The Electronic Absorption Spectra of Carboxylate Derivatives. III. Effects of Solvent and Structure on the Absorption Spectra of α,β-Unsaturated Esters[1,2]

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The energies and intensities of the allowed ($\pi \rightarrow \pi^*$) and forbidden ($n \rightarrow \pi^*$) electronic transitions of a variety of esters of three representative α,β-unsaturated carboxylic acids have been determined. Methyl substitution at the α carbon of the ester appears to decrease the energy of both transitions, while methyl substitution at the β carbon decreases the energy of the $\pi \rightarrow \pi^*$ band but increases that of the $n \rightarrow \pi^*$ transition. The allowed transition is insensitive to the nature of the alkoxy group, but *t*-butyl esters exhibit the same bathochromic shift of the $n \rightarrow \pi^*$ maximum as do *t*-butyl esters of saturated carboxylic acids. An argument is presented indicating this shift to be due to steric interaction between the *t*-butyl group and the nonbonding p orbital of the carbonyl oxygen. The effect of solvent polarity on the spectra of the esters as well as on the spectra of the corresponding acids is also discussed.

The α,β-unsaturated ester system is basically a modified butadiene structure. An approximate energy level diagram, determined from simple Huckel MO calculations (neglecting overlap)[4] is presented in Figure 1. By analogy with α,β-unsaturated ketones and aldehydes,[5] one should expect to observe two different transitions in the accessible ultraviolet, namely $\pi_3 \rightarrow \pi_4^*$ and $n \rightarrow \pi_4^*$, as indicated in Figure 1. Compared with the corresponding ketones and aldehydes, all electronic levels will be modified by the presence of the alkoxy oxygen directly attached to the carbonyl group. In saturated esters this effect results in a hypsochromic shift of the $n \rightarrow \pi^*$ transition of about 70 mμ (*ca.* 33 kcal./mole).[1b] If a similar shift occurs in the spectrum of conjugated ethylenic esters, the $n \rightarrow \pi^*$ band should be near 240 mμ.[6] It has been amply verified that the effect of the alkoxy group on the $\pi \rightarrow \pi^*$ band of α,β-unsaturated esters is relatively minor, being a hypsochromic shift of 5–10 mμ (2–5 kcal./mole) relative to the corresponding transition of methyl vinyl ketone,[5,7] but until recently, evidence for the observation of the $n \rightarrow \pi^*$ transition has been sparse.[8] Lately, Weiss and Ziffer have shown that the vapor phase spectrum of β,β-dimethylacrylic acid exhibits a distinct maximum near 245 mμ which they have assigned to the $n \rightarrow \pi^*$ transition on the basis of its low intensity and the Cotton effects and circular dichroism maxima exhibited by related optically active carboxylic acids near this wave length.[9] These authors also pointed out that the Cotton effects observed in the rotatory dispersion spectra of certain optically active α,β-unsaturated lactones[10] were probably due to this same transition.[9]

As part of a continuing investigation of the spectra of acyl derivatives,[1] we wish to report our results concerning acrylate, methacrylate, and *trans*-crotonate esters. Preliminary work indicated that the $n \rightarrow \pi^*$ band could be observed in the spectra of acrylate esters in nonpolar solvents, but apparently was obscured by the intense $\pi \rightarrow \pi^*$ band in polar media and in the spectra of substituted acrylates.[1a] In the present study, the effects of molecular structure and solvent on both transitions have been examined. In particular, the effects of methyl substitution on the double bond, of alkyl substitution in the alkoxy portion of the ester, and of solvent polarity on each transition have been studied.

Results and Discussion

The wave length of maximum absorption for the high intensity band, and for the low intensity band, whenever it could be observed, were carefully determined in a series of solvents of different polarities. The absorption maxima and molar absorptivities (ϵ) for the $\pi \rightarrow \pi^*$ transitions are presented in Table I. In Table II are shown similar data for the $n \rightarrow \pi^*$ transitions.

The Allowed Transition.—The $\pi \rightarrow \pi^*$ transition of acrylate esters is found between 1917 and 1930 Å. in isooctane. The molar absorptivities (ϵ) are of the order of 10^4, varying between 11,000 and 17,000. On attaching a methyl group to the double bond, a bathochromic shift of 9 to 10 mμ occurs as previously noted.[7] In isooctane the shift is almost identical for methacrylates and crotonates, indicating little difference in effectiveness of substitution at the α or β position. There does seem to be a small but definite difference between crotonate and methacrylate transition energies, the band in crotonates always appearing at a few angstroms longer wave length.

The intensity of the $\pi \rightarrow \pi^*$ transition is affected by the position of the methyl group. The molar absorptivities of crotonates fall in the same range as those of acrylates, with most of the values clustered near 15,000. Methacrylates, on the other hand, tend to have molar

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[1] (a) Paper I: W. D. Closson, S. F. Brady, E. M. Kosower, and P. C. Huang, *J. Org. Chem.*, **28**, 1161 (1963); (b) paper II: W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, **86**, 2384 (1964).

