limits 3.3–3.4 and 3.0–3.1, respectively. These values are consistent with those obtained from the data in Table I through use of Smyth's equations, as indicated in the following paragraph.

Assuming all tetrahedral angles of 109.5° the equations of Lewis and Smyth[2] may be rearranged into the following quadratic form most suitable for algebraic substitution

$$m_3^2 + 6 \cos \theta \, [(m_2 + m_1 \cos \theta)m_3 + m_2(m_1 + m_2) + m_1 \cos \theta(m_1 \cos \theta + 2m_2)] + 3(m_1^2 + m_2^2) - \mu^2 = 0$$

Here m_3 is the P → O (or P → S) bond moment, m_1 the C–O moment, m_2 the covalent P–O moment, $\cos \theta$ is -0.334, and μ is the total moment determined in benzene solution. Using $m_1 = 1.1$, $m_2 = 1.2$, and the appropriate average moments of 3.08 and 2.83 from Table I, the values 3.3 and 3.0 are obtained for the P → O and P → S bond moments, respectively.

The value of 3.5 assigned by Smyth[1] for the P → O moment in $POCl_3$ is based on the addition of the $POCl_3$ moment (2.4) and a value of 1.1 for the PCl_3 moment, the origin of this latter value being obscure. If a P–Cl bond moment of 0.81 (based on 1.1 for PCl_3) is used, and correction made for angles of 106° in $POCl_3$,[12] then the P → O moment calculates about 3.35 D. If the literature value of 0.90 for PCl_3 in benzene solution[13] is accepted and added to 2.4 for $POCl_3$, the value 3.3 is obtained for P → O. The slight additional correction for Cl–P–Cl widening to 106° lowers the value to about 3.15 D. This slightly lower value than 3.3 is easily attributable to a slight polarization of the oxygen atom by the chlorine atoms in a manner similar to that which produced a strong inductive effect on the sulfur atom.

Although an analysis of the nature reported here is necessarily approximate, it appears that 3.3 ± 0.1 and 3.0 ± 0.1 are optimum values for the P → O and P → S semi-polar bond moments, respectively, when these bonds are not appreciably influenced by induction.

[13] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Mass. Inst. of Technology, Cambridge, Mass., 1948.

LUBBOCK, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEXAS TECHNOLOGICAL COLLEGE]

Electric Moments of Some Unsaturated Carbonyl Compounds[1]

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Electric moments have been determined in benzene and dioxane solution for a number of unsaturated methyl ketones and aldehydes having moments in the range 3.20 to 3.58 *D*. The results are interpreted in terms of resonance, preferred configurations and solvent effects. Analysis of this and previous work indicates that aliphatic unsaturated aldehydes, and β-disubstituted ketones, have predominantly the s-*trans*, and s-*cis* configurations, respectively. The β-monosubstituted unsaturated ketones appear to have approximately equal contributions from both the s-*trans* and s-*cis* configurations.

This work may be considered as part two of work previously reported[2] relative to preferred configurations in unsaturated methyl ketones having moments below 3.0 *D*. Results are now reported on molecules having moments greater than 3.0 *D*, with further structural analysis.

Experimental

Preparation and Purification of Compounds.—Boiling points, unless otherwise indicated, have been corrected to 760 mm.

Crotonaldehyde, a Matheson Co. product, was carefully dried and fractionated just prior to use; b.p. 102°, $n^{25}_{\rm D}$ 1.4342, d^{25}_4 0.848.

Ethylideneacetone was prepared by an aldol type condensation in which acetone and acetaldehyde were condensed with dilute NaOH as catalyst.[3] It was purified by careful fractionation at reduced pressure; b.p. 122–123°, $n^{25}_{\rm D}$ 1.4333, d^{25}_4 0.8592.

α-Methylethylidene acetone was prepared by a condensation of acetaldehyde and ethyl methyl ketone at −10°, using dry HCl as catalyst.[4] The product was twice fractionated at reduced pressure; b.p. 138°, b.p. 63° (49 mm.), $n^{25}_{\rm D}$ 1.4469, d^{25}_4 0.8697.

