proportion of saturated atoms to conjugated rings. However, this single example is within the limits for the polycyclic aromatics, a fact which seems to confirm the prediction based on other spectroscopic evidence that the interaction of the sp^2- and sp^3-hybridized orbitals in the highest occupied orbital and first excited state is limited. Thus, the hypothesis of weak polarization of the aromatic ring in most states by saturated groups is supported rather than hyperconjugation. The latter effect would be expected to make an appreciable shift in the excited states.

The work described in this paper seems to provide some justification for the extension of the simple molecular orbital treatment of π-complexes to several cases of hydrocarbons related to the polycyclic aromatic compounds. The comparison of empirical values for complex and donor transitions furnishes further support for the basic theoretical approach. The values determined by the molecular orbital treatment for an additional acceptor, trinitrofluorenone, should further aid in the application of π-complex theory; a number of studies on applications are being carried on at the present time.

Acknowledgment.—The author wishes to thank Professor M. J. S. Dewar for helpful discussions.

[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Alkaline Hydrolysis of Normal and Pseudo Methyl Esters of *o*-Benzoylbenzoates and of Hindered Alkyl Acetates[1]

BY MELVIN S. NEWMAN AND SHINZABURO HISHIDA

RECEIVED MAY 12, 1962

The rates of alkaline hydrolysis in 70% dioxane–30% water at 30° of a series of normal and pseudo methyl esters of methyl substituted *o*-benzoylbenzoic acids have been measured. The high rate for methyl 2-benzoyl-6-methylbenzoate seems best interpreted by initial attack of hydroxide ion on the ketonic carbonyl followed by intramolecular expulsion of a methoxide ion. Certain secondary alkyl acetates have been shown to undergo hydrolysis at rates slower than that of *t*-butyl acetate.

The fact that *o*-benzoylbenzoic acids form two types of esters, normal and pseudo, has long been known.[2] Usually, the point of interest involved in this area has been the determination of structure of each ester. To our knowledge, no measurements of the relative reactivity of such isomeric esters with any reagent have been made. Because of some qualitative observations concerning the rapidity of conversion of ψ-methyl *o*-benzoylbenzoate to the normal ester under alkaline conditions,[3] we decided to measure the rates of alkaline hydrolysis of several pairs of normal and pseudo esters. Accordingly, the second-order rate constants in 70% dioxane–30% water at 30° for the alkaline hydrolysis of five pairs of methyl *o*-benzoylbenzoates were measured. The results are listed in Table I.

The relative rates of hydrolysis of the pseudo esters are roughly what might be expected from the combined steric and inductive effects of methyl groups. Esters IV, VI, VIII and X would all be expected to hydrolyze at rates slower than that of II. Since the steric effects of the methyl groups in IV and VI are approximately the same (in terms of hindrance to addition of hydroxide ion to the carbonyl group) one might explain the slower rate for VI by noting that in VI the methyl group is attached to the ring containing the carbonyl and hence should exert its rate-retarding inductive effect[4a] whereas in IV this effect would not be expected to be felt.

One might have expected a greater steric effect from the methyl group in VIII.[4b] However, because the carbonyl group in VIII is coplanar with the ring and attack by hydroxide ion is surely from a direction perpendicular to the ring,[5] the steric effect of the methyl group is minimized.[6] Finally, the rate for X reflects the two effects of methyl groups in VI and VIII. The above arguments all assume that the same mechanism for hydrolysis, namely, addition of hydroxide ion to the carbonyl group to yield a tetrahedral transition state,[7] applies.

We believe that the alkaline hydrolysis of the normal methyl esters I, III, V, VII and IX is more complicated than that of the pseudo esters because two different mechanisms for hydrolysis are involved. The rate measured, therefore, is a composite of two rates and hence interpretation is difficult. The main fact which demands this explanation is that ester VII hydrolyzes at a rate so much greater than that of any of the others.

