. Patent 2,194,363 (1940); (d) D. R. Jackson and T. H. Vaughn, U. S. Patent 2,205,885 (1940); (e) Union Carbide Corp., Belgian Patent 636,771 (1964).

(17) H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 167 (1935).

(18) E. Gryszkiewicz-Trochimowski and W. Schmidt, *Bull. soc. chim. France*, 593 (1948).

(19) G. C. Morrison and W. O. Fugate, U. S. Patent 3,069,458 (1962).

(20) H. Brintzinger, K. Pfannstiel, and H. Koddebusch, *Angew. Chem.*, **60**, 311 (1948).

trile with F-10 activated alumina (Aluminum Company of America) at 250° and 20 sec. contact time is dehydrochlorinated to 2-chloroacrylonitrile in 86% yield with no trace of the 3-chloro isomers. Similar results were obtained with methyl 2,3-dichloropropionate over alumina at 200° or with toluene at 510° in the absence of catalyst; both gave methyl 2-chloroacrylate as the principal product.

cis-3-Chloroacrylonitrile (42 g.) was eventually obtained in 90% purity by work-up and distillation through an 18-in. packed column of the 550° pyrolysate obtained from 424 g. of 2,3-dichloropropionitrile. The infrared spectrum of this sample of *cis*-3-chloroacrylonitrile, n^{20}_{D} 1.4587, showed bands at 2222 (C≡N), 1613 (C=C), 1333, 961, 775, and 729 cm.$^{-1}$. Hydrolysis of *cis*-3-chloroacrylonitrile with 80% H_2SO_4 at 125–154° for a few minutes or with H_2O_2 and sodium carbonate in aqueous acetone at 50° for 2 hr. failed to give any identifiable products.

2-Chloroacrylonitrile.—A mixture of 38.7 g. of quinoline and 37.2 g. of 2,3-dichloropropionitrile[20] was heated to 60° at 106 mm. The product, 21.9 g. (83%) of 2-chloroacrylonitrile distilled at 36–37° at 106 mm., and gave one peak by vapor phase chromatography; characteristic infrared peaks were 2232 (C≡N), 1603 (C=C), 1370, 1163, 930, and 889 cm.$^{-1}$; n.m.r. had two doublets (J_{gem} = 3.0 c.p.s.) at δ 6.19 and 6.30.

From the pyrolysis of 2,3-dichloropropionitrile described previously there was obtained a distillate fraction, b.p. 35–66° (133 mm.), containing 2-chloroacrylonitrile of *ca.* 90% purity.

Methyl 3-Dimethylaminoacrylate (IIIb).—The addition of methyl propiolate to dimethylamine in ether gave methyl 3-dimethylaminoacrylate (IIIb) in 91% yield; m.p. 44–45.5° (lit.[21] m.p. 48–49°); infrared bands at 1715 (C=O), 1645 (C=C), 1449, 1408, 1353, 1299, 1247, 1164, 1109, 1063, 980, 948, 859, 810, 797, and 679 cm.$^{-1}$; n.m.r. (CCl_4) δ 4.38 (=CHCOO—, doublet, J = 13.0 c.p.s.), 7.30 (=CHN=, doublet, J = 13.0 c.p.s.), 3.53 (OCH_3, singlet), and 2.88 [$-N(CH_3)_2$, singlet], relative areas 1:1:3:6, respectively.

Dimethyl Dimethylaminomaleate (IVb).—Dimethyl acetylenedicarboxylate (71.0 g.) was added to 22.5 g. of dimethylamine in 200 ml. of ether with cooling, giving 89.1 g. (95%) of crude IVb; recrystallization from ether gave an analytically pure product; m.p. 77–79°; infrared bands (KBr pellet) at 1733 (C=O), 1672 (C=C), 1570, 1431, 1408, 1370, 1247, 1190, 1161, 1134, 1067, 1041, 976, 957, 883, 832, 784, 760, 733, 724, and 678 cm.$^{-1}$; n.m.r. (CCl_4), δ 4.50 (=CH), 2.88 [$-N(CH_3)_2$], 3.58 and 3.86 ($-COOCH_3$), all singlets of relative areas 1:6:3:3, respectively.

