6-bromo-2-naphthyl β-D-glucopyruronoside[19] (1.0 mg.) were determined as follows: Equimolar amounts of each substrate in 4 cc. of 10% methanol were adjusted with 0.15 *M* phosphocitrate buffer (1.0 cc.) to *p*H 5.0 and incubated with 0.5 cc. of the supernatant of a centrifuged homogenate (5 mg. per cc. in water) of rat liver and 0.5 cc. of a solution containing 10 mg. of a commercial preparation of bovine β-glucuronidase[20] for 4 hours at 37°. Phenol was measured by adjustment of the *p*H to 9.5 with 0.2 *M* trisodium phosphate (0.5 cc.) followed by addition of 0.5 cc. of a 30% alcoholic solution of 2,6-dibromo-N-chloro-*p*-quinoneimine (1.0 mg. per cc.). The blue color density was measured in a photoelectric colorimeter (Klett) with a 590 mμ filter and conversion to micrograms of phenol was accomplished with an appropriate calibration curve. 6-Bromo-2-naphthol was measured by adjustment of the *p*H to 7.6 with 0.2 *M* trisodium phosphate (0.3 cc.) followed by coupling to an azo dye with tetrazotized diorthoanisidine. The dye was extracted into chloroform (10 cc.) and the color density was measured in a photoelectric colorimeter with a 540 mμ filter. The procedure and calibration curve are given elsewhere.[21] Control tubes without substrate and without enzyme were also prepared.

In 4 hours, commercial β-glucuronidase had hydrolyzed the phenyl compound 7% and the naphthyl compound 52% (0.024 μM. per hour and 0.31 μM. per hour, respectively). Hydrolysis of these substrates by rat liver in 4 hours was 13 and 57%, respectively (0.05 μM. per hour and 0.35 μM. per hour). Apparently bovine glucuronidase hydrolyzes the phenyl compound less readily than does rat glucuronidase, whereas no significant difference in hydrolysis rate was found with the naphthyl compound.

Phenyldiacetyl-β-D-glucofururonolactone (II).—A mixture of triacetyl-β-D-glucofururonolactone[8] (13.5 g.), phenol (12.6 g.) and *p*-toluenesulfonic acid (0.1 g.) was fused *in vacuo* for 25 minutes at 100°. The melt was triturated with 20 cc. of 95% ethanol and the crude product was collected and washed with ethanol; yield 12.0 g., m.p. 178–181°. The product crystallized from methyl cellosolve in fine needles; yield 10.2 g. (70%), m.p. 188–189°, $[\alpha]^{30}D$ +74.5° (*c* 1.85, in chloroform). Its infrared absorption spectrum in chloroform had a 5.59 μ band for γ-lactone, a 5.75 μ band for ester, and 6.30 μ band for the phenyl group.

Anal. Calcd. for $C_{16}H_{16}O_8$ (336.29): C, 57.14; H, 4.80. Found: C, 57.17; H, 4.89.

A sample of II was dissolved in 0.1% hydrochloric acid in dioxane and its rotation of polarized light was observed not to change for 2 hours. Thus, the possibility of an ortho-ester structure (IIa) was excluded.

Deacetylation of II.—A small piece of metallic sodium (about 1–2 mm.[3]) was added to a suspension of II (0.1 g.) in 10 cc. of absolute methanol. The suspension was shaken manually, and in one hour a light yellow solution resulted. After standing for an additional hour, the solution was acidified with acetic acid and evaporated to dryness *in vacuo*. Phenol was sublimed from the mass at 1 mm. and was found to react positively with 2,6-dibromo-N-chloro-*p*-quinoneimine and sodium carbonate. The brown residue was free of phenol. It was extracted with absolute methanol. On concentrating the decolorized alcoholic solution and after 2 days at 4°, a small amount of white clusters of crystals (*ca.* 10 mg.) separated; m.p. 138–140°, $[\alpha]^{30}D$ −49.7° (*c* 1.25, water). This was probably identical with methyl-β-D-glucofururonolactone (lit. m.p. 139°), $[\alpha]^{23}D$ −59°,[22] contaminated with some of the α-isomer. When the reaction was conducted at 0° overnight, only phenol and 50% of the starting material recovered. Only phenol was obtained and no product was isolated when deacetylation was performed in absolute methanol with dry ammonia at 0°, or in absolute methanol with barium methoxide at 0°.

