and sometimes at 146°. This behavior was also shown by an authentic sample of aceto-*p*-toluide.

B. **At 100°.**—Similar results were obtained when aspirin was treated with a hot solution of *p*-toluidine in pyridine and the mixture heated in a boiling water-bath for 10 minutes. The one difference was that F_3 yielded three mg. (0.13%) of salicyclo-*p*-toluide, m.p. 156° (mixed m.p. 157°). This gave no colored complex with aqueous ferric chloride but gave a purple complex with aqueous *methanolic* ferric chloride.

An authentic sample of salicylo-*p*-toluide was prepared by the simpler version of the salol method.[12] The crude product melted at 156°. After recrystallization from ethanol it melted at 158°.

The Reaction of Aspirin with β-Naphthol.—To 1.80 g. (0.010 mole) mixed with 1.01 g. (0.0070 mole) of β-naphthol was added 2 ml. of pyridine. The resulting solution was heated for 10 minutes at 100° and cooled. The addition of 10 ml. of water caused the separation of an oil which soon solidified. The solid was filtered, washed twice with 5-ml. portions of water and air-dried. The product weighed 1.23 g., and melted at 69°. The combination of the wash waters with the original filtrate caused a further precipitation of 0.036 g. of product making the total 1.28 g. or 98% of theory. Recrystallization from aqueous methanol gave a product melting at 71° which exhibited no depression of the m.p. when mixed with authentic β-naphthyl acetate.

At room temperature the reaction between aspirin and β-naphthol was only slightly exothermic and remained incomplete after an hour.

The Reaction of Benzoylsalicylic Acid with *p*-Toluidine.—To 2.42 g. (0.010 mole) of benzoylsalicylic acid[13] was added a solution of 1.7 g. (0.015 mole) of *p*-toluidine in 2 ml. of pyridine. The resulting solution was heated for 10 minutes at 100° after which the mixture was cooled and 10 ml. of water added. The resulting precipitate was filtered (F_1), washed with 5 ml. of water (F_2) and then with a further 10 ml. of water. The precipitate was then ground in a mortar with 10 ml. of *M* sodium hydroxide, filtered (P_1) and washed with 5 ml. of water. The alkaline filtrate and washings were combined and treated with 1.2 ml. of glacial acetic acid. This produced a precipitate (P_2) which was filtered and washed with 10 ml. of water. F_2 was acidified with concd. hydrochloric acid. The resulting precipitate was filtered, washed with 5 ml. of water and treated with 20 ml. of *M* sodium bicarbonate solution which dissolved most of it. Filtration gave a small amount of solid which was treated like the original precipitate but with only 2 ml. of *M* sodium hydroxide (P_1' and P_2'). The filtrate was acidified with concd. hydrochloric acid (P_3).

The yield of benzo-*p*-toluide $[P_1 + P_1']$ was 1.83 + 0.015 = 1.85 g. (87%). The crude product melted at 153°. After recrystallization from methanol it melted at 158° and showed no depression when mixed with authentic benzo-*p*-toluide, m. p. 159°.

The yield of salicylo-*p*-toluide $[P_2 + P_2']$ was 0.182 + 0.008 = 0.19 g. (8%). It melted at 155°. After recrystallization from methanol it melted at 157° and showed no depression when mixed with the product prepared by the action of salol on *p*-toluidine (see above).

P_3 weighed 0.88 g. and melted at 155° indicating the possibility that it was mainly salicylic acid, admixed with a minor amount of benzoic acid.

At room temperature, the reaction of benzoylsalicylic acid with *p*-toluidine was not noticeably exothermic.

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(12) C. F. H. Allen and J. VanAllan, *Org. Syntheses*, **26**, 94 (1946).