Anal. Calcd. for $C_8H_{13}NO_4$: C, 51.33; H, 7.00. Found: C, 51.57; H, 7.01.

cis- **and** *trans*-**2,3-Dichloroacrylonitrile (IId). Pyrolysis Method.**—A total of 285 g. of 2,2,3-trichloropropionitrile[20] was pyrolyzed at 550° with a 10-sec. contact time in a 25-mm. o.d. Pyrex tube packed with 3-mm. Pyrex helices; the effective volume of the reaction zone was 34 cc. The pyrolysate was condensed at −80° and worked up by washing to neutrality with water, drying over calcium chloride, and distilling through an 18-in. vacuum-jacketed Vigreux column to give 130 g. (59.5%) of *cis*- and *trans*-2,3-dichloroacrylonitriles, b.p. 65–66° (73 mm.), n^{20}_{D} 1.4838 (lit.[8] b.p. 130–130.5°, n^{25}_{D} 1.4839). This sample of 2,3-dichloroacrylonitrile showed only one peak by vapor phase chromatography, but the n.m.r. spectrum (neat) showed two individual proton peaks at δ 7.39 and 7.17 in the ratio of 6:4. Pure samples of the *cis* and *trans* isomers were prepared as indicated below.

The addition of 50 mole % of toluene to the pyrolysis feed led to the formation of 2-chloroacrylonitrile and benzyl chloride.

Quinoline Method.—Dehydrochlorination of 2,2,3-trichloropropionitrile by heating with quinoline[8,12] gave the same mixture of isomers of 2,3-dichloroacrylonitrile as that obtained by the pyrolysis method.

cis-**2,3-Dichloroacrylamide** (*cis*-**IIc**).—A mixture of 230 g. of 2,3-dichloroacrylonitrile (60:40 mixture of isomers) and 360 ml. of 80% sulfuric acid was heated at 80° for 3.5 hr. The solid phase was filtered after cooling and washed with water. Recrystallization from chloroform gave 140 g. (53%) of *cis*-2,3-dichloroacrylamide, m.p. 135–138°. An analytical sample melted at 135.8–136.4° (lit.[10a] m.p. 134°): infrared bands (KBr pellet) at 1686 (C=O), 1605 (C=C), 1404, 1379, 1242, 1101, 1019, 881, 845, 765, 722, and 678 cm.$^{-1}$.

Anal. Calcd. for $C_3H_3Cl_2NO$: C, 25.74; H, 2.16. Found: C, 26.32; H, 2.38.

trans-**2,3-Dichloroacrylamide** (*trans*-**IIc**).—The aqueous acidic phase from the 80% H_2SO_4 hydrolysis of 2,3-dichloroacrylonitrile was extracted twice with ether, the extract was combined with the chloroform mother liquors from the preparation of *cis*-IIc, and the combined organic phase was evaporated and distilled to give 46.8 g. of a mixture of a solid and an oil, b.p. 56–108° (0.3 to 1.0 mm.). The solid was washed with pentane and dried, giving 11.9 g. of a mixture of *cis*- and *trans*-2,3-dichloroacrylamide, m.p. 66–118°, rich in the *cis* isomer; recrystallization from chloroform, then hexane, gave 1.7 g. of *trans*-2,3-dichloroacrylamide: m.p. 118–119°; infrared bands (KBr pellet) at 3344, 3145, 1634 (broad), 1487 (sh), 1418, 1267, 1096, 999, 828, 793, 756, and 685 cm.$^{-1}$.

Anal. Calcd. for $C_3H_3Cl_2NO$: C, 25.74; H, 2.16; Cl, 50.66. Found: C, 25.94; H, 1.98; Cl, 50.32.

Irradiation of 3.2 g. of pure *cis*-2,3-dichloroacrylamide in 319 ml. of benzene at 42° for 24 hr. with a 100-w. Hanovia 8A36 mercury lamp in a quartz apparatus gave a 90:10 *cis–trans* mixture of isomers. An additional 24 hr. of irradiation failed to change this ratio significantly. In another test 2.2 g. of 2,3-dichloroacrylamide (40:60 *cis–trans*) in 320 ml. of benzene was irradiated for 18 hr. at 42° to give a 50:50 *cis–trans* mixture of isomers.

cis-**2,3-Dichloroacrylonitrile** (*cis*-**IId**).—A mixture of 8.0 g. of *cis*-2,3-dichloroacrylamide and 8.2 g. of P_2O_5 was heated to 200° and the pressure was reduced to 225 mm.; 5.5 g. (79%) of the product *cis*-IId, b.p. 94° (225 mm.), was collected. The purity of the nitrile was 99% by vapor phase chromatography; the n.m.r. spectrum (CCl_4) showed a singlet at δ 7.37, this being the low-field isomer in the mixture of 2,3-dichloroacrylonitriles obtained above by pyrolysis of 2,2,3-trichloropropionitrile. Characteristic infrared bands (neat) were present at 3049, 2237, 1580, 1264, 1104, 1072, 1025, 876, 823, and 641 cm.$^{-1}$.

