gave 9.5 g. of solid melting at 245–247°. The mixed m.p. with starting material was 220–236°. Crystallization from acetone gave the analytical sample, m.p. 256–258°.

Anal. Calcd. for $C_{25}H_{34}O_5S_2$ (478.64): C, 62.73; H, 7.16. Found: C, 62.72; H, 7.00; $[\alpha]_D$ +210° (0.5% in chloroform); λ_{KBr}, 2.96, 5.74, 5.82, 5.95, 7.30, 7.91, 8.10, 9.52μ.

Saponification with methanolic potassium bicarbonate solution yielded 17α,21-dihydroxy-4-pregnene-3,11,20-trione 3-ethylene mercaptole crystallization from acetone: petroleum ether afforded material melting at 210–213°.

Anal. Calcd. for $C_{23}H_{32}O_4S_2$ (436.61): C, 63.27; H, 7.39. Found: C, 63.18; H, 7.29; λ_{KBr}, 2.96, 5.88, 9.52 μ.

Acknowledgment.—We are grateful to E. A. Brown for the preparation of the ethanedithiol, to Anne Jaeger, Jeanette Mier and Marjorie Ziebell for the chromatographic separations and to R. T. Dillon and his staff for the analytical data.

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A *gem*-Effect in the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to γ,δ-Unsaturated Acids

BY MARCELLO DE MOURA CAMPOS

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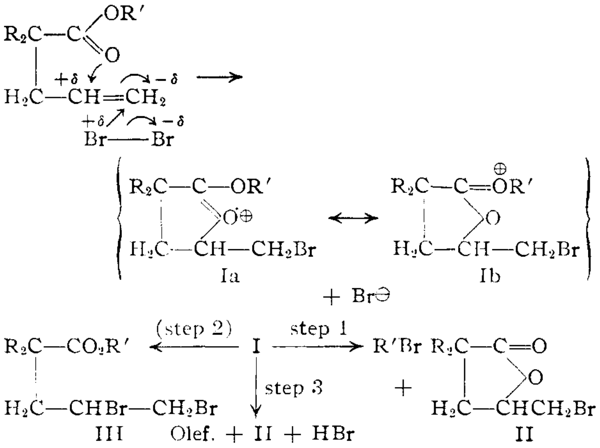
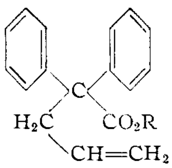
In the reaction of bromine with γ,δ-unsaturated acids and esters the carbonyl oxygen atom is able to participate in the formation of a "resonance stabilized" cyclic oxonium salt (I),[1] in a manner similar to that postulated for the bromination of N-allylbenzamide.[2]

This oxonium salt can undergo three types of transformations: either a bromolactone II or a dibromide III is formed; or, in some cases, the hydrogen bromide formed in the reaction (step 3) can compete with the bromine and simple lactones are formed.[3]

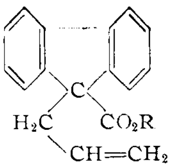


Other electrophilic reagents, like ICN[4] and H^+,[3,5] undergo the same type of reaction.

When methyl 2,2-diphenylpenten-4-oate (IVb) reacts with bromine[3,6] only bromolactone is formed, while the bromination of compound Vb gives rise to a mixture of bromolactone and dibromide.[1]



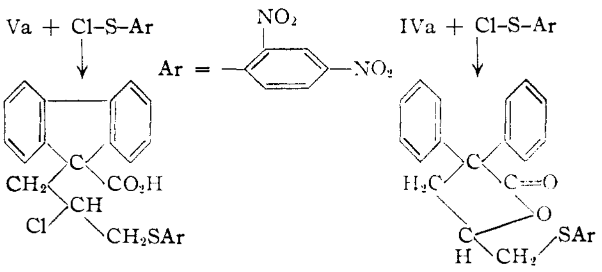
IVa, R = H
b, R = CH_3



Va, R = H
b, R = CH_3

This seems to indicate that the neighboring carbonyl group of the methyl ester IVb participates as a neighboring group in the reactions involving addition at the γ,δ-double bond to a greater extent than the carbonyl group of methyl 9-allyl-9-fluorene carboxylate.