(19) This substrate was synthesized for the histochemical demonstration of the enzyme and its synthesis will be published by Tsou and Seligman elsewhere.

(20) Purchased from Viobin Corp., Monticello, Illinois.

(21) R. B. Cohen, K.-C. Tsou, S. H. Rutenburg and A. M. Seligman, *J. Biol. Chem.*, **195**, 239 (1952).

(22) E. M. Osman, K. C. Hobbs and W. E. Walston, THIS JOURNAL, **73**, 2726 (1951).

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Participation of a Neighboring Carboxyl Group in Addition Reactions. I. The Mechanism of the Reaction of Bromine with γ,δ-Unsaturated Acids and Esters[1]

BY RICHARD T. ARNOLD, MARCELLO DE MOURA CAMPOS[2] AND KENNETH L. LINDSAY

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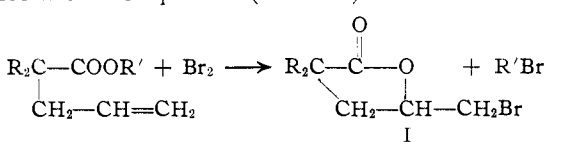
The mechanism of the reaction between bromine and γ,δ-unsaturated acids or esters, which leads to the formation of δ-bromo-γ-pentanolactones, has been investigated in some detail. The formation of alkyl bromides during the bromination of γ,δ-unsaturated esters has been shown to involve essentially complete inversion of the alkyl group. The effect of the structure of the unsaturated acid on the course of the reaction is discussed.

It has long been recognized that γ,δ-unsaturated acids frequently react with bromine to form δ-bromo-γ-pentanolactones and hydrogen bromide instead of the simple addition product, in accordance with the equation (R′ = H)



The bromination of 2,2-diphenylpenten-4-oic acid,[3] diallylmalonic acid[4] and oleanolic acid[5] represent typical examples of this transformation, and several new examples are reported in the Experimental section of this paper.

The rapid formation of δ-bromo-γ-pentanolactones from esters of γ,δ-unsaturated acids is well established in a few cases,[3,4] although the reaction has received little attention and no one has, as yet, reported the isolation of an alkyl halide (R′Br) which might be anticipated as the other product, although Craig[6] has obtained indirect evidence for the formation of methyl bromide during the bromination of methyl 2,2-diphenylpenten-4-oate. The major objective of the present study was to investi-

(1) (a) Presented before the Division of Organic Chemistry during the 122nd Meeting of the American Chemical Society at Atlantic City, N. J., September, 1952; (b) taken in part from the Ph.D. Thesis of Kenneth L. Lindsay, 1952.

(2) Rockefeller Postdoctoral Fellow from the University of Sao Paulo, Brazil.

(3) P. N. Craig and I. H. Witt, THIS JOURNAL, **72**, 4925 (1950).

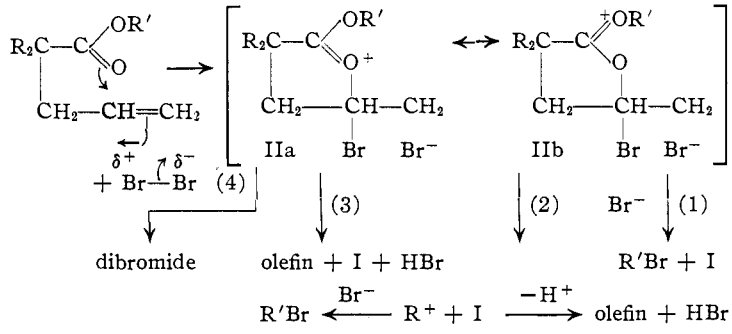
(4) R. Fittig and E. Hjelt, *Ann.*, **216**, 52 (1883).

(5) A. Winterstein and W. Hammerle, *Z. physiol. Chem.*, **199**, 56 (1931).

(6) P. N. Craig, THIS JOURNAL, **74**, 129 (1952).