(13) A. Einhorn, L. Rothlauf and R. Seuffert, *Ber.*, **44**, 3309 (1911).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CONNECTICUT, AND ILLINOIS INSTITUTE OF TECHNOLOGY]

Intermediates in the Reactions of Carboxylic Acid Derivatives. II. Infrared Absorption Spectra as Evidence for the Formation of Addition Compounds of Carboxylic Acid Derivatives[1,2]

BY MYRON L. BENDER

RECEIVED JULY 17, 1953

The infrared absorption spectra of a number of esters, amides and acids have been determined. Addition to the carbonyl group of these compounds was detected by observation of the intense absorption band in the region 1600–1800 cm.$^{-1}$ assigned to the carbon–oxygen double bond. Sodium methoxide, sodium ethoxide, and to lesser extent the corresponding lithium alkoxides add to the carbonyl group of ethyl trifluoroacetate in di-*n*-butyl ether solution whereas water, ethanol and various salts do not. The addition of sodium methoxide to ethyl trifluoroacetate is reversible. The effect of successive substitution by fluorine in ethyl acetate displaces the position of equilibrium toward the addition compound. Increasing the chain length of the ester reduces the extent of addition. Sodium alkoxide adds to ethyl oxalate and partially to trifluoroacetamide. No unequivocal evidence for ortho acid formation with perfluoro acids was obtained. The addition compounds are considered to be examples of stable intermediates in base-catalyzed transesterification. The parallel effect of structure on the addition equilibria and on the rates of basic ester hydrolysis indicates that the slow step in the hydrolysis probably is the addition of hydroxide ion to the carbonyl carbon atom.

Compounds formed by addition to the carbonyl group have been postulated as intermediates in a number of reactions involving acid derivatives and carbonyl compounds. For example, the isotopic oxygen exchange of acetone[3] probably proceeds through the hydrate; the isotopic oxygen exchange of benzoic acid[4] proceeds through the hydrate of the acid (the ortho acid); the hydrolysis of ethyl benzoate under both acidic and basic catalysis proceeds through the hydrate of the ester.[1] Presumably the reverse of the latter reaction, the esterification of benzoic acid with ethanol, proceeds through an intermediate compound formed by the addition of ethanol to the carbonyl group of benzoic acid.[1]

It was considered desirable to obtain information concerning stable representatives of the addition compounds which were postulated as intermediates above. There are several examples in the literature of stable hydrates of aldehydes and ketones in which there is definite evidence that the hydrate consists of the addition of a water molecule to the carbonyl double bond. Some of these are chloral,[5] fluoral,[6] trifluoroacetone,[7] hexafluoroacetylacetone,[8]

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(1) Previous paper: M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

(2) Presented at the Chicago Meeting of the American Chemical Society, September, 1953.

(3) M. Cohen and H. C. Urey, THIS JOURNAL, **60**, 679 (1938).

(4) I. Roberts and H. C. Urey, *ibid.*, **61**, 2580 (1939).

(5) M. M. Davies, *Trans. Faraday Soc.*, **36**, 1114 (1940).

(6) H. Shechter and F. Conrad, THIS JOURNAL, **72**, 3371 (1950).

(7) A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *ibid.*, **69**, 1819 (1947).

(8) B. G. Schultz and E. M. Larsen, *ibid.*, **71**, 3250 (1949).

(a dihydrate), mesoxalic acid,[5] triketohydrindene[5] and diphenyltriketone.[5] Caution must be exercised when speaking of hydrates, for the work of Lauder[9] shows that a hydrogen-bonded complex forms instantaneously when acetaldehyde and water are mixed and that this complex slowly forms the true addition product.

In addition to a hydrate, chloral forms a stable hemiacetal with ethanol.[10] Evidence for hemiacetal formation in alcohol–aldehyde system has been obtained by cryoscopic[11] and refractive index[12] measurements, and infrared,[13] Raman[12] and ultraviolet[11] spectra.

In contrast to the hydrates of aldehydes and ketones there appear to be no examples of stable hydrates of carboxylic acids in which the water molecule has been unequivocally shown to have added to the carbon–oxygen double bond to produce an ortho acid. X-Ray, Raman and infrared spectroscopic studies show that compounds such as oxalic acid dihydrate exist as hydrogen-bonded aggregates in the solid state.[14] Davies[5] reports that trichloroacetic acid hydrate appears to be largely dissociated in chloroform solution.