Benzylideneacetone, an Eastman Kodak Co. white label product, was recrystallized twice from ligroin; m.p. 40°.

Methyl *p*-tolyl ketone, an Eastman Kodak Co. white label product was carefully fractionated twice at reduced pressure; b.p. 116° (26 mm.), $n^{25}_{\rm D}$ 1.5313, d^{25}_4 0.999.

***p*-Tolualdehyde**, an Aldrich Chemical Co. research grade material, was used without further purification; b.p. 204°, $n^{25}_{\rm D}$ 1.5432, d^{25}_4 1.0155.

Benzene and dioxane were purified as indicated in earlier work.[2]

Measurements and Calculations.—The general procedure was as indicated in earlier work.[2] Moments were calculated from the equation

$$\mu = 0.2208(P_{2\infty} - 1.05\, MR_{\rm D})^{1/2}$$

Molar refractions for liquids were calculated from densities and refractive indices; for benzylideneacetone atomic refractions were used with an estimate for a slight exaltation.

Discussion of Results

Table I lists the pertinent data relating to the moments which have been determined. Configurational results based on this and previous work[2,5,6] are indicated in Table II.

Data for β-methylcrotonaldehyde and α,β-dimethylcrotonaldehyde have been estimated. The s-*trans* configuration is indicated for all the aldehydes (except *p*-tolualdehyde, whose two preferred configurations are equivalent). Ketones with residues of three or less carbon atoms as anchorage for the carbonyl group also appear to be predominantly s-*trans*. The s-*cis* configuration is indicated for mesityl- and methylmesityl oxides, in which steric hindrance occurs between the carbonyl

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[1] Presented at the 10th Southwest Regional Meeting of the American Chemical Society, Forth Worth, Texas, December 2–4, 1954.

[2] G. K. Estok and J. H. Sikes, THIS JOURNAL, **75**, 2745 (1953).

[3] V. Grignard and M. Fluchaire, *Ann. Chim.*, **9**, 10 (1928).

[4] L. E. Hinkel, *J. Chem. Soc.*, 817 (1931).

[5] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *ibid.*, **2957** (1949).

[6] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Mass. Inst. of Technology, Cambridge, Mass., 1948.

TABLE I

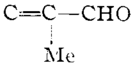
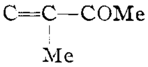
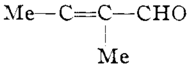
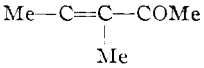
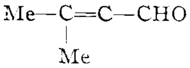
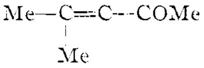
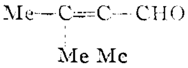
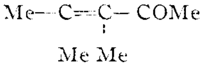
SLOPE-INTERCEPT DATA, POLARIZATIONS AND ELECTRIC MOMENTS (25°)

(Benzene, ϵ = 2.273, d = 0.873; dioxane, ϵ = 2.21, d = 1.028.)

	Solvent	$\frac{\Delta(\Delta\epsilon/w_2)}{\Delta w_2}$	$(\Delta\epsilon/w_2)_\infty$	$\frac{\Delta(\Delta d/w_2)}{\Delta w_2}$	$(\Delta d/w_2)_\infty$	$P_{2\infty}$	MR_D	μ
Crotonaldehyde	Benzene	3.4	18.96	−0.3	−0.013	274.5	(21.52)	3.50
	Dioxane	3.4	22.71	.5	− .227	285.4		3.58
Ethylideneacetone	Benzene	15	13.08	.0	− .032	236.7	(25.45)	3.20
	Dioxane	16	15.70	.0	− .202	243.8		3.26
α-Methylethylideneacetone	Benzene	11	11.25	.0	− .006	241.9	(30.14)	3.20
	Dioxane	1.7	13.57	.0	− .199	252.3		3.28
Benzylideneacetone	Benzene	4.3	8.40	.0	.136	274.0	(45.8)	3.31
	Dioxane	6.3	9.99	.0	− .001	281.3		3.37
p-Tolyl methyl ketone	Benzene	3.7	8.48	.0	.115	254.0	(41.57)	3.20
	Dioxane	3.7	10.20	.1	− .027	263.3		3.27
p-Tolualdehyde	Benzene	3.4	9.72	.0	.123	255.1	(37.30)	3.24

