Tetrahedron, 1963, Vol. 19, pp. 739 to 748. Pergamon Press Ltd. Printed in Northern Ireland

DIARYLIODONIUM SALTS—XIX

REACTIONS WITH DIALKYL MALONATES[1,2]

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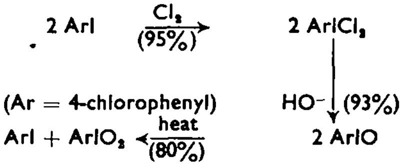
(Received 23 October, revised form 23 November)

Abstract—While diethyl malonate with diphenyliodonium chloride in t-butyl alcohol containing potassium t-butoxide gave only low yields of diethyl phenylmalonate and diethyl diphenylmalonate, reaction with 4,4′-dichlorodiphenyliodonium chloride gave good yields of the corresponding mono- and di-(4-chlorophenyl) derivatives. In methanol, ethanol and 2-propanol arylation was repressed, the main reactions now involving oxidation-reduction: dehydrogenation of the solvent and reduction of the diphenyliodonium ion. Such reactions gave ethylidene-bis-malonic ester in good yield. These observations are discussed in terms of a reaction mechanism of which the first step is electron transfer within an iodonium ion-carbanion pair ($Ar_2I^+R^-$) to form a radical pair ($Ar_2I{\cdot}R\cdot$ or $Ar{\cdot}R\cdot$), whose fate depends in part on the solvent.

PHENYLATION of dimedone,[4,5] di- and triketones[5,6] and esters[2] has been effected by the reactions of their anions with diphenyliodonium salts, usually in t-butyl alcohol. The work presently reported is concerned with the reactions of dimethyl and diethyl malonate with diphenyl- and 4,4′-dichlorodiphenyliodonium chloride in various alcohols.[7]

4,4′-Dichlorodiphenyliodonium chloride

This salt was prepared in two independent ways. The first method started with 4-chloroiodobenzene and proceeded by chlorination to the iodoso dichloride, hydrolysis to the iodoso compound and disproportionation to the iodo and iodoxy compounds. The iodoso and iodoxy compounds were then allowed to react in the



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[1] This article is taken from the dissertation of P. S. Forgione submitted in 1959 for the D. of Phil. (Chem).

[2] Preceding article on the phenylation of esters: F. M. Beringer and P. S. Forgione, *J. Org. Chem.* **28**, (1963) In press.

[3] Alfred P. Sloan Foundation Fellow, 1956–1959.

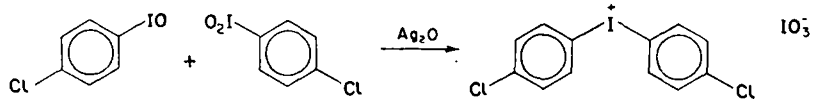
[4] O. Neiland, G. Ia. Vanags and E. Iu. Gudrinietse, *J. Gen. Chem. Moscow*, **28**, 1256 (1958) (In English).

[5] F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron* **8**, 49 (1960).

[6] F. M. Beringer, S. A. Galton and S. J. Huang, *J. Amer. Chem. Soc.* **84**, 2819 (1962).

[7] Much of the early exploratory work with primary and secondary alcohols was carried out before it developed that phenylations were generally more successful in t-butyl alcohol (ref. 2, 5, 6).

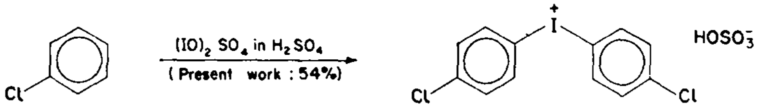
presence of silver oxide, forming 4,4'-dichlorodiphenyliodonium iodate, which was reduced *in situ* to the iodonium iodide.[8]



This salt by two metatheses gave 4,4'-dichlorodiphenyliodonium chloride[9] of unequivocal structure. A much more convenient synthesis used the direct coupling of

$$\begin{tikzcd}
Ar_2I^+ \, IO_3^- \arrow[r, "SO_2", "H_2O"'] & Ar_2I^+ \, I^- \arrow[d, "AgNO_3"'] \\
Ar_2I^+ \, Cl^- & Ar_2I^+ \, NO_3^- \arrow[l, "NH_4Cl", "(52\% \text{ overall})"']
\end{tikzcd}$$

chlorobenzene with iodyl sulfate in sulfuric acid, discovered by Masson[10] and more fully developed in this Laboratory.[11] The iodonium bisulfate was readily recrystallized to remove any isomeric impurities and converted by metathesis to the chloride.



