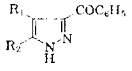
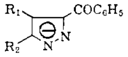
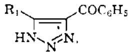
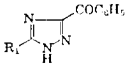
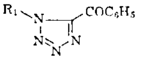
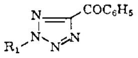
TABLE I

	R_1	R_2	Medium[a]	$\lambda_{max}(\mu)$[b]	Intensity Ratio (ϵ_r)[c]
	C_6H_5	H	N	6.06 10.88[d]	0.7
	C_6H_5	OH	N	6.13 11.02	0.6
	C_6H_5	C_6H_5	D	6.08 11.05	1.1
	H	C_6H_5	D	6.07 11.20[e]	0.6
	OH	C_6H_5	N	6.16 11.05	0.7
	$OCOCH_3$	C_6H_5	D	6.12 11.00	1.2
	COC_6H_5	COC_6H_5[f]	D	6.02 11.00[d]	0.9
	$N_2^{\oplus}$	C_6H_5	D	6.08 11.15[e]	1.0
	C_6H_5	$N_2^{\oplus}$	D	6.06 11.05[e]	1.6
	$NHCOC_6H_5$	...	N	6.11 10.70	1.1
	COC_6H_5	...	N	6.09 10.81[e]	0.7
	$NHCOC_6H_5$	...	N	6.00 10.82[e]	0.5
	H	...	N	6.03 10.80[e]	0.9
	CH_3[g]	...	D	5.99 10.88	1.1
	$CH_2CO_6H_5$	...	D	5.95 10.82[h]	1.0
	$CH_2COC_6H_5$	...	D	5.97 10.80[h]	0.9

[a] N = Nujol mull; D = dichloromethane solution. [b] Where more than one carbonyl-stretching band occurs, only that assignable to the benzoyl group is given. [c] Ratio of apparent extinction coefficients of the benzoyl band and that in the 10.7–11.2-μ region. [d] Compared with the corresponding 2-pyrazoline. [e] Compared with the compound having the C-benzoyl group replaced by a benzyl group. [f] P. Yates and T. J. Clark, *J. Org. Chem.*, **27**, 286 (1962). [g] This compound is either 1-methyl- or 2-methyl-5-benzoyltetrazole. [h] Compared with the corresponding *N*-phenacyltetrazole.

infrared spectra of sixteen compounds which possess the common feature of a benzoyl group attached to a carbon atom of a heteroaromatic system containing two or more nitrogen atoms. We have observed that the spectra of all of these compounds show a strong band in the region 10.7–11.2 μ whose intensity is of the same order as that of the carbonyl-stretching band due to the benzoyl group. Although we have not established the nature of the vibration which gives rise to this band, we report these data here since the correlation has been found to be useful as a diagnostic aid in structural determinations.[4]

The positions of this band and the carbonyl-stretching band of the benzoyl group in each case are given in Table I together with the ratio (ϵ_r) of the apparent extinction coefficients of the two bands.[7] The latter may be seen to fall in the range 0.5–1.6. In several instances it has been possible to examine the spectra of the corresponding compounds in which the benzoyl group is replaced by a benzyl group; in all of these cases, the spectra show only very weak bands or no bands in the 10.7–11.2-μ region. Further, while the spectra of 3-benzoyl-4-phenylpyrazole and 3,4,5-tribenzoylpyrazole show strong bands in this region, those of the corresponding 2-pyrazolines show only weak absorption, although each possesses a strong band at 11.6 μ. It may also be noted that the spectra of 1- and 2-phenacyltetrazole lack the strong bands at 10.8 μ present in the spectra of their 5-benzoyl derivatives.

We have not examined whether this correlation applies also to C-acyl derivatives of these heterocycles, or is restricted to the benzoyl series. However, recently published spectra[8] of 3-acetylpyrazole and 3-pivaloylpyrazole show bands, in the 10.5–11-μ region, whose intensities appear to be of the same order as those of the corresponding carbonyl-stretching bands.

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(3) P. Yates and D. G. Farnum, *Tetrahedron Letters*, No. 17, 22 (1960); D. G. Farnum and P. Yates, *Chem. Ind.* (London), 659 (1960).

(4) It has been suggested[5] that an absorption band at 10.7 μ is characteristic of the pyrazole ring; this view has not been supported by our own studies nor by those of others.[6]

(5) C. S. Rondestvedt and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6532 (1955).

(6) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961).