[2] (a) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Institutes of Health. (b) Presented before the Organic Division at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[3] Supported by a National Institutes of Health Traineeship, Grant No. 1Tl-GM-1130-02, in the Department of Chemistry, Columbia University, 1964–1965.

[4] The procedure used was essentially that discussed in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 133–135, 209. The value for the carbonyl n-electron level was determined from the experimental value of the $n \rightarrow \pi^*$ transition energy of methyl acrylate and the calculated β value for acrylate esters.

[5] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 204–209.

[6] Using methyl vinyl ketone as reference compound: λ_{max} 330 mμ in isooctane.

[7] A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

[8] H. E. Ungnade and J. Ortega, *J. Am. Chem. Soc.*, **73**, 1564 (1951); E. A. Braude, *Ann. Rept. Chem. Soc.*, **42**, 105 (1945); H. Mohler and H. Lohr, *Helv. Chim. Acta*, **21**, 485 (1938); H. Ley and H. Wingchen, *Ber.*, **67**, 501 (1934); W. Luthy, *Z. Phys. Chem.*, **107**, 285 (1923).

[9] U. Weiss and H. Ziffer, *J. Org. Chem.*, **28**, 1248 (1963).

[10] (a) J. A. Giles and J. N. Schumacher, *Tetrahedron*, **14**, 246 (1961); **18**, 260 (1962). (b) See also, P. Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco Calif., 1965, pp. 278–284, and references listed therein.

TABLE I

ABSORPTION MAXIMA OF $\pi \rightarrow \pi^*$ TRANSITIONS OF α,β-UNSATURATED ESTERS

Solvent	λ_{max}, Å. ($\epsilon \times 10^{-3}$) Methyl	Ethyl	Isopropyl	*t*-Butyl
		Acrylate		
Isooctane	1917 (16.3)	1923 (13.9)	1930 (17.1)	1927 (12.5)
Acetonitrile	1923 (16.4)	1930 (10.6)	1933 (13.7)	1935 (14.5)
Ethanol	1922 (15.5)	1936 (14.0)	1946 (14.1)	1939 (16.0)
Methanol	1925 (16.1)	1933 (13.0)	1945 (16.1)	1939 (17.3)
TFP[a]	1929 (16.6)	1937 (11.2)	1946 (14.3)	1941 (16.0)
Water	1949 (15.2)	1958 (11.5)	1959 (*b*)	1963 (*b*)
		Methacrylate		
Isooctane	2016 (10.4)	2012 (11.3)	2007 (12.0)	2015 (10.7)
Acetonitrile	2124 (10.2)	2022 (10.9)	2017 (11.3)	2023 (10.8)
Ethanol	2030 (10.2)	2030 (10.5)	2024 (11.1)	2032 (10.0)
Methanol	2032 (10.1)	2034 (10.5)	2026 (10.5)	2033 (10.0)
TFP[a]	2046 (10.1)	2044 (8.90)	2035 (10.6)	2043 (9.45)
Water	2066 (*b*)	2066 (*b*)	2053 (*b*)	2064 (*b*)
		trans-Crotonate		
Isooctane	2017 (15.1)	2019 (15.6)	2018 (15.2)	2022 (13.9)
Acetonitrile	2048 (15.0)	2049 (15.2)	2046 (15.9)	2051 (12.7)
Ethanol	2053 (15.1)	2047 (14.8)	2047 (15.8)	2050 (11.6)
Methanol	2056 (15.4)	2058 (15.0)	2060 (13.3)	2055 (15.5)
TFP[a]	2077 (16.0)	2075 (16.5)	2073 (14.7)	2071 (16.3)
Water	2099 (16.1)	2089 (16.8)	2097 (14.4)	2097 (*b*)

[a] 2,2,3,3-Tetrafluoropropanol. [b] Saturated solution.

TABLE II

ABSORPTION MAXIMA OF $n \rightarrow \pi^*$ TRANSITIONS OF α,β-UNSATURATED ESTERS

Solvent	λ_{max}, Å. (ϵ_{max}) Methyl	Ethyl	Isopropyl	*t*-Butyl
		Acrylate		
Isooctane	2439 (68)	2430 (72)	2434 (74)	2497 (55)
Acetonitrile	2371 (81)	2391 (92)	2399 (92.5)	2463 (68)
Ethanol	2350 (87)	237[a] (96)	238[a] (96)	2440 (69)
Methanol	234[a] (89)	...	...	2434 (64)
TFP[b]	...	...	...	240[a] (...)
		Methacrylate		
Isooctane	...	...	...	2512 (92)
Acetonitrile	...	...	...	2448 (119)
Ethanol	...	...	...	240[a] (...)
		trans-Crotonate		
Isooctane	...	...	...	2435 (113)
Acetonitrile	...	...	...	241[a] (...)