There appear to be only two examples of stable addition compounds of carboxylic acid derivatives, both involving esters. Ethyl trifluoroacetate and sodium ethoxide are reported to form $CF_3C(OC_2H_5)_2O^-Na^+$, the product being characterized by elemental analysis and ebullioscopic measurement.[15] It is reported that equimolar quantities of sodium ethoxide and diethyl oxalate produced an addition compound, $C_2H_5O_2CC(OC_2H_5)_2O^-Na^+$.[16,17]

In the present work, addition to the carbonyl group was easily detected by observation of the intense infrared absorption band in the region 1600–1800 cm.$^{-1}$, which is characteristic of all carboxylic acid derivatives and has been assigned to the carbon–oxygen double bond. The forward reaction expressed in the equilibrium 1

$$R_1R_2C{=}O + HQ\ (\text{or } Q^-) \rightleftharpoons R_1R_2CQ(OH)(\text{or } O^-) \quad (1)$$

results in a decrease in the intensity of the carbonyl band.

The extent of this reaction was measured by determining the intensity of absorption of the 1600–1800 cm.$^{-1}$ band. Since Beer's law was approximately valid, the quantity of the ester which had lost its carbonyl function could be calculated. This quantity was then assumed to correspond to the formation of the addition compound. Since the solvent used in these studies was either an alcohol or ether, a new band characteristic of the addition compound and corresponding to the carbon–oxygen single bond vibration was necessarily masked.

Experimental

Materials.—Di-*n*-butyl ether (Eastman Kodak Co.) was refluxed over sodium for several hours and then distilled through a packed column; b.p. 139.8–140.0 (746 mm.), $n^{20}D$ 1.3983. Both methanol and ethanol were purified by the method of Lund and Bjerrum quoted by Fieser.[18] After this purification they were subjected to final drying by treatment with calcium hydride. Sodium and lithium alkoxides were prepared by treatment of the above alcohols with the appropriate metal. The final drying of the alcohols, the preparation of the alkoxides, and the storage of these materials were carried out in a nitrogen-filled dry-box using phosphorus pentoxide as a drying agent. Extreme care was taken to exclude water since water produced undesirable side reactions in many cases, as will be noted later. The carboxylic acid derivatives used are listed in Table I.

Infrared Spectra.—Infrared spectra were determined by use of a Perkin–Elmer model 21 double beam recording infrared spectrophotometer. Matched sealed liquid absorption cells approximately 0.1 mm. in thickness were employed. Spectra of all compounds listed in Table I were determined in the region from 1200 to 2000 cm.$^{-1}$ using 0.1, 0.05 and 0.025 *M* solutions of the compounds in di-*n*-butyl ether. Using the absorption band of the carbonyl group, listed in Table I, Beer's law curves were constructed for each of the compounds.

To study the addition of various reagents to the carboxylic acid derivatives, 0.1 *M* solutions of the carboxylic acid derivatives in di-*n*-butyl ether were shaken with measured amounts of the addition reagents. When the addition reagent was a metallic alkoxide, an aliquot of the alkoxide in alcohol was evaporated to dryness *in vacuo* and the solid was employed in suspension. In other cases, amounts of the addition reagents determined gravimetrically or volumetrically were added to the carboxylic acid derivatives. After shaking the addition reagent and the di-*n*-butyl ether solution of the carboxylic acid derivative for a specified time, the resulting solutions were then analyzed by means of the infrared spectrophotometer. Operations described above were carried out in a nitrogen swept dry-box to minimize side reactions brought about by water. By the determination of the concentration of the carboxylic acid derivative before and after reaction with the addition reagent, it was possible to calculate the percentage addition. In the subsequent discussion, the results are tabulated in terms of percentage addition rather than an equilibrium constant because most of the systems investigated contained solid and liquid phases and the solubilities of the various systems were not determined. A typical infrared absorption spectrum is shown in Fig. 1.

Results and Discussion

Esters.—Ethyl trifluoroacetate was studied most extensively, because it contains a highly electronegative group which should enhance the electrophilic character of the carbonyl carbon atom and thus promote addition to the carbonyl double bond. The data obtained for this ester are presented in Table II.