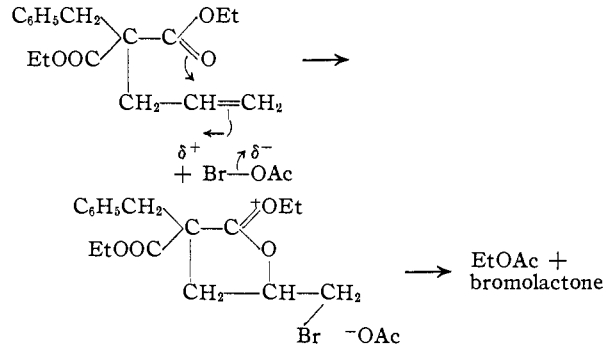
gate the bromination of γ,δ-unsaturated esters and to determine if possible the fate of the group R′.

Stereochemically, the proximity of the carbonyl oxygen atom to the γ-carbon atom of the unsaturated acid or ester allows it to participate in the formation of a resonance stabilized, cyclic oxonium salt (II) in a manner similar to that postulated for the bromination of N-allylbenzamide.[7] Of the several limiting structures which contribute to II, only IIa and IIb are indicated.



The possible reactions of II are outlined above. Reaction (1) corresponds to an S_N2 substitution of an alkyl halide and should go with complete Walden inversion. Process (2) is related to the S_N1 and E-1 elimination of an alkyl halide. Reaction (3) corresponds to an E-2 elimination and step (4) to the second stage in the normal addition to a double bond.

Ethyl bromide has now been isolated in considerable quantities from the bromination without solvent of diethyl allylbenzylmalonate and of diethyl cyclopenten-2-ylmalonate. When diethyl allylbenzylmalonate was added to a solution containing one equivalent of acetyl hypobromite (formed in acetic acid solution with sodium acetate and bromine) there was isolated ethyl acetate (50–65%) and the expected bromolactone (63%).. This reaction is assumed to take the course



When *d,l*-2-octyl 2,2-diphenylpenten-4-oate was treated with bromine at 0–10° in chloroform solution there was isolated 2-bromoöctane in a yield of 39%. The dextro and levo forms of this ester were separately brominated under the same conditions and optically active enantiomorphs of 2-bromoöctane were isolated whose rotations were opposite in sign (and configuration[8]) to those of the alcohols used in the preparation of the esters (*via* a method which does not affect the asymmetric center and therefore does not affect the configuration). From the rotations of these 2-bromoöctanes, it was calculated[9] that inversion of configuration had occurred to the extent of 97.5 and 98.5%, respectively. This establishes that the optically active bromides obtained in our work resulted overwhelmingly by way of an S_N2 type substitution.

Evidence for the formation of bromolactone *via* route (2) was obtained by examining the bromination of neopentyl 2,2-diphenylpenten-4-oate. In this case the expected bromolactone was isolated in a yield of 41% and in addition hydrogen bromide formation to the extent of 59% was observed. The formation of hydrogen bromide from the neopentyl ester must arise from an S_N1 type ionization of the neopentyl cation from the preformed oxonium salt followed by carbon skeleton rearrangement and elimination.

The evolution of hydrogen bromide during the bromination of several secondary alkyl esters can be accounted for by either path (2) or path (3) above, although path (3) appears the most likely, for if hydrogen bromide were formed by path (2) one would expect that alkyl bromide would be formed by this path in sufficient quantity to bring about an appreciable racemization of the optically active center in 2-bromoöctane. The formation of hydrogen bromide in 84% yield during the bromination of diethyl allylbenzylmalonate in chloroform solution is probably best explained by an E-2 elimination as described in path (3) above. This experiment indicates the importance of the medium in controlling the type of decomposition which the intermediate oxonium salt (II) undergoes, for it will be recalled that ethyl bromide was the predominant product when the bromination was carried out in the absence of a solvent.