[a] Approximate position of shoulder in millimicrons. [b] 2,2,3,3-Tetrafluoropropanol.

absorptivities near 10,000. This is probably due to a somewhat greater deviation from copolanarity of the π system in methacrylates than in the cases of the other two types of ester. While the conformation about the central single bond in simple dienes[11] and ethylenic aldehydes[12] is preferably *s-trans*, in more substituted cases such as ethylenic ketones and α,β-unsaturated carboxylates, the situation is much less clear, and the preferred conformation is often probably solvent and/or structure dependent.[12a,13] Assuming that the preferred conformation about the carbon–oxygen single bond is *s-trans* as in most esters,[15] the two most likely conformations are the *s-trans–s-trans* and *s-cis–s-trans* as shown. In either of these, it would seem reasonable that methacrylates (R′ = CH_3) should have the carboxyl group somewhat more twisted from coplanarity with the double bond than the other two esters. This deviation would exhibit itself more quickly in diminished intensity than in increased energy of the $\pi \rightarrow \pi^*$ band,[12a] and a minor enhancement of twist would accommodate the data.

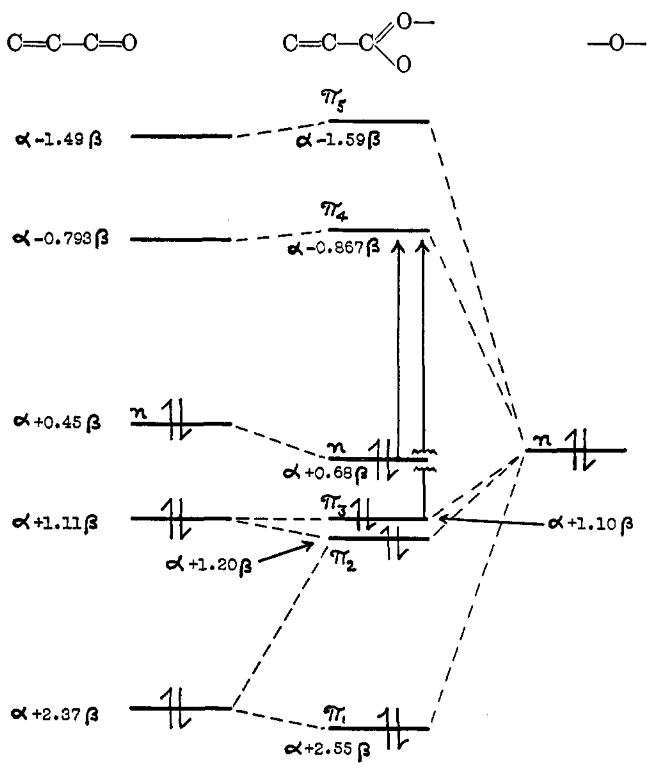
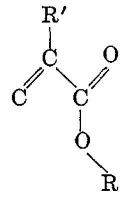
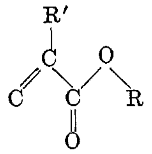


Figure 1.—Energy level scheme for the α,β-unsaturated ester system.



s-trans–s-trans
I



s-cis–s-trans
II

Variation of the alkoxy group of the esters seems to have no major effect on the $\pi \rightarrow \pi^*$ transition. The differences in energy and intensity of the intense band of the methyl, ethyl, isopropyl, and *t*-butyl esters of a given ethylenic acid appear to be small and random in nature (Table I).

The effect of solvent polarity on the energy of the $\pi \rightarrow \pi^*$ transition is similar to that observed for α,β-unsaturated ketones.[13c,14] In Table III are presented data describing the solvent sensitivity of the various ester $\pi \rightarrow \pi^*$ bands and those of certain ketones. The data in the second column [E_T(isooctane) − E_T(water)] are self-explanatory; the *m* values

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(11) J. G. Aston, G. Szasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); R. G. Parr and R. A. Mulliken, *ibid.*, **18**, 1338 (1950).

(12) (a) J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949); (b) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951).

(13) (a) E. A. Braude and E. S. Waight, *Progr. Stereochem.*, **1**, 126 (1954), and references listed therein; (b) M. C. Whiting, quoted by Kosower[14a]; (c) E. M. Kosower, G.-S. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **83**, 3147 (1961); (d) R. S. Armstrong, M. J. Aroney, and R. J. W. LeFevre, *Australian J. Chem.*, **15**, 703 (1962).

(14) (a) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958); (b) E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 281 (1959).

(15) (a) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960), and references listed therein; (b) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 303-309; (c) D. J. Millen, *Progr. Stereochem.*, **3**, 138 (1962); (d) R. J. W. LeFevre and A. Sundaram, *J. Chem. Soc.*, 3904 (1962).