Dissolution of the sodium alkoxides in an ether solution of the ester occurred readily and attainment of equilibrium was complete within a few minutes at room temperature. The addition 2 was reversible as implied by the work of Swarts.[15]

$$CF_3CO_2C_2H_5 + OR^- \rightleftharpoons CF_3C(OC_2H_5)(OR)O^- \quad (2)$$

Both the solvent and the cation determined the position of equilibrium. The sodium alkoxides added almost completely in di-*n*-butyl ether while addition of the lithium alkoxides was only partial, probably due to the fact that sodium alkoxides are

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[9] I. Lauder, *Trans. Faraday Soc.*, **44**, 732 (1948).

[10] H. Meerwein, T. Bersin and W. Burneleit, *Ber.*, **62**, 1002 (1929).

[11] F. E. McKenna, H. V. Tartar and E. C. Lingafelter, This Journal, **71**, 729 (1949).

[12] F. E. McKenna, H. V. Tartar and E. C. Lingafelter, *ibid.*, **75**, 604 (1953).

[13] A. Ashdown and T. A. Kletz, *J. Chem. Soc.*, 1454 (1948).

[14] R. Brill, *Z. Elektrochem.*, **50**, 47 (1944); J. W. Robertson, *Trans. Faraday Soc.*, **36**, 913 (1940).

[15] F. Swarts, *Bull. soc. chim. Belg.*, **35**, 414 (1926).

[16] F. Adickes, *Ber.*, **58B**, 1992 (1925).

[17] L. Claisen, *ibid.*, **20**, 649 (1887), reported the isolation of a stable addition compound from methyl benzoate and sodium alkoxide which was subsequently shown to be a mixture of sodium benzoate and sodium alkoxide by both Adickes[16] and Tischenko (V. Tischenko, I. F. Welz and I. L. Rabzewitsch-Subkowski, *J. prakt. Chem.*, [2] 86, 325, 334 (1913)).

[18] L. F. Fieser, "Experiments in Organic Chemistry," D. Heath and Co., New York, N. Y., 1941, p. 359.

TABLE I

CARBOXYLIC ACID DERIVATIVES

Compound	B.p., °C.[k]		n^{20}D		Source	ν(C=O) (cm.$^{-1}$)[l] Di-*n*-butyl ether solution
	Obsd.	Lit.	Obsd.	Lit.		
$CF_3CO_2C_2H_5$	60.3-60.6	60.5	1.3072	1.3073	[a]	1790
$CF_2HCO_2C_2H_5$	98-98.5	99.5	1.3470	1.3463	[b]	1780
$CFH_2CO_2C_2H_5$	114	114-115	1.3747	1.3753	[c]	1749, 1776[i]
$CH_3CO_2C_2H_5$	....	77	1.3718	1.3718	[d]	1749
$C_2F_5CO_2C_2H_5$	76-77	75-75.6	1.3006	1.3010	[e]	1784
$C_3F_7CO_2CH_3$	78.8-79.5	79	1.2928	1.293	[e]	1787
$C_3F_7CO_2C_2H_5$	96-96.5	95	1.3027	1.3032	[e]	1786
$C_3F_7CO_2CH(CH_3)_2$	105.5-106.5	106	1.3105	1.310	[e]	1777
$(CO_2C_2H_5)_2$	....	186	1.4101	1.4101	[d]	1747, 1771
$CCl_3CO_2C_2H_5$	....	168	1.4509	1.4507	[d]	1770
CF_3CONH_2	73-74 (m.p.)	75			[f]	1750
CF_3CO_2H	70.3-70.4	71	Hygroscopic		[d]	1783[j]
$C_2F_5CO_2H$	95	95.5	Hygroscopic		[g]	1773[j]
$C_3F_7CO_2H$	119.5-120	120	Hygroscopic		[g]	1773[j]
CH_3CO_2H	15.5 (m.p.)	16.6	1.3726	1.3727	[h]	1720, 1753