In considering the factors which influence the relative extent to which dibromide formation (path 4) competes with bromolactone formation, a study of the early literature[4] indicated that bromolactone formation is facilitated by substitution in the α-position of penten-4-oic acid. This substituent effect is similar to the so-called "*gem*-dimethyl effect" which renders dimethyl- and tetramethylsuccinic acids more easily convertible to their respective anhydrides than is succinic acid itself.[10] In considering such steric effects, a comparison between 2,2-diphenylpenten-4-oic acid and 9-allyl-9-fluorenecarboxylic acid appeared to be of interest, since these compounds differ only in the bridging of the two phenyl groups into the fluorene ring system in the latter. Sterically, these two very similar compounds could be expected to behave differently, for the benzene rings of 2,2-diphenylpenten-4-oic acid should not be able to achieve coplanarity and should therefore exhibit a large *gem* effect, whereas there should be no steric interference between the neces-

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

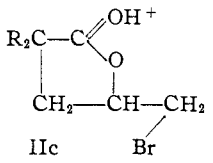
(8) E. D. Hughes, C. K. Ingold and S. Masterson, *J. Chem. Soc.*, 1196 (1937).

(9) Based upon H. Brauns' value of ±40.64° for the rotation of optically pure 2-bromoöctane; *Rec. trav. chim.*, **65**, 805 (1946).

(10) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 373.

sarily coplanar benzene rings of the fluorene derivative.

Only bromolactone (in 85% yield) was isolated from the bromination of 9-allyl-9-fluorenecarboxylic acid, but from the methyl ester dibromide was obtained in 33% yield in addition to a 48% yield of bromolactone despite the fact that methyl 2,2-diphenylpenten-4-oate gave virtually quantitative yields of bromolactone.[3,6] The difference in reactivity between the acid and the methyl ester suggests that a hyperconjugative resonance form (IIc) contributes to the structure



IIc

of II in the case of the acid, but not in the case of the ester, or that bromolactone formation is acid catalyzed.

Experimental

Diethyl Allylmalonate.—To 500 ml. of absolute alcohol in a 1-l. three-necked flask equipped with a sealed stirrer, a reflux condenser, and a dropping funnel was added 23 g. (1 gram atom) of sodium. The flask was cooled with ice during the addition of the sodium and was then protected with a calcium chloride tube. When all the sodium had reacted, 166 g. (1.03 moles) of diethyl malonate was added through the dropping funnel in a steady stream. Then 121 g. (1.00 mole) of allyl bromide was added with stirring over a period of 40 minutes, and the solution was refluxed for 15 hours until it was neutral to litmus. The reflux condenser was exchanged for a downward condenser and the alcohol was removed by distillation. The residue was shaken with water and the oily layer separated. The oil was dried azeotropically by distilling benzene from it and was then distilled *in vacuo*, yielding 135 g. (67%) of diethyl allylmalonate, b.p. 103–107° (17 mm.).

Diethyl Allylbenzylmalonate.—By using the same procedure as above, 101 g. (0.52 mole) of diethyl allylmalonate, was converted to 65 g. (43%) of diethyl allylbenzylmalonate, b.p. 142–147° (1 mm.), through the use of benzyl chloride as an alkylating agent.

Allylbenzylmalonic Acid.—A mixture of 56 g. (0.193 mole) of diethyl allylbenzylmalonate, 65 g. (1.16 moles) of potassium hydroxide and 65 g. of water was stirred vigorously and heated under reflux for nine hours. The mixture was then extracted with ether to remove any unreacted ester, and the aqueous layer was acidified with concentrated hydrochloric acid. An oil separated which was extracted with ether. The ether solution was dried over sodium sulfate, filtered and evaporated, leaving an oily residue which crystallized slowly to give 43.5 g. (98%) of allylbenzylmalonic acid as colorless needles, m.p. 113–115.5°. This compound was previously reported as an oil.[11]

Allylbenzylacetic Acid.—In a 100-ml. claisen flask, 42 g. (0.179 mole) of allylbenzylmalonic acid was heated to 180–200° until the evolution of carbon dioxide was complete (about 30 minutes). The residue was distilled *in vacuo*, yielding 30 g. (88%) of allylbenzylacetic acid, b.p. 139–147° (2.5 mm.). The acid was redistilled for analysis, b.p. 144–146° (1.7 mm.), $n^{25}D$ 1.5180.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.41; neut. equiv., 190.23. Found: C, 75.31; H, 7.67; neut. equiv., 191.3.

Diethyl Cyclopenten-2-ylmalonate.—This ester was prepared by Dr. George Scott by the method of Moffett.[12]

2,2-Diphenylpenten-4-oic Acid and 9-Allyl-9-fluorenecarboxylic Acid.—These acids were prepared according to the method of Arnold, Parham and Dodson.[13]

Methyl 9-Allyl-9-fluorenecarboxylate.—This ester was obtained in 96% yield by treating the acid with diazomethane in the usual way. It was recrystallized for analysis from methanol–water, m.p. 76–76.5°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.9; H, 6.32.