RESULTS

Attempted arylations in methanol, ethanol and 2-propanol. In the present work the first attempts to phenylate esters were made in methanol and ethanol. Such reactions gave low yields of phenylmalonic esters and other, unexpected products.[12–15] Thus, in methanol dimethyl malonate gave with diphenyliodonium chloride the desired dimethyl phenylmalonate (25%), the expected iodobenzene (77%) and the unexpected benzene[12] (15%).

It seems likely that there were at least two competing reactions: the desired

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[8] This sequence is well exemplified by the synthesis of diphenyliodonium iodide from iodobenzene as reported by H. C. Lucas and E. R. Kennedy; E. C. Horning, *Organic Synthesis, Coll.* Vol. III, John Wiley, New York (1955): (a) chlorination, p. 482; (b) hydrolysis (co-authored by M. W. Formo), p. 483; (c) oxidation or disproportionation, p. 485; (d) coupling, p. 355.

[9] L. W. Wilkinson [*Ber. Dtsch. Chem. Ges.* **28**, 99 (1895)] presumably used this sequence to prepare 4,4'-dichlorodiphenyliodonium salts, but no details of synthesis are given.

[10] I. Masson *et al.*, Nature, Lond. **139**, 150 (1937); *J. Chem. Soc.* **1937**, 1718; *ibid.* **1938**, 1999 and 1702.

[11] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, *J. Amer. Chem. Soc.* **81**, 349 (1959).

[12] When this research has started in 1956, the common mode of reaction of the diphenyliodonium ion with bases seemed to be simple phenylation (ref. 13, 14), although several reactions were recognized as probably involving free radicals (ref. 13, footnote 15). In this sense some of the reactions encountered in runs of iodonium ions with carbanions (dehydrogenation of solvent and formation of benzene, iodide ion and "dimer-like" products) and with organometallic compounds (ref. 15) were unexpected.

[13] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Amer. Chem. Soc.* **75**, 2708 (1953).

[14] F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3203 (1955).

[15] F. M. Beringer, J. W. Dehn, Jr. and M. Winicov, *ibid.* **82**, 2948 (1960).

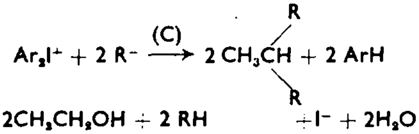
phenylation and an unexpected oxidation-reduction forming benzene. If RH represents a malonic ester and Ar_2I^+ an iodonium ion, the overall reactions may be tentatively formulated as follows:

$$Ar_2I^+ + R^- \xrightarrow{(A)} ArR + ArI$$

$$\begin{array}{ll} Ar_2I^+ + R^- \xrightarrow{(B)} & RH + ArH + ArI \\ + CH_3OH & + H_2C{=}O \end{array}$$

While the formation of formaldehyde was not established here, related reactions of diethyl malonate with diphenyl- and 4,4′-dichlorodiphenyliodonium chloride in ethanol gave evidence for the formation of acetaldehyde, as ethylidene-bis-malonic ester[16] was isolated in surprisingly high yield (70–72%). The unsubstituted iodonium salt gave some benzene, while its 4,4′-dichloro derivative gave chlorobenzene. In both cases some iodide ion was formed.

As iodide ion is not formed in reactions A or B above, a new reaction is required, one possibility is formulated as reaction C:



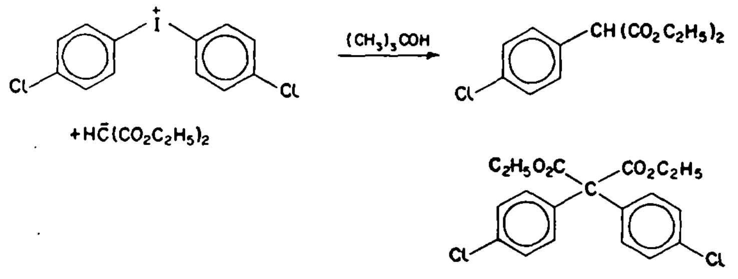
$$\begin{array}{ll} Ar_2I^+ + 2\,R^- \xrightarrow{(C)} & 2\,CH_3CHR_2 + 2\,ArH \\ 2CH_3CH_2OH + 2\,RH & + I^- + 2H_2O \end{array}$$