trans-**2,3-Dichloroacrylonitrile** (*trans*-**IId**).—A mixture of 1.5 g. of *trans*-2,3-dichloroacrylamide and 1.6 g. of P_2O_5 was heated to 175° at a pressure of 200 mm. The distillate of 1.0 g. (77%) was pure by vapor phase chromatography; the n.m.r. spectrum showed a singlet at δ 7.17, this being the high-field isomer in the mixture of 2,3-dichloroacrylonitriles obtained above by pyrolysis of 2,2,3-trichloropropionitrile.

Anal. Calcd. for C_3HCl_2N: C, 29.55; H, 0.83; Cl, 58.14. Found: C, 29.97; H, 0.78; Cl, 57.94.

cis-**2,3-Dichloroacrylic Acid** (*cis*-**IIa**).—A mixture of 20.0 g. of 2,3-dichloroacrylonitrile (40:60 *trans–cis*) and 50 g. of 80% aqueous sulfuric acid was stirred and heated at 140° for 2 hr. Upon cooling, the reaction mixture crystallized to a semisolid and was extracted twice with two 300-ml. portions of ether. Evaporation of the ether gave 16.0 g. (67%) of *cis*-IIa, m.p. 83–86°. Two recrystallizations from chloroform gave 7.5 g., m.p. 85.0–87.5° (lit.[22] m.p. 85–86°); characteristic infrared bands appeared at 3030, 2950, 2841, 2618, 2494, 1709, 1595 (w), 1425, 1274, 1239, 1145 (w), 1029, 909 (sh), 883, 840, 746, and 723 cm.$^{-1}$. This acid is a dangerous vesiccant.

Methyl *cis*-**2,3-Dichloroacrylate** (*cis*-**IIb**).—Esterification of 10.0 g. of *cis*-2,3-dichloroacrylic acid with 50 ml. of methanol and 1.0 g. of *p*-toluenesulfonic acid gave 5.0 g. (45%) of *cis*-IIb, b.p. 72–74° (13 mm.), n^{20}_{D} 1.4812 (lit.[9] $n^{21.5}_{\mathrm{D}}$ 1.4788).

Methyl *cis*- **and** *trans*-**2,3-Dichloroacrylate** (*cis*- **and** *trans*-**IIb**).—A solution of 15.5 g. (0.21 mole) of chlorine in 90 ml. of CCl_4 was added over a period of 3 hr. to a stirred solution of 18.0 g. (0.21 mole) of methyl propiolate in 35 ml. of CCl_4 under nitrogen. After stirring for an additional 76 hr., distillation through a 12-in. Vigreux column gave unreacted methyl propiolate and 7.0 g. (21%), n^{20}_{D} 1.4830, of a mixture of the *cis* and *trans* methyl esters of IIb showing one peak by vapor phase chromatography. The n.m.r. spectrum (neat) showed two olefinic singlet protons at δ 7.71 and 7.01 in the ratio 41:59, and a singlet methyl at δ 3.88; the relative area of the methyl proton to the sum of the two olefinic protons was 3.2:1.0. Chlorination of methyl propiolate as above but with ultraviolet irradiation gave the same 41:59 distribution of *cis–trans* methyl esters IIb.

2-Chloromercuri-3-chloroacrylic Acid (VIb).—Addition of mercuric chloride to 10.0 g. of propiolic acid by a literature[23] method gave 11.0 g. (23%) of 2-chloromercuri-3-chloroacrylic

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[21] V. K. Antonov and A. Y. Berlin, *Zh. Obshch. Khim.*, **29**, 4003 (1959).

[22] F. K. Beilstein, "Handbuch der organischen Chemie," Vol. II, 1920, p. 401, Suppl. I, 1929, p. 186.