[a] Columbia Organic Chemical Co. [b] Matheson Co. [c] Gift of Dr. O. R. Pierce, Purdue University. [d] Eastman Kodak Co. [e] Prepared according to D. R. Husted and A. H. Ahlbrecht, THIS JOURNAL, **75**, 1605 (1953). [f] Prepared according to H. Gilman and R. G. Jones, *ibid.*, **65**, 1458 (1943). [g] Gift of Minnesota Mining and Manufacturing Co. [h] Merck and Co., Inc. [i] Unlike all other monofunctional esters, ethyl fluoroacetate exhibits two absorption bands in the region usually assigned to the carbonyl group. This phenomenon cannot be attributed to impurities because of the constancy of the boiling point and the reproducibility of the refractive index. It may, however, be attributed to a dimer, which in the case of acids gives rise to a second carbonyl peak. This explanation is in agreement with the abnormally high boiling point of ethyl fluoroacetate. [j] No carbonyl absorption due to a dimer was observed with the perfluoroacids, although acetic acid showed absorption bands due to both monomer and dimer. [k] 735-750 mm. [l] Frequencies are reliable to ±2 cm.$^{-1}$.

TABLE II

ADDITION TO ETHYL TRIFLUOROACETATE[a]

Addend	Addend/ester	Solvent	Addition, %
H_2O	1:1	Ethyl ether	0
C_2H_5OH	1:1	Ethyl ether	0
CH_3OH	Solvent	Methanol	0[b]
C_2H_5OH	Solvent	Ethanol	0
$C_3H_7NH_2$	1:1	Ethyl ether	0[c]
NaCl	1:1	Ethyl ether	0[d]
NaF	1:1	Ethyl ether	0[d]
NaCN	1:1	Ethyl ether	0[d]
$NaHSO_3$	1:1	Ethyl ether	0[d]
$LiOCH_3$	1:1	Butyl ether	11 ± 3[d]
$LiOC_2H_5$	1:1	Butyl ether	60 ± 2[e]
$NaOCH_3$	1:1	Butyl ether	99 ± 1[e,f,g]
$NaOC_2H_5$	1:1	Butyl ether	99 ± 1[e]
$LiOCH_3$	1:1	Methanol	0
$NaOCH_3$	1:1	Methanol	0

[a] These data were determined from the magnitude of the 1790 cm.$^{-1}$ absorption band of ethyl trifluoroacetate. [b] The extinction coefficient of the ester was reduced in going from ethyl ether to methanol, but only in the same ratio as the reduction in the extinction coefficient of ethyl acetate, indicating no specific interaction. [c] The sum of the amide spectrum and the ester spectrum equaled 100%. [d] Heterogeneous system. [e] Average of at least five runs. Initially a heterogeneous system. [f] Addition of water to the addition compound produced sodium trifluoroacetate quantitatively. [g] Addition of acetic acid or phenol reversed the equilibrium, re-forming half of the original ester. Addition of pentafluoropropionic acid or gaseous hydrogen chloride reversed the equilibrium completely.

more highly ionized than lithium alkoxides and therefore the former add to the polarized carbonyl carbon atom more readily. Neither sodium nor lithium methoxide added to the ester in methanol solution. In this medium of relatively high dielectric constant, the electrostatic energy of the methoxide ion with its highly concentrated charge renders it more stable relative to the addition compound.[19]

The addition of equimolar quantities of acetic acid or phenol produced a reversal of the equilibrium shown in equation 3 as detected by the reappearance of the ester carbonyl band. This reappearance amounted to only half of the original ester present and may indicate that acetate ion

$$CF_3C(OR)_2O^- + HA \longrightarrow CF_3CO_2R + ROH + A^- \quad (3)$$

and phenolate ion produced in the reaction add partially to ethyl trifluoroacetate. The addition of perfluoropropionic acid or anhydrous hydrogen chloride to the addition product produced a complete reversal of the equilibrium as indicated by the complete reappearance of the ester carbonyl band. These experiments prove conclusively that the reaction under question is a true equilibrium and that the disappearance of the carbonyl absorption band indicates the formation of an addition compound.