Dehydrogenation of the solvent was also observed in similar runs with diethyl malonate and diphenyliodonium chloride in 2-propanol.[6] Such a run gave a low yield of diethyl phenylmalonate (10%) along with benzene (11%), acetone (27%) and the acetonemalonic ester condensation product diethyl isopropylidenemalonate (14%).

Diethyl malonate in t-*butyl alcohol.* The least successful phenylation of an ester in t-butyl alcohol was that of diethyl malonate. Only small yields of diethyl phenylmalonate (6%) and diethyl diphenylmalonate (10%) were obtained, along with 82% of iodobenzene, 19% of benzene and 46% of acetone. In addition there were obtained small yields of tetraethyl 1,1,2,2-ethanetetracarboxylate, isolated as the tetraanilide, and another high-boiling ester, possibly t-butyl diethyl 1,2-diphenylethane-1,1,2-tricarboxylate.

On the other hand a successful arylation was achieved in a similar reaction of malonic ester with 4,4′-dichlorodiphenyliodonium chloride.[17] Products included diethyl 4-chlorophenylmalonate (23%), diethyl bis-(4-chlorophenyl) malonate (36%), 4-chloroiodobenzene (63%), chlorobenzene (6%) and acetone (10%).

The structure of the monoaryl derivative was proved by the identity of its I.R.



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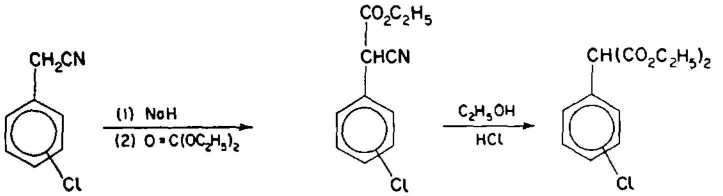
[16] F. E. Ray, *J. Amer. Chem. Soc.* **50**, 661 (1928).

[17] The origin of the difference in results with the unsubstituted and the 4,4′-dichlorodiphenyliodonium salts is not known.

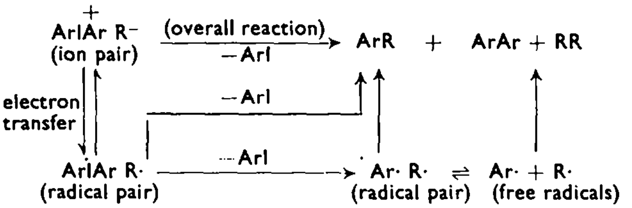
spectrum with that of an authentic sample of diethyl 4-chlorophenylmalonate but not of diethyl 3-chlorophenylmalonate. To make these esters, the chlorobenzyl cyanides were first carbethoxylated with diethyl carbonate to give ethyl chlorophenylcyanoacetates, which on treatment with ethanol saturated with hydrogen chloride gave diethyl chlorophenylmalonates.



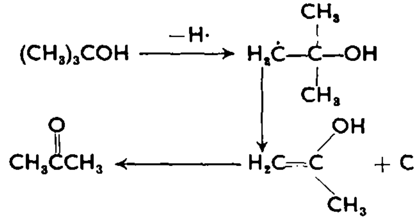
The diethyl bis-(4-chlorophenyl) malonate was shown to have the structure assigned by oxidation to 4,4'-dichlorobenzophenone, subsequently converted to the 2,4-dinitrophenylhydrazone. Also, saponification and decarboxylation gave the known bis-(4-chlorophenyl) acetic acid in high yield.