(7) It must be noted that the solvent used for the solution spectra, dichloromethane, is not that of choice since it has a weak absorption band at 11 μ; the values of ϵ_r quoted are thus approximate in nature.

(8) Yu. N. Sheinker, I. Ambrush, and N. K. Kochethov, *Doklady Akad. Nauk S.S.S.R.*, **123**, 709 (1958).

Inductive Constants for the Cyclohexyl and 3-Cyclohexenyl Radicals

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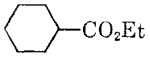
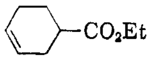
Received February 5, 1962

In connection with another study[2] concerning neighboring double-bond participation in cyclohexenylcarbinyl systems it was desired to have σ^* constants for the cyclohexyl and 3-cyclohexenyl groups. Although a σ^* value for cyclohexyl has been reported,[3] it is based on a secondary comparison rather than the fundamental definition of σ^* in terms of rates of acidic and basic ester hydrolyses;[4] no σ^* value for the 3-cyclohexenyl group has been reported. This note reports the required acid and base catalyzed rates of hydrolysis of the ethyl esters of cyclohexanecarboxylic acid (I), and 3-cyclohexenecarboxylic acid (II). From these data and the corresponding rates for ethyl acetate are calculated the desired σ^* constants.



I



II

Table I summarizes the measured rate data; the footnotes of this table cite relevant literature data for comparison. In making these comparisons, it will be noted that the previous data was for hydrolysis in a slightly more aqueous solvent than that employed here. Consideration of the effect of water on hydrolysis rates in other acetone–water mixtures[6] indicates that the extra water has no significant effect here and that the rates may be compared directly without correction. Although the internal and external agreement in Table I is only fair (± 6–10%) in some cases, it is quite adequate for calculating σ^* constants, since as logarithmic quantities they are insensitive to small changes in rate.

TABLE I

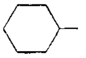
SECOND-ORDER RATE CONSTANTS FOR ACID AND BASE HYDROLYSIS AT 25.0° IN 70% (v./v.) ACETONE–WATER[a]

Compound	Nature of Hydrolysis	k, Mole^{-1} Sec.$^{-1}$
Ethyl acetate[b]	Base	5.4×10^{-2}
Ethyl acetate[c]	Acid	4.6×10^{-6}
Ethyl cyclohexanecarboxylate	Base	$(1.74 \pm 0.03) \times 10^{-3}$
Ethyl cyclohexanecarboxylate[d]	Acid	$(7.2 \pm 0.4) \times 10^{-6}$
Ethyl 3-cyclohexenecarboxylate	Base	$(4.86 \pm 0.00) \times 10^{-3}$
Ethyl 3-cyclohexenecarboxylate	Acid	$(8.8 \pm 0.4) \times 10^{-6}$

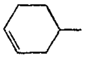
[a] This corresponds to *ca.* 65% (w./w.) acetone–water. [b] A rate constant of 4.9×10^{-2} can be estimated from a plot of log k *vs.* $1/T$ for the eight rates measured by Davies and Evans,[5] Nair and Anantakrishnan,[6] and Rylander and Tarbell[7] at eight different temperatures all in *ca.* 62% (w./w.) acetone–water. The slope of this plot yields an E_a of 11.8 kcal. [c] Reported value,[5] 4.6×10^{-6} (extrapolated from 24.8°). [d] Reported value,[8] 7.4×10^{-6}.

Insertion of the data from Table I (using the value of 4.9×10^{-2} for the basic ethyl acetate hydrolysis) into equation (1)[4] yields the σ^* values shown below. The deviations

$$\sigma^* = \frac{1}{2.48}\left[\log(k/k_0)_B - \log(k/k_0)_A\right] \qquad (1)$$



$\sigma^* = -0.26 \pm 0.02$



$\sigma^* = -0.12 \pm 0.02$

ascribed to these values are based on the observed deviations in the rate constants of Table I. By way of comparison the average of the probable errors in fit of other σ^* constants is greater than 0.03 unit.[3]