When the addition compound formed from equimolar quantities of ethyl trifluoroacetate and sodium methoxide was treated with a drop of water, a quantitative yield of sodium trifluoroacetate was produced within a few minutes. The latter substance was determined by measurement of the infrared band at 1681 cm.$^{-1}$, which incidentally provided an extremely sensitive test for the presence of water in all of the experiments with the alkoxides. This experiment demonstrates the reversal of the equilibrium by the water, acting as a proton donor.

$$CF_3C(OR)_2O^- + H_2O \longrightarrow CF_3CO_2R + ROH + OH^- \quad (4)$$

$$CF_3CO_2R + OH^- \longrightarrow CF_3C(OR)(OH)O^- \longrightarrow CF_3CO_2^- + ROH$$

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[19] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 80.

An attempt was made to add a number of other species, including various salts, water and ethanol, to ethyl trifluoroacetate. These experiments, presented in Table II, produced negative results. Whereas fluorinated aldehydes and ketones readily add water and ethanol to the carbon–oxygen double bond, fluorinated esters do not. The fluorinated esters can undergo addition only if the addend is hydroxide ion or alkoxide ion. The hypothetical hydroxide ion addition product, $CF_3C(OH)(OC_2H_5)O^-$, decomposes readily to the highly resonance stabilized trifluoroacetate ion; decomposition of the alkoxide ion addition product can only lead to an ester.

The effect of fluorine substitution in the ester on the position of equilibrium is summarized in Table III. Such substitution successively increases the electrophilic character of the carbonyl carbon atom and displaces the position of equilibrium toward the addition compound.

TABLE III

THE EFFECT OF FLUORINE SUBSTITUTION ON THE ADDITION REACTION OF ESTERS WITH SODIUM METHOXIDE IN DI-*n*-BUTYL ETHER

Ester	Addition, %
Ethyl acetate	0
Ethyl fluoroacetate	26 ± 2
Ethyl difluoroacetate	77 ± 2
Ethyl trifluoroacetate	99 ± 1

The effect on addition of lengthening the perfluoroalkyl chain is summarized in Table IV. The change in the acid portion of the ester from two to three carbon atoms reduces the amount of addition significantly, whereas the change from three to four carbon atoms does not. These addition compounds may be compared with those of Brown[20] formed from the reaction of amines with suitable reference acids. He attributed the abnormally high dissociation of addition compounds involving triethylamine to F-strain. The same factor may be operative here since the propionate addition compound approximates a homomorph of the triethylamine–trimethylboron addition compound.

TABLE IV

THE EFFECT OF CHAIN LENGTH ON THE ADDITION REACTION OF PERFLUORO ESTERS WITH SODIUM ALKOXIDES IN DI-*n*-BUTYL ETHER SOLUTION

Ester	Addition, %	
	$NaOCH_3$	$NaOC_2H_5$
Ethyl trifluoroacetate	99 ± 1	99 ± 1
Ethyl pentafluoropropionate	75 ± 2	83 ± 2
Ethyl heptafluorobutyrate	75 ± 2	90 ± 1

An attempt was made to add sodium alkoxide to esters other than the fluorinated esters. Confirming the work of Adickes,[16] the addition of sodium ethoxide to ethyl oxalate in di-*n*-butyl ether solution took place readily. The two original ester carbonyl bands at 1747 and 1771 cm.$^{-1}$ were converted to a single carbonyl band at 1718 cm.$^{-1}$ when one mole of sodium ethoxide was dissolved in the ether solution. The spectrum of this addition compound exhibited a new band characteristic of the monofunctional ester as well as the absence of the original ester bands.