DISCUSSION OF RESULTS

A mechanism proposed[6] for the phenylation of carbanions by iodonium salts may allow partial explanation of the above observations.[18] The proposed mechanism starts with electron transfer within ion pairs from carbanions to iodonium ions to give radical pairs. The members of such radical pairs in t-butyl alcohol largely react together, either by radical displacement of R· on diaryliodine[19] or by coupling of R· and aryl radicals. Some free radicals, formed by diffusion apart of the members of the members of the radical pairs, later couple to give ArR, ArAr and RR. Coupled radicals in the form of RR have been observed in the present work. The low yields of biphenyl may be accounted for by the ability of free phenyl radicals to abstract hydrogen from solvent, even t-butyl alcohol, to form benzene; in the phenylation of 2-phenyl-1,3-indandiones the presence of biphenyl has been reported.[6]



t-Butyl alcohol is a superior solvent for at least three reasons: its low acidity



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[18] The present discussion specifically includes the phenylations of esters previously reported (ref. 2), as mechanisms were not discussed in that article.

[19] A possible role of diaryliodines in chemical reactions was first mentioned in an article concerned with the electroreduction of iodonium salts: H. E. Bachofner, F. M. Beringer and L. Meites, *J. Amer. Chem. Soc.* **80**, 4269 (1958).

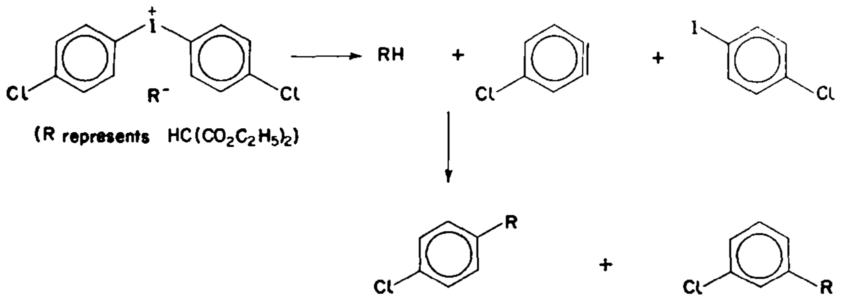
(pK_a — 19), its relative unreactivity toward free radicals[20] and the lower reactivity of its decomposition product, acetone, toward carbanions as compared to formaldehyde and acetaldehyde. The first of these is important in converting the esters to carbanions, the second minimizes destruction by solvent of the proposed radical pairs, while the third simplifies work-up.

With malonic and oxalacetic esters it was observed that much better yields of products were obtained when there was only one acidic hydrogen on the carbon to be phenylated.[2] This can be understood in part as arising from the easier work-up of a reaction mixture containing one major product rather than two (mono-and diphenyl derivatives). This cannot be the whole story, as the yield of oxidation-reduction products, especially of benzene, was smaller when the reactant had only one acidic hydrogen. A possible explanation is that the substituents (alkyl, phenyl, acetamido) stabilize the free radicals more than they do the carbanions from which they are derived. Thus, the substituents both faciliate the original electron transfer and make the ester radical more selective and thus less apt to react with the solvent. The effect of the substituent should also favor diphenylation.

As indicated in the discussion of reactions of diethyl malonate, reduction of the diphenyliodonium ion apparently proceeds to different extents: with formation of benzene and iodobenzene (reaction B), and with formation of benzene and iodide ion (reaction C). The extent of oxidation-reduction was less with esters having a single acidic hydrogen than those having two. Further, oxidation-reduction was generally less in t-butyl alcohol than in primary or secondary alcohols. The most extensive oxidation-reduction was observed with malonic ester and diphenyliodonium chloride in ethanolic sodium ethoxide, with substantial formation of benzene, iodide ion and ethylidene-bis-malonic ester. The pathway for the formation of iodide ion is not presently known. One possibility is the acceptance by the diphenyliodonium cation of two electrons, in one or more steps. Further work in this area is anticipated.

$$(C_6H_5)_2\overset{+}{I} + 2\,R^- \longrightarrow I^- + 2\,C_6H_5\cdot + 2\,R\cdot$$

At the time the present work was begun the above mechanism for the phenylation of carbanions had not been formulated,[6,19] and it was felt desirable to seek evidence for the possible intermediacy of benzynes in the reactions of iodonium ions with strong bases such as carbanions. If 4,4′-dichlorodiphenyliodonium ion reacted with sodiomalonic ester *via* a chlorobenzene both 3- and 4-chlorophenylmalonic ester,



(R represents $HC(CO_2C_2H_5)_2$)