Because of the lack of data for reactions or equilibria of known freedom from steric influences, it is difficult to assess independently the validity of these two σ^* constants. The previously assigned σ^* for cyclohexyl (0.15)[3] was based on the acidity of cyclohexanecarboxylic acid in water at 25°. Unfortunately, as Taft has pointed out,[9] acid equilibria are susceptible to steric influences and both the cyclohexyl and 3-cyclohexenyl groups would be expected to exhibit steric complications. The enhanced acidity of α-ethylbutyric acid (R = diethylcarbinyl) computed from the $\rho^*\sigma^*$ plot corresponds to a σ^* deviation of *ca.* +0.16 unit. If cyclohexyl were assigned the same positive deviation, the corrected σ^* estimated from its pK_a would be −0.31. The less negative observed value of −0.26 is in line with the idea that steric effects are less important with cyclohexyl than with diethylcarbinyl. Moreover, from an inductive point of view, it would be supposed that the cyclohexyl σ^* should be very slightly more negative than that of the diethylcarbinyl group ($\sigma^* = -0.23$) as is observed. Finally, in support for at least the difference between the σ^*'s of cyclohexyl and 3-cyclohexenyl, it should be mentioned that the assigned values correlate well with nine pairs of solvolysis rates.[2]

Experimental

Ethyl 3-Cyclohexene-1-carboxylate (II).—In a steel bomb containing 20 g. (0.2 mole) of ethyl acrylate and 0.5 g. of hydroquinone was condensed 13.5 g. (0.25 mole) of butadiene. The sealed bomb was heated at 160–165° for .5 hr. Distillation of the crude product gave 28.3 g. (93%) of ethyl 3-cyclohexene-1-carboxylate, b.p. 84° (23 mm.), n^{25}D, 1.4540 (lit.,[10] b.p. 194–195°, n^{20}D, 1.4578).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 69.96; H, 9.20.

Ethyl Cyclohexanecarboxylate (I).—A solution of the

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[1] Taken from the dissertation submitted by S. S. Chibber to Cornell University for the Ph.D. degree, September, 1961.

[2] C. F. Wilcox, Jr., and S. S. Chibber, manuscript submitted for publication.

[3] R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, 1956, p. 619.

[4] R. W. Taft, *ibid.*, p. 587.

[5] G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940).

[6] P. M. Nair and S. V. Anantakrishnan, *Proc. Indian Acad. Sci.*, **32A**, 187 (1950).

[7] P. M. Rylander and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3021 (1950).

[8] H. A. Smith and J. H. Steele, *J. Am. Chem. Soc.*, **63**, 3466 (1941).

[9] R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, 1956, ref. 5 in Table IX.

[10] N. Chayanov, *Zhur. Obshchei Khim.*, **8**, 460 (1938).

cyclohexenyl ester II in 95% ethanol was reduced over 10% palladium on charcoal in a Parr hydrogenation apparatus. Fractional distillation of the product gave a 62% yield of the saturated ester, b.p. 97° (23 mm.), $n^{25}D$ 1.4387 (lit.,[11] b.p. 195–200, $n^{25}D$ 1.4396).

Alkaline Hydrolyses.—Except in the case of ethyl acetate, approximately 0.1 *M* solutions of the esters were prepared by dissolving the required amount of ester in 70 ml. of anhydrous acetone and diluting with 30 ml. of water. In the case of ethyl acetate an approximately 0.4 *M* aqueous solution was prepared and 30 ml. of this solution diluted with 70 ml. of acetone. The concentration of each ester solution was checked before use by complete hydrolysis with excess base and back titration with acid.

For the alkaline hydrolyzing agent, 30 ml. of *ca.* 0.33 *M* carbonate free sodium hydroxide was diluted with 70 ml. of acetone.[12] The concentration of this solution was determined by titration immediately before use.

After the ester and base solutions had both equilibrated at 25.0°, 50 ml. of each solution was transferred into a 100-ml. volumetric flask which was stoppered, well shaken and quickly returned to the thermostat. The reaction was followed by withdrawing 5-ml. aliquots at suitable time intervals, running them into 10 ml. of 0.05 *N* hydrochloric acid, and finally titrating the excess acid with 0.05 *N* sodium hydroxide solution against phenolphthalein.

The second-order rate constants were computed by the Widequist technique.[13]

Acid Hydrolyses.—The ester and hydrochloric acid solutions were prepared in the same manner as described under the base hydrolyses. Because of the slow rate of reaction and the volatility of the solvent, 5-ml. aliquots were sealed in glass ampoules and these equilibrated at 25.0°. At suitable time intervals the contents of a tube were titrated with sodium hydroxide solution.

The rate constants were calculated in the standard fashion.[5]

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[11] S. Ono and T. Yamauchi, *Bull. Chem. Soc. Japan*, **25**, 404 (1952).