Esters of 2,2-Diphenylpenten-4-oic Acid.—The following general method was employed for the preparation of all esters of this acid. The purification of the crude ester is indicated separately for each ester. 2,2-Diphenylpenten-4-oic acid was allowed to stand overnight with an excess of thionyl chloride. By morning only one phase was present and the excess thionyl chloride was removed *in vacuo*. The residue of 2,2-diphenylpenten-4-oyl chloride was poured slowly into a solution of the appropriate alcohol in equal amounts of carbon tetrachloride and pyridine. After several days standing, the reaction mixture was poured into 10% hydrochloric acid, extracted twice with ether, and the combined ether solutions washed with 10% hydrochloric acid, water, 10% sodium carbonate and water. The ether solution was dried over magnesium sulfate, filtered, and evaporated, leaving a residue of crude ester.

2-Butyl 2,2-Diphenylpenten-4-oate.—The crude ester was fractionated through a 6-in. glass helices-packed column and the pure ester was obtained in 53% yield, b.p. 167° (1.2 mm.) to 170° (1.5 mm.), $n^{22}D$ 1.5441.

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.86; H, 7.80.

Neopentyl 2,2-Diphenylpenten-4-oate.—The crude ester was heated to 100° (0.2 mm.) to remove any volatile contaminants. The residue was then dissolved in B petroleum ether and chromatographed through an alumina column by eluting with the same solvent. The eluent (27% yield) was distilled for analysis, b.p. 125–130° (0.09 mm.), $n^{20}D$ 1.5382, $n^{25}D$ 1.5370.

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.79; H, 8.43.

Benzyl 2,2-Diphenylpenten-4-oate.—The crude ester was heated to 100° (0.2 mm.) to remove any volatile contaminants and the residue (66% yield) was not further purified, since an earlier sample had decomposed on distillation.

2-Octyl 2,2-Diphenylpenten-4-oate.—The crude ester was dissolved in B petroleum ether and chromatographed through an alumina column by eluting with the same solvent. The eluent was heated to 100° (0.2 mm.) to remove any volatile contaminants, leaving 97% of a light orange oil, $n^{25}D$ 1.5230, which was not purified further because a previous sample had decomposed on distillation.

Optically Active 2-Octyl 2,2-Diphenylpenten-4-oate.—The resolution of 2-octanol was accomplished in the usual manner,[14] and the resulting optically active 2-octanols ($[\alpha]^{17}D$ −9.47°, optical purity 97.8%, and $[\alpha]^{17}D$ +9.33°, optical purity 97.2%) were separately converted to the esters in 81 and 85% yields, respectively, by the method described above, except that the esters were not chromatographed, but were heated to 100° (0.2 mm.) directly.

Brominations.—The various bromination experiments were carried out by the three general methods described below.

Method A.—To a cooled solution of the unsaturated acid or ester in chloroform, a solution of one equivalent of bromine in chloroform was added dropwise with stirring or swirling. The chloroform solution was washed with 10% sodium carbonate, then with water, dried over magnesium sulfate, filtered and evaporated. The residue was distilled *in vacuo* or crystallized from ethanol–water. If the starting material was an acid, the sodium carbonate extract was acidified and examined for the presence of unreacted starting material or a dibromoacid.

Method B.—A solution of 1.00 g. of the unsaturated compound in 75 ml. of chloroform was placed in a 200-ml., three-necked, round-bottomed flask fitted with a glycerol-sealed stirrer, a dropping funnel, and a tube connecting the third neck with the top opening of the dropping funnel (so that pressure will be equalized throughout the closed system). The flask was cooled well in ice and a solution of one equivalent of bromine was added slowly through the dropping funnel with stirring and continued cooling. Stirring was

(11) T. B. Johnson and A. J. Hill, *Am. Chem. J.*, **46**, 548 (1911).

(12) R. B. Moffett, *Org. Syntheses*, **32**, 52 (1952).

(13) R. T. Arnold, W. E. Parham and R. M. Dodson, THIS JOURNAL, **71**, 2439 (1949).