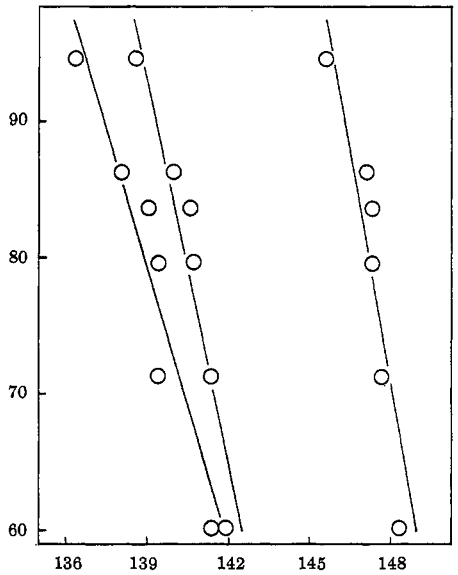


Figure 2.—E_T (transition energies) *vs.* Z (solvent polarity values) for the $\pi \rightarrow \pi^*$ transition of *trans*-*t*-butyl crotonate (left), *t*-butyl methacrylate (middle), and *t*-butyl acrylate (right).

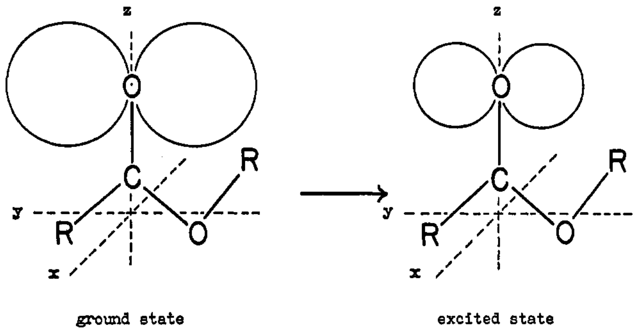


Figure 3.—Approximate volume change of the oxygen p_Y orbital during the $n \rightarrow \pi^*$ transition of an ester.

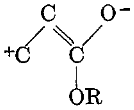
TABLE III

SOLVENT SENSITIVITIES OF $\pi \rightarrow \pi^*$ TRANSITIONS

Compound	E_T(isooctane) − E_T(water)[a]	m[b]
Methyl acrylate	2.45	−0.085
Ethyl acrylate	2.65	−0.084
Isopropyl acrylate	2.19	−0.068
t-Butyl acrylate	2.72	−0.085
Methyl methacrylate	3.43	−0.110
Ethyl methacrylate	3.72	−0.112
Isopropyl methacrylate	3.19	−0.095
t-Butyl methacrylate	3.37	−0.102
Methyl crotonate	5.53	−0.158
Ethyl crotonate	4.74	−0.142
Isopropyl crotonate	5.33	−0.154
t-Butyl crotonate	5.05	−0.147
Mesityl oxide		−0.18[c]
Δ^2-Cyclohexenone	7.4	−0.20[c]
Isophorone	9.0	−0.24[c]
2,2-Dimethyl-3,4-dihydro-4-pyrone	6.9	−0.20[c]

[a] In kcal./mole. [b] Slope of plot of E_T *vs.* Z ($E_T = mZ + b$). [c] Data taken from ref. 13c.

in the third column are slopes of the least-square plots of E_T *vs.* Z, where Z is Kosower's solvent polarity value.[14a,16,17] The magnitude of the m values is similar to the approximate value of −0.10 observed for ethyl β-aminocrotonate by Hofmann, Kosower, and Wallenfels,[18] but smaller than that of the ethylenic ketones shown in Table III. The greater solvent sensitivity of the $\pi \rightarrow \pi^*$ band of the ketones may simply be due to their degree of substitution and, in the cases of cyclic compounds, greater rigidity and lack of steric interference with solvation. Of more interest are the pronounced differences in solvent sensitivities of acrylates, methacrylates, and crotonates themselves. The excited state resulting from the allowed transition should receive a greater contribution from the polarized structure (III) below than does the ground-state hybrid. Substitution at the terminal carbon should stabilize the dipolar form and increase charge density at the ends of the conjugated system in the excited state, as well as bring about a lesser contribution of the dipolar form to the ground-state structure. Thus, interaction of the excited state with solvent should increase, since the solvent molecules in the cybotactic region are already close to the proper orientation for solvation of the "Franck–Condon excited state."[19] It is not surprising, then, that crotonates exhibit the largest solvent sensitivity and acrylates the smallest. The intermediate position of methacrylates is probably due to a slightly higher degree of ground-state solvation as compared with acrylate esters. This could result from the modest inductive effect of the methyl group on the carbonyl oxygen. A small increase in ground-state solvation will of course result in a magnified increase in solvation of the excited state. A plot of transition energy *vs.* Z for the $\pi \rightarrow \pi^*$ transition of *t*-butyl crotonate, methacrylate, and acrylate is shown in Figure 2.