There is a still greater difference in the behavior of the two acids when they are allowed to react with 2,4-dinitrobenzenesulfenyl chloride. This sulfenyl chloride reacts with olefins giving rise to 2,4-dinitrophenyl β-chloroalkyl sulfides.[7] This is also the result of the reaction of 9-allyl-9-fluorenecarboxylic acid (Va) with 2,4-dinitrobenzenesulfenyl chloride, where a simple addition occurs. However, when the reaction is performed with 2,2-diphenylpenten-4-oic acid (IVa), 2,2-diphenyl-5-(2,4-dinitrophenylmercapto)-4-pentanolactone (VI) is obtained.



VII VI

This difference in the behavior of the two γ,δ-unsaturated acids is probably due to the fact that in acid Va the fluorene nucleus has a planar configuration whereas in acid IVa the two benzene rings cannot achieve coplanarity,[1] thus occupying a greater space and establishing a conformation of the molecule more favorable for cyclization. This effect is similar to the so-called "*gem*-dimethyl effect" that makes the formation of dimethyl- and tetramethylsuccinic anhydride easier than that of succinic anhydride itself.[8]

In order to compare the behavior of the two acids by means of quantitative data, we measured the reaction of iodine with acids IVa and Va in chloroform solution at 0°. It can be seen from Table I that the values obtained for the rate of reaction agree with the qualitative results, acid IVa reacting much faster than acid Va.

This seems again to indicate that in acid IVa the neighboring carbonyl group participates in the addition reaction to a greater extent, increasing the rate of the reaction. We are studying the reaction

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[1] R. T. Arnold, M. de Moura Campos and L. K. Lindsay, THIS JOURNAL, **75**, 1044 (1953).

[2] S. Winstein, L. Goodman and R. Boschan, *ibid.*, **72**, 2311 (1950).

[3] P. N. Craig and I. H. Witt, *ibid.*, **72**, 4925 (1952).

[4] R. T. Arnold and K. L. Lindsay, *ibid.*, **75**, 1408 (1953).

[5] (a) G. Darzen, *Compt. rend.*, **183**, 748, 1110 (1926); (b) R. F. Raffauf, THIS JOURNAL, **74**, 4460 (1952).

[6] P. N. Craig, *ibid.*, **74**, 129 (1952).

[7] (a) N. Kharasch, L. Wehrmeister and H. Tigerman, *ibid.*, **69**, 1612 (1947); (b) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949); (c) N. Kharasch, *ibid.*, **74**, 3427 (1952).

[8] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 373.

of some derivatives of γ,δ-unsaturated acids substituted in the carboxyl group with iodine, in order to determine whether the participation of the carbonyl group is increased or decreased.

Experimental

2,2-Diphenyl-5-(2,4-dinitrobenzenemercapto)-4-pentanolactone (VI).—To 550 mg. of 2,2-diphenylpenten-4-oic acid dissolved in 15 ml. of chloroform was added 507 mg. of 2,4-dinitrobenzenesulfenyl chloride dissolved in 50 ml. of chloroform. The mixture was refluxed for four hours, washed with sodium carbonate solution (10%), twice with water, and dried with sodium sulfate. By evaporation of the chloroform, a solid yellow residue was obtained. By acidifying the carbonate solution, only starting material was recovered. After two recrystallizations from a mixture of benzene and ethanol, pale yellow needles were obtained, m.p. 222–225°, yield 410 mg. (41%). The compound does not contain chlorine.

Anal. Calcd. for $C_{23}H_{18}N_2O_6S$: N, 6.22. Found: N, 6.19.

9-[3-(2,4-Dinitrobenzenemercapto)-2-chloropropyl]-9-fluorenecarboxylic Acid (VII).—A solution of 400 mg. of 2,4-dinitrobenzenesulfenyl chloride and 495 mg. of 9-allyl-9-fluorenecarboxylic acid in 10 ml. of chloroform was refluxed for six hours. The solvent was evaporated at room temperature and a yellow residue was left. The residue was treated with benzene, and the yellow, insoluble crystals were collected and dried on a porous plate. The yield was 580 mg. (64.8%), m.p. 173–176°.