[23] A. N. Nesmeyanov and N. K. Kochetkov, *Izv. Akad. Nauk SSSR*, 77 (1950).

acid, m.p. 217–218° dec. (lit.[23] m.p. 178–179°). Characteristic bands in the infrared spectrum (KBr pellet) appeared at 2941, 2597, 1689, 1595, 1418, 1302, 1256, 989, 919, 855 (w), 825 (w), and 761 cm.$^{-1}$.

trans-**3-Chloro-2-methylacrylic acid** (VII) was prepared by the method of Ferris and Marks.[14] The n.m.r. spectrum in CCl$_4$ showed a quartet olefinic proton at δ 7.48 (J = 1.5 c.p.s.), a doublet methyl at δ 1.98 (J = 1.5 c.p.s.), and a singlet carboxyl proton at δ 12.7 in the ratio 1:3:1. The infrared spectrum showed characteristic peaks at 3077, 2985, 2865, 2632, 2564, 1709, 1631, 1429, 1391 (w), 1332, 1316 (w), 1267, 1175 (w), 1135, 1101 (w), 1013, 926, 866, 790, and 741 cm.$^{-1}$.

Acknowledgment.—The authors wish to thank Mr. C. B. Strow, Jr., who first measured the n.m.r. spectra of methyl *cis*-3-chloroacrylate and methyl *trans*-3-chloroacrylate.

The Base-Catalyzed Oxidation of Organic Sulfides with Molecular Oxygen[1a]

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The base-catalyzed autoxidation of α-sulfido carbanions has been investigated with several benzyl-type sulfides, aralkyl sulfides, and dialkyl sulfides. The observed rates of oxygen consumption were found to be dependent on sulfide structure, base strength, and the solvent. The results obtained suggest that the rate-determining step in these reactions is proton abstraction from the sulfide to form an α-carbanion which reacts rapidly with oxygen to produce both carboxylic and sulfonic acids. An anion-radical mechanism involving the formation of unstable α-hydroperoxide anions is proposed and discussed.

The oxidation of organic sulfides has been studied with a variety of oxidizing agents. Reagents such as nitric acid,[1] potassium permanganate,[1] chromic acid,[2] perbenzoic acid,[3] hydrogen peroxide,[4] manganese dioxide,[5] and periodate[6] produce sulfoxides, sulfones, and mixtures of sulfoxides and sulfones. Elegant work on the reactions of sulfides with hydroperoxides and the effect of hydrocarbon and hydroxylic solvents on such reactions has also been carried out.[7,8]

The radical-induced oxidation of organic sulfides with molecular oxygen in the liquid phase at moderate temperatures (45–75°) is reported to yield a complex mixture of products. The proposed mechanism of oxidation involves introduction of oxygen into the sulfide at the α-carbon atom followed by several secondary and competing reactions.[7] Alkyl and benzyl sulfides are resistant to oxidation by molecular oxygen in the absence of free-radical initiators.[9]

Recently, it has been demonstrated that polar solvents have a marked effect on the anionic oxidation of mercaptans[10–13] and weakly acidic hydrocarbons such as toluene.[14] Studies in the absence of oxygen have demonstrated that various sulfones, sulfoxides, sulfides, and disulfides are decomposed to olefins in the presence of potassium *t*-butoxide and a polar solvent.[15–17] Owing to the unreactivity of aliphatic and benzylic sulfides toward molecular oxygen in the absence of free-radical initiators, the base-catalyzed oxidation of these compounds has been investigated in the polar solvent, hexamethylphosphoramide (HMPA).

Results

The base-catalyzed oxidation of benzyl sulfide with molecular oxygen has been studied under a variety of conditions. In potassium *t*-butoxide–HMPA, benzyl sulfide yielded benzoic acid and stilbene as the reaction products at 23.5 and 80°. When potassium hydroxide was employed as the base in HMPA, the reaction products were benzoic acid and a trace of stilbene. In potassium *t*-butoxide–*t*-butyl alcohol media a low yield of benzoic acid was obtained after 22 hr. of oxidation at 80°. Specific reaction conditions employed and product yields obtained under these conditions have been summarized in Table I. Other suspected intermediates such as benzaldehyde, benzyl alcohol, α-toluenesulfonic acid, and benzyl sulfoxide could not be detected by the analytical methods employed. The rates of oxidation of benzyl sulfide under the above conditions are also included in Table I. Each rate of oxidation was calculated from the moles of oxygen consumed as a function of time during the initial stages of the reaction using the oxidation apparatus described in the Experimental section. When necessary, corrections for solvent oxidation were made. All rate plots obtained were similar to those shown in Figure 1. Initially, the oxidation is rapid and the moles of oxygen consumed are linear with time. As the reactions progressed oxygen consumption decreased as indi-

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[1a] NOTE ADDED IN PROOF.—For a preliminary account, see T. J. Wallace *et al.*, *Chem. Ind.* (London), 945 (1965).

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