III

Further conjugation of the acrylate system has the expected effect of increasing the intensity of the $\pi \rightarrow \pi^*$ transition and decreasing its energy.[5] Thus methyl β-vinylacrylate (IV) has λ_{max} 2428 Å. (ϵ 24,000) (isooctane) and λ_{max} 2450 Å. (ϵ 26,100) (acetonitrile). Conjugation of a triple bond with the carboxylate group, as in ethyl propiolate (V), appears to be poorer than that of a double bond. The maximum of the intense band in V appears to lie below 186 mμ, the limit of the instrument used.[20] This is contrary to the case with enynes,[21] but more work is needed on acetylenic systems before any conclusion can be drawn.

$CH_2{=}CH{-}CH{=}CHCO_2CH_3$
IV

$HC{\equiv}CCO_2CH_2CH_3$
V

The Forbidden Transition.—Originally, the prime problem of the $n \rightarrow \pi^*$ transition of α,β-unsaturated esters was simply one of seeing it, let alone investigat-

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(16) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3267 (1958).

(17) The Z value used for 2,2,3,3-tetrafluoropropanol was 86.3,[16] rather than the value 96.3 suggested in ref. 13c.

(18) D. Hofmann, E. M. Kosower, and K. Wallenfels, *J. Am. Chem. Soc.*, **83**, 3314 (1961).

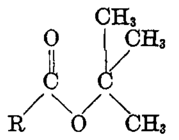
(19) G. C. Pimentel, *ibid.*, **79**, 3323 (1957).

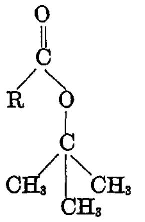
(20) Neither IV nor V exhibited a distinct maximum corresponding to an $n \rightarrow \pi^*$ transition. The spectrum of the propiolate ester in isooctane showed a shoulder near 242 mμ (ϵ 18) that may be due to this transition. The spectrum of IV is quite smooth, indicating its $n \rightarrow \pi^*$ transition is completely submerged.

(21) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold (Publishers) Ltd., London, 1954, pp. 88–90.

ing its properties.[1a,9] Fortunately, application of information gained from studies on saturated esters[16] allowed resolution of weak transition in all three classes of esters. This was done by using the bathochromic effect of a *t*-butyl group, attached to the ether oxygen. The resulting 5- to 6-mμ shift was sufficient to isolate even the $n \rightarrow \pi^*$ transition of crotonate esters. The technique can probably be applied to other carboxylate systems.

The origin of this "*t*-butyl effect" is of considerable interest. Previously, it was indicated that it was probably due to steric interaction with the carbonyl group, but the mechanism of interaction remained in doubt.[1b] As mentioned above, the nature of the alkoxy group has no particular effect on the $\pi \rightarrow \pi^*$ transition in any of the 72 cases investigated. Therefore, it is very unlikely that the *t*-butyl group has any effect on the π orbitals of the conjugated system. The source of the effect clearly involves raising the energy of the n-orbital. In the $n \rightarrow \pi^*$ transition, one of the major changes between the ground and the "Franck-Condon excited state" is a sharp decrease in electron-density of the nonbonding p_y orbital on oxygen, as shown in Figure 3. In the preferred *s-trans* conformation of an ester (VI), a *t*-butoxy group will sterically interfere with the p_y orbital, while the other alkoxy groups investigated can always direct a hydrogen toward the carbonyl group. In *t*-butyl esters, this steric interference will result in compression of the p_y orbital, raising its ground-state energy, but in the excited state this compression will be much smaller or absent. The overall effect should be a decrease in the $n \rightarrow \pi^*$ transition energy. In most of the cases studied this shift is about 3 kcal./mole. Assuming this is entirely due to increase in the ground-state energy as outlined above, it would appear that the *s-trans* (VI) and *s-cis* (VII) conformations of a *t*-butyl ester would be of about equal stability.[22] However, the dipole moment of *t*-butyl acetate[23] (1.93 D.) is about normal for an *s-trans* ester[14b] and far from the value expected for the *s-cis* conformation.[24] One can only conclude that the *s-trans* arrangement is still favored. (The *s-cis* arrangement would be expected to have its $n \rightarrow \pi^*$ band at longer wave lengths also,[1b] and thus a change in conformation would only be detectable through an increase in dipole moment.) This "*t*-butyl effect" has an interesting relationship to the "methyl effect" observed in the spectra of 2,4,6-trimethyl-3,5-dicarbethoxy-1,4-dihydropyridine (VIII) where it has been suggested that steric repulsion between the 4-methyl group and the carbethoxy carbonyl oxygen in the *excited state* ($\pi \rightarrow \pi^*$) leads to a hypsochromic shift of about 4.4 kcal./mole.[18] The steric relationship between carbonyl oxygen and alkyl group in VIII and in a *t*-butyl ester are not quite the same (at least one of the methyls of the *t*-butyl group in an *s-trans* ester must be closer to the carbonyl oxygen than is the 4-methyl group in VIII), but it is not clear why one case apparently results in a ground-state and the other case an excited-state effect.