This compound contains chlorine and was recrystallized from a mixture of benzene and ethanol, giving yellow crystals, m.p. 176–178.5°.

Anal. Calcd. for $C_{23}H_{17}N_2O_6SCl$: C, 56.97; H, 3.53; N, 5.74. Found: C, 57.23; H, 3.73; N, 5.75.

Quantitative Measurements of the Reaction of Compounds IVa and Va with Iodine.—A solution of 0.5434 g. of 9-allyl-9-fluorenecarboxylic acid (Va) in 20 ml. of chloroform at 0° was mixed with 0.5511 g. of iodine dissolved in 23.43 ml. of chloroform at 0°. The initial concentration of the acid and iodine was 0.05 mole/l. The mixture was kept in a thermostat at 0 ± 0.02° and aliquots of 10 ml. were titrated with a $N/50$ $Na_2S_2O_3$ solution.

In the same manner, starting with 0.5467 g. of acid IVa and 0.5501 g. of iodine, a 0.05 mole/l. solution of these compounds was prepared.

Table I gives the values obtained in these experiments.

TABLE I

REACTION OF IODINE WITH ACIDS Va AND IVa IN CHLOROFORM SOLN. AT 0°

Time, min.	Reaction, %	
	Cmpd. Va	Cmpd. IVa
15	6.6	
20		39.2
30	10.1	
60	14.9	43.2
130		46.6
160	22.2	
240		49.2
360	28.3	
480		50.2
1380	36.8	

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The Relative Reactivity of Functional Groups toward Diazomethane

BY ALVIN I. KOSAK,[1] CARL W. HUNTINGTON AND IAN R. MACGREGOR

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The relative reactivity of various functional groups toward diazomethane is of considerable interest when polyfunctional compounds are treated with this reagent. The data recorded in the literature are generally not adequate for the construction of a reactivity series,[2] as such a comparison was usually not the primary objective of previous investigators, and the yields (or presence) of side-reaction products are sometimes not given.

We have run a series of competition reactions between five substituted benzenes wherein equimolar quantities of each of two reactants and of diazomethane were allowed to react at −10° for two hours, and the amounts of each product and of unchanged reactant were determined. The results listed in Table I indicate that the relative reactivities of the groups studied are $-CO_2H > -COBr > -COCl > -OH > -COCH_3$. This order is in agreement with the following observations. The carbonyl chloride group of 9-oxo-4-fluorenoyl chloride reacts preferentially to the carbonyl group[3]; the carbonyl halide reacts faster than the hydroxy group in 2-hydroxy-3-naphthoyl chloride[4]; the carboxy function of 4-hydroxyphthalic acid is attacked in preference to the hydroxy substituent[5]; and the hydroxy group in *p*-hydroxyacetophenone is more reactive than the carbonyl toward diazomethane.[6]

Experimental

General Procedure.—Ethereal diazomethane solutions were prepared by the method of Arndt[7] and were standardized by adding aliquots to excess benzoic acid and titrating the unreacted acid with standard sodium hydroxide solution. The average of three such determinations was used to determine the volume of solution containing 8.41 g. (0.20 mole) of diazomethane.

A solution of 0.20 mole of each reactant in 150 ml. of anhydrous ether contained in a 1-l. erlenmeyer flask was maintained at approximately −10° by means of an ice-salt mixture. The diazomethane solution (0.20 mole) was added, the flask was protected against moisture by means of a calcium chloride drying tube, and the reaction was allowed to proceed for 2 hr. If the yellow color of unreacted diazomethane were still noticeable, the excess reagent was destroyed by shaking the solution with a small volume of hydrochloric acid or by passing in hydrogen chloride.

All reactants were reagent grade or were center cuts of freshly distilled samples. All figures cited below represent the average of two runs.

Benzoic Acid–Phenol.—The solution was extracted with dilute sodium bicarbonate solution, then with several portions of 10% sodium hydroxide solution, and was finally distilled to give 18.1 g. (0.13 mole) of methyl benzoate, b.p. 84–85° (17 mm.); $n^{18.5}D$ 1.5167.

The bicarbonate extract yielded no benzoic acid upon

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[2] For a review see B. Eistert in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 513 ff.

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