The two mechanisms are: an ester carbonyl addition mechanism (1) similar to that involved in ordinary carboxylic esters,[5] and a ketone carbonyl addition mechanism (2).

The key feature to mechanism 2 is the cyclization of intermediate A to B. In this step, *the preferred geometry would have the plane of the ester group roughly perpendicular to the plane of the ring so that the negatively charged oxygen atom can approach the carbonyl group from a direction per-*

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[1] This research was supported by grant G 10345 of the National Science Foundation.

[2] Probably the first example of an acid which formed normal and pseudo esters was that of opianic acid; H. Wegscheider, *Monatsh.*, **13**, 252 (1892). A list of known isomeric esters (as of 1940) may be found in the Ph.D. thesis of C. D. McCleary, O.S.U., 1940.

[3] See the Ph.D. thesis of C. D. McCleary, Ohio State University, 1940.

[4] (a) Ethyl *m*-toluate hydrolyzes in alkali at a rate about 0.7 that of ethyl benzoate; D. P. Evans, *et al.*, *J. Chem. Soc.*, 1430 (1937). (b) The rate for ethyl *o*-toluate is about 0.13 that of ethyl benzoate.

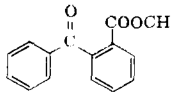
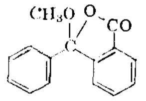
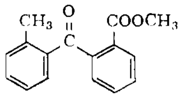
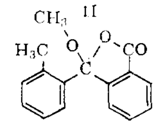
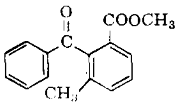
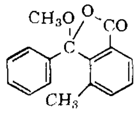
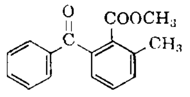
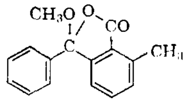
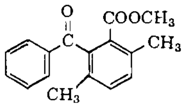
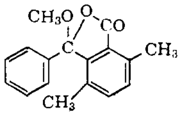
[5] See M. L. Bender, *Chem. Revs.*, **60**, 60 (1960).

[6] Stated in another way, the transition state for hydrolysis of such a lactone (pseudo ester) is not greatly crowded by an *o*-methyl group.

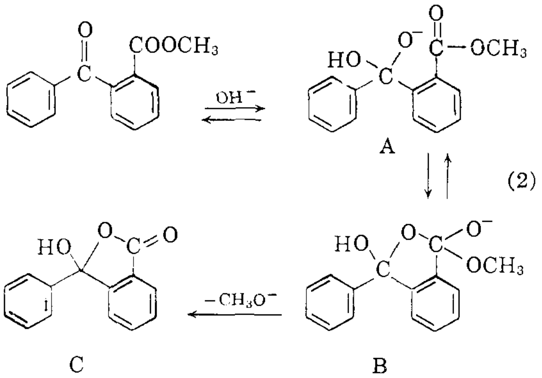
[7] Reference 5, page 59.

TABLE I

ALKALINE HYDROLYSIS RATES OF *n*- AND *ψ*-METHYL *o*-BENZOYLBENZOATES

Normal esters	10^4k, l./mole/sec.	Pseudo esters	10^4k, l./mole/sec.
 I	34.7 (33.1, 36.2)	 II	205 (204, 205)
 III	25.2 (24.9, 25.5)	 IV	129 (128, 131)
 V	13.5 (13.4, 13.6)	 VI	56.1 (54.0, 58.1)
 VII	315 (300, 330)	 VIII	44.4 (44.1, 44.7)
 IX	1.9 (1.8, 2.0)	 X	12.5 (12.4, 12.6)

pendicular[5] *to it to yield B.* In esters I, III and V the plane of the ester group is essentially that of the ring since resonance stabilization of the ester group should tend to orient it so. Hence, hydrolysis of esters I, III and V probably occurs mainly by mechanism 1. Ester V must hydrolyze almost exclusively by mechanism 1 because the diortho-substituted ketonic carbonyl group is too sterically hindered to add an hydroxyl ion readily. However, in VII, the methyl and ketone groups cause the ester group to lie almost perpendicular to the plane of the ring. Hydrolysis by mechanism 1 would be sterically hindered because of the two bulky *ortho* groups and hence we believe that *VII is hydrolyzed almost exclusively by mechanism 2.* The increased rate for VII is mainly a consequence of the fact that the plane of the ester group is roughly perpendicular to that of the ring and hence is ideally oriented for attack by the neighboring O^-.