VI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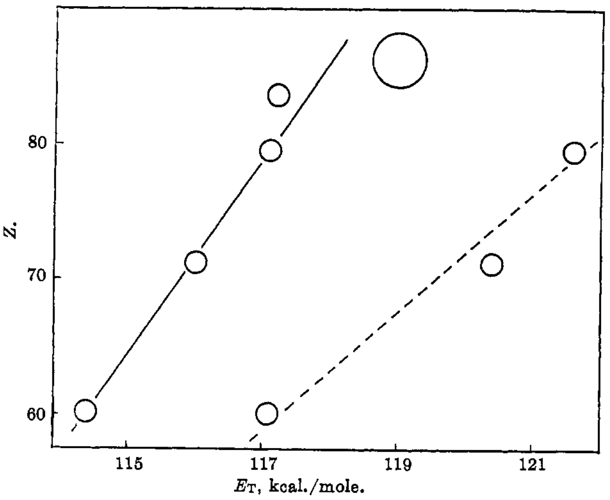
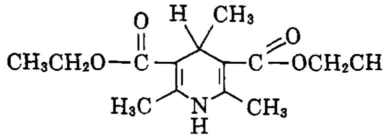


Figure 4.—E_T (transition energies) *vs.* Z (solvent polarity values) for the $n \rightarrow \pi^*$ transition of *t*-butyl acrylate (left) and methyl acrylate (right).


VIII

The positions of the $n \rightarrow \pi^*$ maxima of a series of acrylate esters (Table II) clearly show the operation of this "*t*-butyl effect." In isooctane the $n \rightarrow \pi^*$ transitions of *t*-butyl crotonate and *t*-butyl methacrylate are separated from the $\pi \rightarrow \pi^*$ band far enough to allow resolution of maxima. Normally, attachment of electron-supplying substituents such as alkyl groups to the π system has a hypsochromic effect on the $n \rightarrow \pi^*$ band.[13c] Assuming there is no peculiar effect of the *t*-butoxy group on the positioning of the forbidden band, one would expect the band in crotonates and methacrylates at shorter wave length than in the case of acrylates. The maximum for *t*-butyl crotonate is displaced 6 mμ to shorter wave length from that of the acrylate ester, and thus falls into line. *t*-Butyl methacrylate, however, has its forbidden transition at slightly *longer* wave length.[26] This could be due to a greater inductive effect of an α-methyl group or to an enhancement of the "*t*-butyl effect" from additional steric interaction of the

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[22] R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959); N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 264 (1963).

[23] H. L. Donle, *Z. physik. Chem.*, **B14**, 326 (1931).

[24] The dipole moment of the *s-cis* conformation of an ester should be similar to that of a lactone[22]; *i.e.*, it should be close to 4 D., the magnitude of the dipole moment of butyrolactone.[25]

[25] G. R. Clemo and J. H. Jack, *Chem. Ind.* (London), 195 (1953); G. F. Longster and E. E. Walker, *Trans. Faraday Soc.*, **49**, 228 (1953); R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

[26] It is likely that the observed maxima of the $n \rightarrow \pi^*$ transitions of all three esters are at shorter wave length than the position of the true maximum, owing to the effect of overlap with the more intense $\pi \rightarrow \pi^*$ band. This shift would be greater for crotonates and methacrylates where the intense band is closer, and thus the anomalous position of *t*-butyl methacrylate is even more striking. The higher molar absorptivities of the $n \rightarrow \pi^*$ bands of *t*-butyl crotonate and methacrylate are a reflection of this overlap. Initially,[1a] on the basis of unresolved spectra, it was postulated that the $n \rightarrow \pi^*$ bands of the three types of esters fall in the expected order.

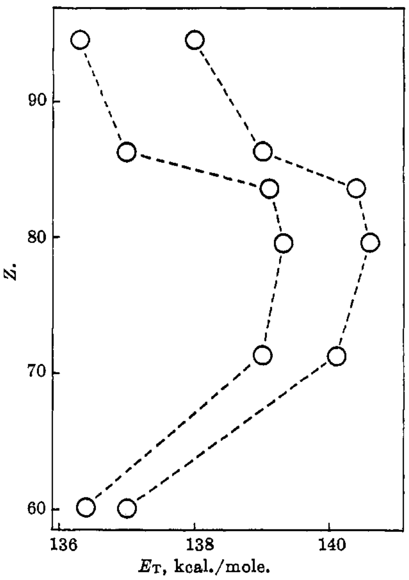


Figure 5.—E_T (transition energies) *vs.* Z (solvent polarity values) for the $\pi \rightarrow \pi^*$ transition of *trans*-crotonic acid (left) and methacrylic acid (right).

carbonyl oxygen with the neighboring methyl group. Not enough data are available to distinguish between these possibilities, but the later reason seems more plausible.