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[20] The poor yields of phenylated products from malonic ester and the relative complexity of reaction products even in t-butyl alcohol suggest that the radical $H\dot{C}(CO_2C_2H_5)_2$ abstracts hydrogen from solvent readily; this may be due to its electronegativity.

would be expected as products. The observed identity of the spectra of 4-chlorophenymalonic ester from the arylation reaction and from 4-chlorobenzyl cyanide may be interpreted as meaning that no more than about 5% of 3-chlorophenylmalonic ester was formed in the arylation.[21] However, this result still does not exclude reaction *via* 4-chlorobenzyne, as it is not known in what proportions this benzyne would add malonic ester to form 3- and 4-chlorophenylmalonic esters.[22]

While the above work does not exclude arynes as intermediates in the arylation of carbanions with iodonium salts in t-butyl alcohol, it is felt that the observed[2,5,6] dehydrogenation of alcohols and the observed[6] influence of oxygen and of styrene on phenylations in t-butyl alcohol are better explained as arising from electron-transfer reactions.

EXPERIMENTAL

4,4′-*Dichlorodiphenyliodonium chloride*

(a) *From chlorobenzene, with iodyl sulfate*[11]. To a suspension of 0·5 mole $(IO)_2SO_4$ prepared by the oxidation of iodine with nitric in fuming sulfuric acid and held at 5–10°, 310 ml acetic anhydride and 338 g (3 moles) chlorobenzene were added in succession dropwise over 3 hr. Stirring (20°, 12 hr; 45°, 2 hr), hydrolysis (one l. water, at 5°) and chilling of the reaction mixture, followed by collection and recrystallization of the precipitate from methanol gave 243 g (0·54 moles, 54%) 4,4′-*dichlorodiphenyliodonium bisulfate;* after 3 recrystallizations from methanol, m.p. 191–192°. Metathesis with ammonium chloride in hot aqueous methanol gave, quantitatively, 4,4′-*dichlorodiphenyliodonium chloride*. Three recrystallizations from acetonitrile gave 171 g (0·45 mole, 45%) of the pure salt, m.p. 204°; reported[9,11] m.p. 202°, 210°.

(b) *From 4-chloroiodobenzene.*[9] Chlorination[8a] of 145 g (0·61 mole) of 4-chloroiodobenzene in chloroform at 0° gave 180 g (0·58 mole, 95%) of yellow 4-*chloroiodosobenzene dichloride*, m.p. 115–116°; reported[18] m.p. 116–117°. This was hydrolyzed[8b] by grinding with 300 g crushed ice and 145 g anhydrous sodium carbonate and slowly adding 410 ml 5N NaOH. Water was added as needed to facilitate grinding. After several hours treatment the product was collected, washed with water, air-dried and washed with chloroform to give 136 g (0·154 mole, 93%) yellow 4-*chloroiodosobenzene* which slowly decomposed on heating, reported[26] m.p. over 85° (Exp.). 4-*Chloroiodoxybenzene* was prepared in 80% yield by the disproportionation[8c] of the iodoso compound by boiling an aqueous suspension for 6 hr; m.p. 245° (Exp.); reported[26] m.p. 243° (Exp.).

A mixture of 81·8 g (0·40 mole) 4-chloroiodosobenzene, 106 g (0·4 mole) 4-chloroiodoxybenzene and silver oxide freshly precipitated from 170 g (1 mole) silver nitrate in 2 l. water was shaken for 36 hr. After removal of the silver salts, the solution was treated with sulfur dioxide. The precipitated iodonium iodide was filtered and washed with water, and the aqueous phase on treatment with iodide ion afforded a small additional amount of iodide salt. The damp 4,4′-dichlorodiphenyliodonium iodide was added to a large volume of boiling ethanol and carefully treated with the alcoholic silver nitrate until metathesis was complete. The solution was boiled for an additional ½ hr, filtered and concentrated under red. press. The residue dissolved in hot water was treated with NH_4Cl aq to give the iodonium chloride. Filtration and crystallization from acetonitrile gave 79 g (0·21 mole, 52%) 4,4′-*dichlorodiphenyliodonium chloride*, m.p. 202–204°; reported[9,11] m.p. 202°, 210°.