TABLE II

MOMENTS AND CONFIGURATIONS OF UNSATURATED ALDEHYDES AND KETONES

Config.	μ benz.	Aldehyde	Ketone	μ benz.	Config.
s-*trans*	(2.90)[5]	$C{=}C{-}CHO$	$C{=}C{-}COMe$	(2.98)[6]	s-*trans*
s-*trans*	(2.72)[6]	 $C{=}\underset{\substack{\vert\\ Me}}{C}{-}CHO$	 $C{=}\underset{\substack{\vert\\ Me}}{C}{-}COMe$	(2.74)[2]	s-*trans*
s-*trans*	3.50	$Me{-}C{=}C{-}CHO$	$Me{-}C{=}C{-}COMe$	3.20	(both)
s-*trans*	(3.39)[6]	 $Me{-}C{=}\underset{\substack{\vert\\ Me}}{C}{-}CHO$	 $Me{-}C{=}\underset{\substack{\vert\\ Me}}{C}{-}COMe$	3.20	(both)
s-*trans*	3.6 estimated	 $Me{-}\underset{\substack{\vert\\ Me}}{C}{=}C{-}CHO$	 $Me{-}\underset{\substack{\vert\\ Me}}{C}{=}C{-}COMe$	(2.79)[2]	s-*cis*
s-*trans*	3.5 estimated	 $Me{-}\underset{\substack{\vert\\ Me}}{C}{=}\underset{\substack{\vert\\ Me}}{C}{-}CHO$	 $Me{-}\underset{\substack{\vert\\ Me}}{C}{=}\underset{\substack{\vert\\ Me}}{C}{-}COMe$	(2.88)[2]	s-*cis*
s-*trans*	(3.63)[5]	$C_6H_5{-}C{=}C{-}CHO$	$C_6H_5{-}C{=}C{-}COMe$	3.31	(both)
(both)	3.24	$Me{-}C_6H_4{-}CHO$	$Me{-}C_6H_4{-}COMe$	3.20	(both)

methyl group and one of the two β-methyl groups. In the remaining cases the ketones appear to have approximately equal contributions from both the s-*cis* and s-*trans* preferred configurations (except p-tolyl methyl ketone, whose two configurations are equivalent).

In this last connection three points of interest need be considered which, when taken together, indicate that some of the ketones exist about equally in both configurations.

First, it is to be noted that the moments for ethylideneacetone, α-methylethylideneacetone and benzylideneacetone (3.20, 3.20 and 3.31, respectively) are considerably lower than those for the analogous aldehydes (3.50, 3.39 and 3.63). This would be expected if the ketones have approximately equal contributions of s-*trans* (high moment) and s-*cis* (low moment) configurations.

Secondly, it is noted that the α-methyl group of tiglaldehyde (α-methylcrotonaldehyde) causes a lower moment (3.39) than that for crotonaldehyde (3.50), an effect typical of the s-*trans* configuration.[2] However the α-methyl group of α-methylethylideneacetone does not produce any change in the moment of this molecule (3.20) from that for ethylideneacetone itself (3.20). If the s-*cis* configuration predominated the moment would be expected to be a little higher.[2] Thus the indication is for about equal contributions of the s-*cis* and s-*trans* forms, with the influence of the α-methyl group being cancelled.

Thirdly, the question of the differences in the moments of these aldehydes and ketones being due to their difference in functionality must be answered. To check the comparative influences of the formyl and acetyl groups, two molecules were chosen each of whose two preferred configurations are identical (p-tolualdehyde and p-tolyl methyl ketone). Since moments of 3.30[6] and 3.21,[5] respectively, were previously reported for these compounds, it was felt desirable to redetermine these moments to see if the difference might not be smaller when determined by the same worker. The values of 3.24 and 3.20 found indicate very little difference due to functionality.

It is thus indicated that the lower moments of the ketones under discussion arise because these compounds exist about equally in both the s-*cis* and s-*trans* forms.

The moment values in dioxane solution lead to the same configurational conclusions as those in benzene solution, and further indicate that only the normal solvent effect is operative.

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