(2)

The slow rate of hydrolysis of ester IX provides further evidence in favor of our hypothesis that VII hydrolyzes mainly by mechanism 2. If VII hydrolyzed mainly by mechanism 1, one would expect IX to hydrolyze at a much greater rate (*i.e.*, in the 100 region; Table I) since IX differs from VII only in having an additional methyl group *meta* to the ester function, a change which would not be expected to have a large effect.[4] Also, a similar substitution of a methyl group cuts the rate of the parent ester to about one third (esters I and V).

Assuming the correctness of our hypothesis concerning the mechanism of hydrolysis of VII by route 2, it is of interest to point out two other cases in which a steric factor causes an increase in rate of a reaction involving a five-atom cyclic transition state (or intermediate). In one, the rate of rearrangement (Smiles) of 2-hydroxy-2′-nitrophenyl sulfones (XI) to 2-*o*-nitrophenoxybenzenesulfinic acids (XII) under alkaline conditions is remarkably accelerated (*ca.* 5 × 10^5 fold) by substituents (CH_3, Cl, Br) in the 6-position.[8] In the second case, the rearrangement (Hayashi) of 3-nitro-2-(2-thenoyl)-benzoic acid (XIII) to 6-nitro-2-(2-thenoyl)-benzoic acid (XVI) is undoubtedly due to an acceleration of the rate of formation of the cyclic ion XV from the acyclic oxocarbonium ion XIV as compared to cyclization to form a quinone.[9]

Interestingly, 2-benzoyl-6-methylbenzoic acid, the parent acid of ester VII, esterifies with methanol and hydrogen chloride[10] to give 35% of the

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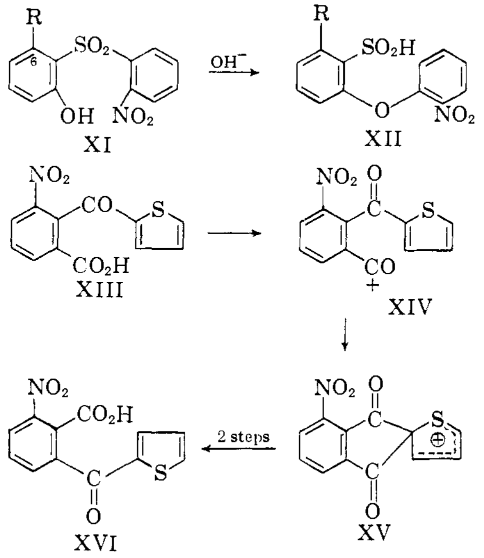
[8] J. F. Bunnett and T. Okamoto, *J. Am. Chem. Soc.*, **78**, 5357 (1956). The authors are indebted to Dr. Bunnett for pointing out this analogy at the Washington A.C.S. Meeting, March, 1962.

[9] M. S. Newman and K. G. Ihrman, *ibid.*, **80**, 3652 (1958). In this paper, similar rearrangements occur when groups other than nitro groups are involved.

[10] M. S. Newman and C. W. Muth, *ibid.*, **73**, 4627(1951).



pseudo methyl ester (in addition to 65% of the normal ester). The formation of pseudo ester under acid-catalyzed esterification conditions probably occurs by a mechanism which involves primary attack at the ketonic carbonyl.[11] Thus, both esterification of this ketoacid and alkaline hydrolysis of its normal ester probably proceed by initial attack on the ketonic carbonyl group.