(14) J. Kenyon, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 418.

continued for an hour (the addition of bromine required 30 minutes to one hour) and any residual bromine color was discharged by the addition of a few drops of cyclohexene. The chloroform solution was extracted with three 100-ml. portions of distilled water, and the combined aqueous extracts were immediately titrated for hydrobromic acid with standard sodium hydroxide solution (approximately 0.1 *N*) to the phenolphthalein end-point. Bromolactone was isolated if desired by evaporation of the chloroform and crystallization of the residue from ethanol–water.

Method C.—The unsaturated ester (with or without the appropriate solvent) was placed in a 250-ml., three-necked, round-bottomed flask equipped with a sealed stirrer, a dropping funnel, and a nitrogen inlet and outlet. The ester was cooled in ice and stirred during the addition of one equivalent of bromine. A stream of nitrogen was passed through the flask, and the effluent gases were swept through a trap containing copper wool (to retain bromine vapor), a trap containing potassium carbonate (to retain hydrogen bromide), and finally through a trap cooled in Dry Ice and isopropyl alcohol to collect any evolved ethyl bromide. After the addition of the bromine was complete, the flow of nitrogen was continued for two hours with the flask at 0–10°. Then the temperature was raised to 60° and the flow of nitrogen was continued for another six hours. The material which collected in the cold trap was examined to determine its identity.

Bromination of Diethyl Allylbenzylmalonate.—The bromination was carried out by method A, and bromolactone was was obtained in 75% yield, b.p. 188–191° (1.3 mm.).

Anal. Calcd. for $C_{15}H_{17}O_4Br$: C, 52.79; H, 5.02. Found: C, 52.90; H, 5.36.

Using method C, 30 g. (0.103 mole) of diethyl allylbenzylmalonate was converted to the bromolactone in 79% yield, and 6.3 g. (56%) of ethyl bromide was collected in the trap and identified by conversion to the Grignard reagent and preparation of the anilide,[15] m.p. 105–107°, mixed m.p. with an authentic sample, 107–107.5°. No solvent was employed during this bromination.

Bromination of Diethyl Cyclopenten-2-ylmalonate.—Using method C, 30 g. (0.133 mole) of diethyl cyclopenten-2-ylmalonate was brominated without solvent, and 3.06 g. (21%) of ethyl bromide was collected in the trap and identified as the anilide, m.p. 106–107°, mixed m.p. 106–107.5°. Carbon–hydrogen analyses indicated that a mixture of bromolactone and dibromoester was obtained from this reaction. The mixture could not be completely separated by distillation.

Bromination of Diethyl Allylbenzylmalonate in Acetic Acid Solution.—When the bromination of this compound was carried out by method C, using acetic acid as a solvent, ethyl bromide was obtained in 68% yield, b.p. 37–38°. It was identified as the anilide, m.p. 106–107.5°, mixed m.p. 105.5–107.5°. A trace of ethyl acetate could be detected by odor, but none could be isolated.

Bromination of Diethyl Allylbenzylmalonate in Chloroform Solution.—When this compound was brominated by method B, the yield of hydrogen bromide was 84%.

Bromination of Diethyl Cyclopenten-2-ylmalonate in Chloroform Solution.—The bromination of this compound by method B gave a 27% yield of hydrogen bromide.

Bromination of Allylbenzylacetic Acid.—This bromination was carried out according to method A, except that the acid was added to the bromine (in order to prevent competition between bromine and evolved hydrogen bromide as electrophilic reagents). The yield of bromolactone was 40%, b.p. 155–170° (0.4 mm.). The bromolactone was redistilled for analysis, b.p. 137° (0.07 mm.), $n^{25}D$ 1.5590.

Anal. Calcd. for $C_{12}H_{13}O_2Br$: C, 53.54; H, 4.89. Found: C, 53.67; H, 4.86.

From the sodium carbonate extract, dibromoacid was obtained in 29% yield, and the crude dibromoacid was analyzed, since this compound tended to decompose on distillation.

Anal. Calcd. for $C_{12}H_{14}O_2Br_2$: C, 41.16; H, 4.03. Found: C, 41.99; H, 4.41.