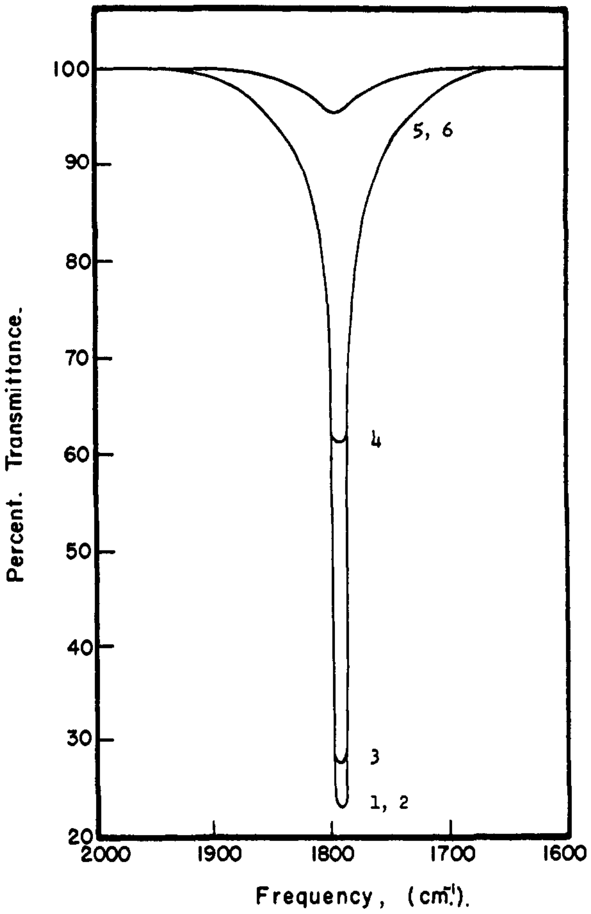

Fig. 1.—Infrared absorption of ethyl trifluoroacetate in the presence of various substances in di-*n*-butyl ether: 1, 0.1 *M* ethyl trifluoroacetate; 2, 0.1 *M* ethyl trifluoroacetate and water, ethanol or salts; 3, 0.1 *M* ethyl trifluoroacetate and 0.1 *M* lithium ethoxide; 4, 0.1 *M* ethyl trifluoroacetate and 0.1 *M* lithium ethoxide; 5, 0.1 *M* ethyl trifluoroacetate and 0.1 *M* sodium ethoxide; 6, 0.1 *M* ethyl trifluoroacetate and 0.1 *M* sodium methoxide.

Sodium ethoxide did not dissolve readily in an ether solution of ethyl trichloroacetate. Infrared analysis showed that the ester band had diminished to the extent of 15%. However, a new carbonyl band appeared to that extent, identical with that of ethyl carbonate. This indicated that any addition compound formed had decomposed by the cleavage of the carbon–carbon bond. This is not observed in the case of the fluorinated esters because of the enhanced stability of the carbon–carbon linkages in such compounds, a fact which is reflected in the difference in the rate of decarboxylation of trichloroacetate and trifluoroacetate ions.[21]

Acids.—As mentioned previously, several structures have been proposed for the so-called hydrates of various acids. Among these are an ortho acid formed by true addition, a hydrogen-bonded association and hydronium carboxylate formed by proton transfer. It was thought that the perfluoro acids

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(20) H. C. Brown and M. D. Taylor, THIS JOURNAL, **70**, 1332 (1947); H. C. Brown and S. Sujishi, *ibid.*, **70**, 2878 (1948).

(21) I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).

would provide the best possibility for the formation of an ortho acid because of the strong inductive effect of the fluorine atoms and because of the analogy with the fluoroketones and esters. Trifluoroacetic, pentafluoropropionic and heptafluorobutyric acids form azeotropes with water,[22] the first two having a composition approximating one mole of acid and one mole of water. Infrared spectra of these acids in di-*n*-butyl ether solution and of a mixture of these acids and a molar equivalent of water in di-*n*-butyl ether solution produced the following results: (1) a 15% diminution in the carbonyl absorption upon the addition of water; (2) no carbonyl absorption due to a dimeric product or perfluorocarboxylate ion either before or after the addition of water. It can only be concluded that the 15% diminution in the carbonyl absorption is due either to ortho acid formation or more probably to a solvent effect due to hydrogen-bonding.

Amides.—Sodium methoxide adds to trifluoroacetamide in di-*n*-butyl ether solution forming an addition compound, $CF_3C(OC_2H_5)(NH_2)O^-Na^+$. The addition in this reaction is about 50% complete, much less than that of the corresponding ester. This decrease may be due to comparatively greater ability of nitrogen to reduce the electrophilic character of the carbonyl carbon atom.