The reasons for measuring the rates of alkaline hydrolysis of various alkyl acetates have been stated.[12] In Table II are listed the rates of hydrolysis of other secondary alkyl acetates, together with certain rates previously determined. Probably the main point of interest is the fact that several of the secondary alkyl acetates hydrolyze at rates considerably slower than that of *t*-butyl acetate.

TABLE II

ALKALINE HYDROLYSIS OF ALKYL ACETATES IN 70% DIOXANE-WATER

R in CH_3COOR	$\frac{k_{30}{}^0\ (CH_3COOCH(CH_3)_2{}^a}{k_{30}{}^0\ (CH_3COOR)}$
CH_3CHCH_3	1.0^b
$CH_3CHCH_2CH_3$	2.2
$CH_3CH_2CHCH_2CH_3$	3.9
$CH_3CHCH(CH_3)_2$	5.8^c
$CH_3CH_2CHCH(CH_3)_2$	12.1^d
$CH_3CHC(CH_3)_3$	13.0^d
$[(CH_3)_2CHCH_2]_2CH-$	21.6^d
$CH_3CH_2CHC(CH_3)_3$	135
$(CH_3)_2CHCHCH(CH_3)_2$	151
$(CH_3)_2CHCHC(CH_3)_3$	151
$(CH_3)_3CCHC(CH_3)_3$	200
$(CH_3)_3C-$	15.1^d

[a] The rates of alkaline hydrolysis were determined essentially as described; all esters were essentially pure as determined by vapor phase chromatography. [b] The rate determined in the present work for isopropyl acetate as standard, 10^3k, l./mole/sec., 12.1, was very close to that, 10^3k, l./mole/sec., 12.4, determined previously.[2] [c] The relative rate for this compound determined in the present work did not agree with that (2.4) determined previously[13]; we believe the present value to be correct. [d] These values are calculated from rate constants reported previously.

In conclusion, the authors would like to thank Drs. H. Shechter and W. N. White for interesting discussions concerning mechanisms of alkaline hydrolysis.

Experimental

The rate constant determinations were carried out essentially as described.[12] The esters of the substituted *o*-benzoylbenzoic acids had the physical constant reported.[11,13] The alkyl acetates used were all homogeneous as judged by vapor phase chromatographic analysis. The rate constants reported in Tables I and II are the average of at least two determinations.

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[11] See M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941). The addition product shown in brackets for the first step would, according to more modern concepts, go to a carbonium ion which, by intramolecular attack on the oxygen (an attack on either oxygen could be rationalized) of the carbonyl group, would lead to the pseudo ester.

[12] S. Sarel, L. Tsai and M. S. Newman, *ibid.*, **78**, 5420 (1956).

[13] M. S. Newman and B. T. Lord, *ibid.*, **66**, 731 (1944).

COMMUNICATIONS TO THE EDITOR

REDUCTION OF ALKYL HALIDES BY ORGANOTIN HYDRIDES. EVIDENCE FOR A FREE RADICAL MECHANISM[1]

Sir:

It has been shown that organotin hydrides are capable of bringing about replacement of the halogen in alkyl,[2,3] aryl,[2,4] and acyl[5] halides by hydrogen. We have extended the fragmentary observations on the reduction of alkyl halides to include examination of the scope and mechanism of reaction (1).

$$(4 - n)RX + R'_nSnH_{4-n} \longrightarrow (4 - n)RH + R'_nSnX_{4-n} \quad (1)$$

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[1] This research was supported by the National Science Foundation under grant NSF-G-10,000.

[2] J. G. Noltes and G. J. M. van der Kerk, *Chem. and Ind.*, 294 (1959).

[3] E. J. Kupchik and R. E. Connolly, *J. Org. Chem.*, **26**, 4747 (1961).

[4] L. A. Rothman and E. I. Becker, *ibid.*, **24**, 294 (1959); **25**, 2203 (1960).

[5] H. G. Kuivila, *ibid.*, **25**, 284 (1960).