[12] In an attempt to prepare 0.2 *N* solutions of sodium hydroxide in 70% acetone–water, a difficulty visible phase separation occurred. The volumes and composition of the two phases appears to be critically dependent on the concentration of base. With the 0.1 *N* base employed here no phase separation was noted.

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, 1953, p. 18.

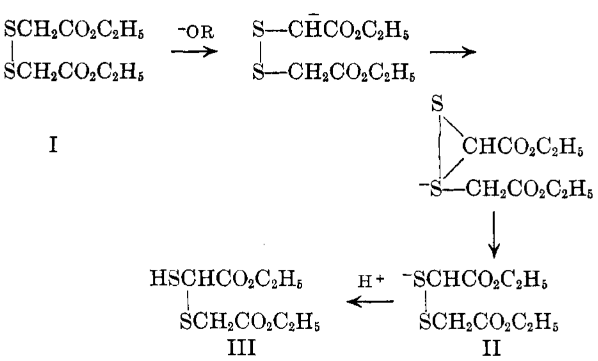
Base-Catalyzed Rearrangement of Diethyl Dithiodiglycolate

E. G. Howard

Contribution No. 695 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del.

Received June 8, 1961

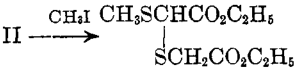
The diethyl ester of dithiodiglycolic acid (I) has been found to undergo a rapid rearrangement, even at −50°, when treated with sodium alkoxide, and the product has proved to be the sodium salt of diethyl 2-mercapto-3-thiaglutarate (II). The ionization of a methylene group is pictured as being the first step in the rearrangement. The carbanion possibly forms a three-membered ring that rearranges to the product II.



The assignment of structure is based on the following physical and chemical properties of compound III. (1) The infrared absorption spectrum possesses a band at 3.95 μ, which is indicative of the mercaptan group. (2) Slow distillation of III gives ethyl mercaptoacetate and a liquid believed to be a trimer of ethyl thioglyoxylate. (3) Compound III gives a positive sodium nitroprusside test. (4) Titration of III with iodine solution requires more titer when smaller samples or more dilute solutions are used or when the titrations are carried out over an extended period of time. These are conditions which would permit the hydrolysis of an unstable hemimercaptal group to a mercaptan

$$\mathrm{III} \xrightarrow[\text{vacuum}]{\text{heat}} HSCH_2CO_2C_2H_5 + (SCHCO_2C_2H_5)_n$$
$$\xrightarrow{H_2O} H_2S + HSCH_2CO_2C_2H_5 + OCHCO_2C_2H_5$$

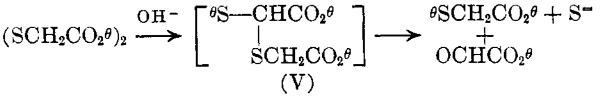
(5) Methylation of the anion II with methyl iodide gave IV which is stable and easily purified by distillation



$$\mathrm{II} \xrightarrow{CH_3I} \begin{array}{l} CH_3SCHCO_2C_2H_5 \\ \quad | \\ \quad SCH_2CO_2C_2H_5 \end{array}$$

IV

It is suggested that compounds of type III are involved in the cleavage of dithiodiglycolic acids by aqueous base where the product is in turn hydrolyzed to salts of hydrogen sulfide, mercaptoacetic acid, and glyoxylic acid.[1] Supporting evidence is found in the fact that I gave the typical yellow color of II even when treated with 30% aqueous sodium hydroxide at 0°. A yellow color similar to that of II has also been observed in the rearrangement of dithiodiglycolic acid.[2]



$$(SCH_2CO_2^{\ominus})_2 \xrightarrow{OH^-} \left[\begin{array}{l} {}^{\ominus}S{-}CHCO_2^{\ominus} \\ \quad | \\ \quad SCH_2CO_2^{\ominus} \end{array}\right] \longrightarrow \begin{array}{c} {}^{\ominus}SCH_2CO_2^{\ominus} + S^{=} \\ + \\ OCHCO_2^{\ominus} \end{array}$$

(V)

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[1] A. Schobel, *Ber.*, **70**, 1186 (1937), *et seq.*

[2] N. A. Rosenthal and G. Oster, Organic Section, 126th Meeting of the American Chemical Society, September, 1954, New York, N. Y., report that a chromophore is produced in the reaction. We found the color to be yellow.