Conclusions

The transesterification reaction has been shown to follow the same pattern as ester hydrolysis with regard to kinetics, type of fission and effect of structure.[23] Addition compounds should then be expected as intermediates in the transesterification reaction as well as in ester hydrolysis,[1] and all the foregoing compounds with the general formula $RC(OR)_2O^-Na^+$ can be considered to be examples of stable intermediates in base-catalyzed transesterification.

The striking increase in percentage addition of sodium alkoxide in the series ethyl acetate, ethyl fluoroacetate, ethyl difluoroacetate and ethyl trifluoroacetate—each an equilibrium process—parallels an enormous increase in the rates of alkaline hydrolysis in the series, ethyl acetate, ethyl chloroacetate, ethyl dichloroacetate and ethyl trichloroacetate.[24] The parallel effect of structure on the addition equilibria and the rates of hydrolysis indicates that the slow step in the alkaline hydrolysis of esters may be the addition of hydroxide ion to the carbonyl carbon. It was mentioned previously that the hydrolysis intermediate $RC(OR)(OH)O^-Na^+$ is not stable because of its seeming instantaneous decomposition to carboxylate ion. This again suggests that in the basic hydrolysis of an ester the slow step is the addition of an hydroxide ion to the ester, which is then followed by a fast decomposition to carboxylate ion.

The addition compound $RC(OR)(NH_2)O^-Na^+$ may be a stable prototype of the intermediate in the amination of esters or in the reverse reaction.

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[22] D. R. Husted and A. H. Ahlbrecht, This Journal, **75**, 1605 (1953).

[23] R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, *ibid.*, **72**, 4511 (1950).

[24] D. Flom, Ph.D. Thesis, Pennsylvania State College, 1952. Unpublished results of D. Flom and of this Laboratory indicate a similar increase in the rates of alkaline-hydrolysis of the fluorinated esters.

[Contribution from the Cobb Chemical Laboratory, University of Virginia]

Evidence for the *cis–trans* Configurations and Effective Conjugations of α-Phenylchalcones

By W. Bruce Black[1] and Robert E. Lutz

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Determination and interpretation of the ultraviolet absorptivities of the *cis-* and *trans*-α-phenylchalcones and of their 2-(4-nitro) and 3-(4-nitro) derivatives have demonstrated the configurations and conformations of the isomers. The conclusion has been drawn that the *cis* isomers involve effective conjugation of the *trans*-stilbene system only, whereas the *trans* isomers involve effective contributions of both the *cis*-stilbene and *trans*-chalcone conjugations. The greater reactivity of the *trans* isomers toward nucleophilic 1,4-additions has been demonstrated and is consistent with and supports this conclusion.

This investigation is a part of a broader study of stereoisomeric pairs of chalcones (benzalacetophenones) (*cf.* III, Fig. 1) carrying α, β, or α,β-di-substituents,[2] which deals particularly with the important differences in ultraviolet absorptions exhibited by each of a *cis–trans* pair, and also the difference shown by α- and β-structural isomers of either the *cis*- or the *trans*-chalcone molecule, differences which should be (and are) in some degree a measure of the steric and electronic effects of the substituent, and of the effectiveness and reactivities of the conjugated systems present. The work stemmed from a restudy of Stobbe's supposed three isomers of α-phenyl-(4-nitrobenzal)-acetophenone[3a] (Ib, IIb), in which we have been able to find evidence for only two isomers.[3b]

The configurations of the three *cis–trans* pairs under study, the α-phenylchalcones and two of the three possible pairs of mono-(*p*-nitro) derivatives, are shown in formulas I and II. The spectra of

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[1] Philip Francis du Pont Fellow, 1952–1953.

[2] (a) R. E. Lutz and R. H. Jordan, This Journal, **72**, 4090 (1950); (b) L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950); (c) R. E. Lutz, D. F. Hinkley and R. H. Jordan, *ibid.*, **73**, 4647 (1951).

[3] (a) H. Stobbe and F. J. Wilson, *Ann.*, **374**, 237 (1910); (b) W. B. Black and R. E. Lutz, This Journal, **75**, 4578 (1953).