In the case of *t*-butyl acrylate, the $n \rightarrow \pi^*$ band is separated far enough from the intense absorption to allow determination of its solvent sensitivity. A plot of transition energy *vs.* Z is shown in Figure 4 for *t*-butyl acrylate, as well as a few points for methyl acrylate. For the former ester, the solvent sensitivity, m, determined from the least-squares line fitted to the first four points, is +0.129. This is well within the range of m values observed for saturated esters (0.10 to 0.15)[1b] and quite similar to that observed for many saturated ketones.[14a,27] It is, however, less than the values observed for several cyclic α,β-unsaturated ketones (0.27 to 0.36).[13c] The three points obtained for methyl acrylate indicate a somewhat greater solvent sensitivity (m = *ca.* 0.2).

α,β-Unsaturated Carboxylic Acids.—In Table IV are presented the absorption maxima and molar absorptivities of the $\pi \rightarrow \pi^*$ bands of the three ethylenic acids in several solvents. It was not possible to observe the $n \rightarrow \pi^*$ transition clearly in any case. As can be seen from the data of Table IV and plots of E_T *vs.* Z for crotonic acid and methacrylic acid (Figure 5), the relationship between solvent polarity constant and $\pi \rightarrow \pi^*$ transition energy is far from linear. The evidence clearly indicates that isooctane is as polar a medium for crotonic acid as is water. The most likely cause of this anomalous behavior is variation in degree of dimerization of the free acids. In polar solvents, such as water and methanol, the equilibrium is probably far on the side of the dissociated species, while in nonpolar solvents, the dimer is probably the favored form.[28] While the association constants of these acids in isooctane are not known, that for crotonic acid in benzene is quite large (390 l./mole),[29] and in solvents such as heptane or carbon tetrachloride most acids apparently have association constants of several thousand liters per mole.[30] Thus, one is safe in assuming that, even at the concentrations used for our measurements (~10^{-3} M), the acids are completely dimerized in isooctane. It appears that this "self-solvation" stabilizes the ground (and excited states) as effectively as does the most polar solvent (water) used. It also implies that, as far as modification of electronic transitions of these acids is concerned, solvation of the carboxyl end of the molecule is most important.

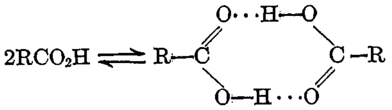


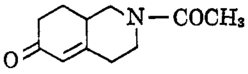
TABLE IV

ABSORPTION MAXIMA OF THE $\pi \rightarrow \pi^*$ TRANSITION OF α,β-UNSATURATED ACIDS

Solvent	Acrylic acid	Methacrylic acid	*trans*-Crotonic acid
	λ_{max}, Å. ($\epsilon_{max} \times 10^{-3}$)		
Isooctane	1967 (13.1)	2083 (11.3)	2091 (14.8)
Acetonitrile	1915 (14.4)	2037 (11.2)	2054 (16.4)
Ethanol	(15.0)[a]	2032 (11.0)	2047 (15.9)
Methanol	(15.7)[a]	2035 (11.5)	2052 (15.6)
TFP[b]	1927 (14.4)	2057 (10.8)	2082 (16.1)
Water	1944 (15.0)	2070 (10.1)	2094 (16.0)

[a] Molar absorptivity at 186 mμ; the absorption maximum is at shorter wave length. [b] 2,2,3,3-Tetrafluoropropanol.

The pattern of the E_T *vs.* Z plots for the $\pi \rightarrow \pi^*$ transition of α,β-unsaturated acids (Figure 5) is reminiscent of that for the $\pi \rightarrow \pi^*$ transition of 3-acetyl-3-azabicyclo[4.4.0]dec-6-en-8-one (IX), reported by McElvain and Remy[31] and discussed by Kosower, Wu, and Sorensen.[13c] One might consider dimerization of IX rather than the suggested intramolecular solvation[13c] as an explanation of its anomalous spectral behavior.



IX

Experimental Section

Solvents.—All solvents were of at least Spectrograde quality. The 2,2,3,3-tetrafluoropropanol was a gift from Dr. E. O. Langerak of the Organic Chemicals Department, E. I. du Pont de Nemours and Co., and was purified by the method of Kosower and Huang.[27]

Materials.—Most of the esters and the α,β-unsaturated acids were obtained from commercial sources. The esters were distilled and their purity was checked by gas chromatography prior to use. Acrylic and methacrylic acid were carefully distilled before use, and *trans*-crotonic acid was recrystallized from pentane: m.p. 71–72°.

***trans*-*t*-Butyl Crotonate.**—To 17.2 g. (0.20 mole) of crotonic acid in a gas-washing bottle was added 25 ml. of ether and 2 ml. of concentrated sulfuric acid. Isobutene was then bubbled through the solution at a slow rate for 30 hr.; the solution was then washed with 10% sodium carbonate solution and dried with magnesium sulfate. Vacuum distillation afforded the colorless ester, b.p. 80–82° (97 mm.), $n^{20.5}_D$ 1.4250.

