tected from moisture by Drierite. The remaining solution was stirred for 6 hr. to complete saponification of the ester. Then enough deuterium chloride of approximately 20% concentration was added to the solution to bring the pH to 1, the solution was then frozen and placed on a rotary evaporator connected by way of a lyophilization trap to a high capacity oil pump, and lyophilized. The residue was rinsed to the bottom of the flask with anhydrous ether, the ether removed *in vacuo* and the flask was fitted with a condenser and placed in an oil bath at 180°. The tricarboxylic acid was decarboxylated producing succinic acid which sublimed either as the free acid or as the anhydride and collected at the neck of the flask.

A solution of 2.15 g. of barium hydroxide octahydrate in 10 ml. of hot water was added to the sublimate in a 40ml. centrifuge tube. Any undissolved barium hydroxide was transferred with another 10 ml. of hot water to the centrifuge tube, and the solution was heated with stirring for 15 min. for complete precipitation of the barium succinate. The solution was then centrifuged for 5 min., and the precipitate dissolved in 10 ml. of 2.4N hydrochloric acid. The solution was frozen immediately and lyophilized. The residue was extracted with ether in a Soxhlet apparatus for 24 hr. The succinic acid so obtained was recrystallized from acetonitrile several times, m.p. 189-190°.

Deuterium analysis. Calcd. for 2 atoms, 33.33 atom % excess D. Found, 33.67 atom % excess D.

The dimethyl esters were made by using diazomethane and distilled at reduced pressure.

Saponification of diethyl succinate in deuterium oxide.¹⁶ Diethyl succinate, 871 mg. was added to 10 ml. of deuterium oxide and then 500 mg. of sodium hydroxide was added and the mixture was stirred at room temperature with a magnetic stirrer for 1 hr. by which time saponification appeared to be complete.

Phosphorus oxychloride (0.5 ml.), freshly distilled from quinoline, was added to acidify the solution to a ρ H less than 1. The solution was then continuously extracted with ether for 24 hr., the ether removed *in vacuo*, the residue dissolved three times in 10 ml. of water, and the water lyophilized. The succinic acid was then recrystallized several times from acetonitrile, and analyzed for deuterium. Deuterium analysis showed 0.515 atom % excess deuterium.

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(16) This experiment was run as a control experiment, in order to show that very little deuterium is introduced into the succinic acid when the diethyl ester is saponified in deuterium oxide. The succinic acid was found to contain 0.515 atom % excess D or only 0.773% of the quantity calculated for complete exchange of the 4-methylene hydrogens.

The Amount of *para*-Isomer Formed in the Bromination of Biphenyl¹

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The amount of *p*-isomer formed in electrophilic substitution in biphenyl is known for bromination by positive bromine,² as well as for chlorination³ and nitration,^{4,5} but no direct value has been determined for bromination by molecular bromine, although indirect evidence indicates that it may be large.⁶ Having recently studied the kinetics of bromination of biphenyl in 50% aqueous acetic acid under conditions under which molecular bromine was identified as the only substituting agent,⁷ it was of interest to learn how much substitution took place in the 4-position under those conditions.

The amount of *p*-bromination in biphenyl was determined by the isotopic dilution method, using molecular bromine containing the radioactive isotope Br^{s_2} , exactly as described for the determination of the amounts of β -isomer in the bromination of naphthalene.⁸ The conditions in the individual determinations were similar to those in the kinetic runs,⁷ *i.e.* reactions were carried out at 25° in 50% (by volume) aqueous acetic acid, which was 0.01*M* (0.1*M* in one run) in sodium bromide, 0.4*M* in sodium perchlorate, 0.006*M* in biphenyl and approximately 0.002*M* in bromine.

Four independent determinations were carried out and the weighted average of the percentages of 4-bromobiphenyl formed was found to be 93.9 \pm 2.4, which represents the amount of 4-isomer in the total bromination product. Disubstitution is not likely to occur under those conditions, and the remaining material probably consists chiefly of 2-bromobiphenyl, with perhaps a small amount of the 3-isomer.

In bromination of biphenyl by positive bromine $(H_2OBr^+ \text{ or } Br^+)^2$ the amount of *para*-substitution is 41.7%; in molecular chlorination³ it is about 47% and in nitration in acetic anhydride 23⁴-32⁵%. The results for bromination by molecular bromine are therefore reasonable, because molecular bromine is a more selective substituting agent than either positive bromine, molecular chlorine or the nitronium ion. It is also in agreement with a value of 90% of 4,4'-dibromobiphenyl obtained with an excess of bromine in the bromination of biphenyl in acetic acid.⁹

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EXPERIMENTAL

Materials. The 50% aqueous acetic acid was prepared from purified acetic acid as before.⁸ Biphenyl (Distillation Products Industries) was recrystallized three times from ethanol (m.p. 69.1-69.7°, cor.); the purified p-bromobiphenyl¹⁰ melted at 89.9-90.6°. All inorganic materials were best reagent grade chemicals.