Reaction of Diethyl Allylbenzylmalonate with Acetyl Hypobromite.—Acetyl hypobromite was prepared by dissolving 19.5 g. (0.122 mole) of bromine in 50 ml. of glacial acetic acid, cooling with ice, and adding 10.0 g. (0.122 mole) of sodium acetate in small portions. In the same apparatus described in method C, except that the potassium carbonate trap was replaced with a potassium hydroxide trap, 35.4 g. (0.122 mole) of diethyl allylbenzylmalonate was added to the acetyl hypobromite solution and nitrogen was swept through at 0° for an hour. Then the temperature was raised to 60–65° for 10 hours and the solution was swept with nitrogen during this time. Ethyl acetate collected in the trap and was washed with 10 ml. of 10% sodium carbonate solution. After distillation, the yield of ethyl acetate was 5.3 g. (50%), b.p. 75.5–78°, $n^{19}D$ 1.3745, saponification equivalent 91.1 (calcd. 88.1). The yield of bromolactone was 63%.

Bromination of 2-Butyl 2,2-Diphenylpenten-4-oate.—Using method A, this ester was converted to the bromolactone in 70% yield, and a copious evolution of hydrogen bromide could be detected by blowing across the mouth of the flask and by placing a piece of moist blue litmus above the mouth of the flask.

Bromination of Benzyl 2,2-Diphenylpenten-4-oate.—The bromination of this ester by method A gave a 73% yield of bromolactone and no hydrogen bromide could be detected.

Bromination of Neopentyl 2,2-Diphenylpenten-4-oate.—The bromination of this compound by method B gave a 59% yield of hydrogen bromide. Bromolactone was isolated in 41% yield.

Bromination of 2-Octyl 2,2-Diphenylpenten-4-oate.—Racemic 2-octyl 2,2-diphenylpenten-4-oate was brominated by method B in duplicate experiments which gave 25.9% and 27.0% yields of hydrogen bromide. The yield of bromolactone was determined in one experiment and was found to be 83%.

The racemic ester was also brominated by method A. The chloroform solution was distilled carefully through a 6-in. Vigreux column. After most of the chloroform had been distilled, the residue was distilled through the same column *in vacuo*, giving 2-bromoöctane in 39% yield, b.p. 67–68° (12 mm.), $n^{20}D$ 1.4448, $n^{25}D$ 1.4428. Bromolactone was isolated in 69% yield.

Bromination of the ester derived from (−)-2-octanol by method A as described above for the racemic ester gave 2-bromoöctane in 32% yield, b.p. 71° (14 mm.), $n^{25}D$ 1.4490, $[\alpha]^{29}D$ +37.7°. Assuming the rotation of optically pure 2-bromoöctane to be ±40.64°,[9] this sample of 2-bromoöctane is 96.3% optically pure. Since the starting alcohol was 97.8% optically pure, inversion of configuration has occurred to the extent of 98.5%.

In a similar fashion, bromination of the ester derived from (+)-2-octanol of 97.2% optical purity gave a 44% yield of 2-bromoöctane, b.p. 77–78° (19 mm.), $n^{25}D$ 1.4488, $[\alpha]^{29}D$ −36.6°. This corresponds to an optical purity of 94.8% and a 97.5% inversion of configuration. The yields of bromolactone from the bromination of the two optically active esters were 82 and 81%, respectively.

Bromination of 9-Allyl-9-fluorenecarboxylic Acid.—The bromination of this compound by method A gave an 85% yield of bromolactone, m.p. 156–158°. This compound was recrystallized for analysis from absolute ethanol until the melting point reached 162–163°.

Anal. Calcd. for $C_{17}H_{13}O_2Br$: C, 62.02; H, 3.98. Found: C, 62.0; H, 4.19.

Bromination of Methyl 9-Allyl-9-fluorenecarboxylate.—This ester was brominated by method A, and bromolactone was obtained by crystallization from absolute ethanol in 48% yield, m.p. 158–161°. Evaporation of the filtrates to dryness and crystallization of the residue from ethanol–water yielded 33% of dibromoester, which was recrystallized from absolute ethanol for analysis, m.p. 75–76°.

Anal. Calcd. for $C_{18}H_{16}O_2Br_2$: C, 50.97; H, 3.80. Found: C, 50.79; H, 3.66.

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(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., third edition, 1948, p. 192.