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Anal. Calcd. for $C_8H_{14}O_2$: C, 67.61; H, 9.86. Found: C, 67.53; H, 10.05.

t-**Butyl Methacrylate.**—To a solution of 11.5 g. (0.12 mole) of sodium *t*-butoxide in dry tetrahydrofuran under nitrogen was slowly added 10.4 g. (0.10 mole) of methacrylyl chloride with cooling. After addition of the acid chloride was complete, the solution was stirred for 30 min. and then poured into 100 ml. of ice–water. The organic layer was extracted with ether, and the ether layer then washed with dilute sodium bicarbonate solution and dried with magnesium sulfate. Distillation yielded 4.5 g. (26%) of pure *t*-butyl methacrylate, b.p. 134–136° [lit.[32] b.p. 135.8–136.3° (762 mm.), 72–74° (93 mm.)], $n^{20.5}_D$ 1.4169.

t-**Butyl acrylate** was prepared by a procedure similar to that used for *t*-butyl crotonate. It was purified by evaporative distillation at about 100 mm., $n^{20.5}_D$ 1.4100 (lit.[33] $n^{19.4}_D$ 1.4074).

Methyl β-vinylacrylate was prepared by the method of Kohler and Butler,[34] b.p. 78–79° (24 mm.) [lit.[34] b.p. 77–80° (25 mm.)].

Spectra.—All spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 0.01- and 0.1-cm. quartz cells. The details of the technique have been described previously.[1b]

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The Thermal Stability of (2-Substituted ethyl)diphenylphosphines. The Potent Neighboring Group Effect of the Trivalent Phosphorus Atom[1]

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(2-Hydroxyethyl)diphenylphosphine (Ib) underwent thermal decomposition to give *s*-ethylenebis(diphenylphosphine oxide). Similar cleavages were observed for its acetate (Ic) and benzoate (Id) derivatives with the formation of *s*-ethylenebis(diphenylphosphine). A common mechanism is proposed for these decompositions, involving the initial formation of a 1,1-diphenylphosphoniacyclopropane salt intermediate, owing to the anchimeric effect of the trivalent phosphorus atom.

Neighboring group participation by the nitrogen, oxygen, and sulfur atoms in promoting certain nucleophilic displacements is well documented,[2] but only recently has evidence emerged supporting such an anchimeric effect occurring in the case of a trivalent phosphorus atom.[3–6] The powerful nucleophilic properties of trivalent phosphorus compounds are well known,[7] and it was on this basis that a study of the chemical properties of several (2-substituted ethyl)diphenylphosphines was initiated to determine the feasibility of synthesizing potential antineoplastic phosphines.

Mann and Hitchcock[3] have reported the self-quaternization of (2-bromoethyl)ethylphenylphosphine at room temperature with the formation of 1,4-diethyl-1,4-diphosphoniacyclohexane dibromide. Rauhut, *et al.*,[4] have demonstrated the exothermic self-quaternization of dialkyl-2-acetoxyethylphosphines to give 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane diacetates at temperatures in excess of 80°, and in a number of examples, when a strict temperature control was imposed during the exothermic reaction, poly(dialkyl)ethylenephosphonium acetates were isolated. The analogous 3-acetoxypropylphosphines did not undergo a similar self-quaternization reaction even when heated to 300°.[4] Recently, Schweizer and Bach[8] have shown the unexpected formation of 1,2-ethylenebis(triphenylphosphonium bromide) from triphenyl phosphorus and 2-bromophenetole. A vinyl phosphonium salt was indicated as a reactive intermediate in the sequence of this reaction. The results which we have obtained with several (2-substituted ethyl)diphenylphosphines corroborates the observations of these researchers as to the unusual properties of the trivalent phosphorus atom and its interaction with potential phosphoniaethylation agents, generated from phosphonium salts.

2-(Butoxyethyl)diphenylphosphine (Ia), synthesized from diphenylphosphine and *t*-butoxyethyl chloride,[6] was stable at least to 350° without any apparent decomposition. Cleavage[9] of the ether gave (2-hydroxyethyl)diphenylphosphine (Ib) and, contrary to recent reports,[10] it was readily distilled under reduced pressure without decomposing into diphenylvinylphosphine. However, at elevated temperatures (305°) a violent exothermic reaction occurred with the formation of III[11] (55%) and diphenylvinylphosphine[10] (12%). Both the acetate Ic and the benzoate Id, prepared from the alcohol Ib were also thermally labile, decomposing into *s*-ethylenebis(diphenylphosphine) (IV),[12,13] diphenylvinylphosphine, and the appropriate acid. While Ib and Ic were stable at normal temperature, Id slowly underwent self-quaternization

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