Determination of percentage of 4-bromobiphenyl. The procedure, instrumentation and method of calculation were as described before.⁸ The only difference was that the amount of 4-bromobiphenyl formed during reaction could not be neglected in relation to the amount of inactive material added and was taken into consideration in the final calculations. In a typical run, 12.5 ml. of a solution containing the radioactive bromine (about 5-10 μ c) and a known, small amount of bromide, was added to 487.5 ml. of a solution containing the other reagents in such concentrations that the final solution was 0.01M in sodium bromide, 0.4M in sodium perchlorate, 0.006M in biphenyl, and 0.002194M in bromine as determined by titration of a 10-ml. sample. After about 50 hr., two 10-ml. samples were withdrawn and titrated for the extent of reaction (84.01%); the excess of bromine was destroyed with sodium bisulfite. Two 5-ml. samples were withdrawn for determining the activity of the total reaction mixture. Inactive 4-bromobiphenyl (1.8128 g.) was added to the reaction mixture followed by sufficient acetone to make the solution homogeneous. Ice and water was then added and the precipitated material was recrystallized from ethanol. After four recrystallizations there was obtained Sample A (0.7135 g.) of m.p. 90.0-90.6°, which, dissolved in acetone to exactly 5 ml., had an activity of 97.24 c/s. Assuming as a first approximation that all of the bromination products formed consisted of the *µ*-isomer, the amount of total p-bromobiphenyl (added and formed) is 2.0104 g., and the recovery of pure isomer was therefore 35.49%. Hence the activity for total p-bromobiphenyl is 97.24/0.3549 = 274.0 c/s. The activity of the total amount of bromine that had reacted was 292.1 c/s. The amount of p-bromobiphenyl formed is therefore 93.8%. Using this value, the recalculated amount of total p-bromobiphenyl becomes 1.9981 g. and the percentage of *p*-isomer 93.2. No further correction was necessary. Sample A was recrystallized once more and 0.4780 g. of sample B of m.p. 90.2-90.7° was obtained; the per cent of p-isomer was similarly calculated to be 95.8. In all cases the specific activity was slightly higher after the last recrystallization and these values were used in the final average.

One of the major uncertainties was in the determination of the exact extent of reaction, because reaction is very slow, and a slight loss of bromine through reaction with the solvent is known to occur.⁷ Under the present conditions this loss was about 2-3% at the end of the reaction period, as determined by a blank. To minimize this factor, the concentration of bromide was kept low, at 0.01*M*, in order to speed up the reaction, although the kinetics had previously been studied at at least 0.1*M* bromide ion concentrations.⁷ In one case (sodium bromide = 0.1*M*), the extent of reaction was calculated from careful determinations of the rate constants under identical conditions with inactive materials. Since for this run the per cent of *p*-bromobiphenyl was the same as that for runs whose extent of reaction was found by titration, no blank corrections were applied.

Independent values for four runs were 91.9, 88.3, 96.0, and 95.8%. The weighted average is 94.0 \pm 2.6%. The

weighting was based on the estimated errors and uncertainties in the individual runs. Finally, the figure of 94.0% was used to recalculate the amount of 4-bromobiphenyl formed in all runs, and the new weighted average per cent thus obtained is 93.9 ± 2.4 .

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β -Oxoadipic Esters

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 β -Oxoadipic esters have been used as starting materials for the synthesis of several useful compounds.¹⁻⁵ Amongst the various methods^{1,6-9} for the preparations of these esters, the best yields have been reported by Viscontini and co-workers.⁸ Following their procedure we could obtain the reported yield (81%) of ethyl methyl or diethyl α -acetyl- β -oxoadipate, but ammonolysis of the crude α -acetyl esters according to their procedure, using 5% ethanolic ammonia, furnished ethyl methyl, or diethyl β -oxoadipate in an overall yield (36%) less than that reported (56-60%). However, we found that ammonolysis according to Ruggli and Maeder⁶ by passing a stream of dry ammonia into an ethereal solution of the crude α -acetyl ester at 0° furnished ethyl methyl or dimethyl β -oxoadipate in an overall yield of 60%.

The dimethyl ester of β -oxoadipic acid, however, could not be prepared in quantity either by the aforementioned procedure or by Bardhan's method,¹ the yields being 5–7%. Korman⁹ reported the preparation of this diester in 38% yield, but we found that the product obtained by his method was not

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