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[21] It is believed that 5 percent or more of the m-isomer in the arylation product would have been detected in the infrared spectrum.

[22] The reported reaction of p-dichlorobenzene with sodamide in liquid ammonia to give p-chloroaniline may be taken as evidence that 4-chlorobenzene reacts with anions preferentially to give p-isomers: J. H. Wotiz and F. Huba, *J. Org. Chem.* **24**, 555 (1959).

[23] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y. and by Dr. K. Ritter, Basel, Switzerland.

[24] Capillary melting points, taken in a Hershberg apparatus, are corrected.

[25] Infrared spectra were taken with a Perkin-Elmer 21 double-beam spectrophotometer, while ultraviolet spectra were taken with a Process and Instruments Co. model RS-3 recording spectrophotometer using Fisher Spectral Grade methanol.

[26] C. Willgerodt, *Ber. Dtsch. Chem. Ges.* **26**, 1947 (1893).

Diethyl m- *and* p-*chlorophenylmalonates*

Ethyl p-*chlorophenylcyanoacetate*. To 300 ml anhydrous ether containing 24 g (1·0 mole) sodium hydride there was added dropwise with stirring 147 g (1·0 mole) freshly distilled *p*-chlorobenzyl cyanide. After heating under reflux for ½ hr and cooling to room temp, 159 g (1·0 mole) freshly distilled diethyl carbonate was added over 2 hr at 20–30°. Stirring was continued for 1 hr at room temp and for ½ hr under reflux. Decomposition of a small amount of unreacted sodium hydride with ethanol, dilution with 300 ml water, acidification with dil. HCl, extraction with ether and distillation of the dried extract gave 134 g (0·60 mole, 60%) *ethyl* p-*chlorophenylcyanoacetate*, b.p. 140–146°/0·4 mm., n_D^{25} 1·5181. An analytical sample, b.p. 118°/0·05 mm., n_D^{25} 1·5171, was prepared by redistillation. (Found: C, 59·23; H, 4·56. Calc. for $C_{11}H_{10}ClNO_2$: C, 59·06; H, 4·50%).

Diethyl p-*chlorophenylmalonate*. A rapid stream of hydrogen chloride was passed into a solution of 59·5 g (0·265 mole) ethyl *p*-chlorophenylcyanoacetate in 80 g 95% ethanol and 2 g water. The reaction mixture was saturated first hot and then cold and after standing at room temp overnight, was heated 1 hr on the steam bath, cooled and treated with 500 ml water to dissolve the ppt. ammonium chloride. After ether extraction, 4·2 g insoluble material was filtered from the aqueous phase. Distillation of the dried ethereal solution gave 47·2 g (0·175 mole, 61%) *diethyl* p-*chlorophenylmalonate*, b.p. 115–116°/0·1 mm. An analytical sample, b.p. 123°/0·2 mm, n_D^{25} 1·4999, was prepared by redistillation. (Found: C, 57·77; H, 5·50. Calc. for $C_{13}H_{15}ClO_4$: C, 57·67; H, 5·58%).

The insoluble material obtained from the aqueous phase (see above) gave white needles, m.p. 158–159°, of *ethyl* p-*chlorophenylmalonamate* when recrystallized from Skellysolve C. I.R. analysis (KBr pellet) showed bands at 2·94 μ and 3·13 μ (NH stretching for bonded primary amide), 5·74 μ (ester), and 6·02 μ (C—O adsorption for primary amide). This amide ester with hot aqueous methanolic potassium hydroxide gave ammonia. Careful treatment of the basic solution with excess hydrochloric acid and heating at reflux for 1 hr gave *p*-chlorophenylacetic acid, m.p. 102–103°; reported[27] m.p. 104–105°. (Found: C, 54·95; H, 5·16. Calc. for $C_{11}H_{12}ClO_3N$: C, 54·66; H, 5·02%).

Heating of 1 g ethyl *p*-chlorophenylmalonamate under nitrogen at 180° for 4 hr gave 0·2 g p-*chlorophenylmalonamide*, m.p. 243–244°, when crystallized from ethanol. (Found: C, 50·81; H, 4·05. Calc. for $C_9H_9ClN_2O_2$: C, 50·84; H, 4·21%).

m-*Chlorobenzyl cyanide*. To 200 g (1·57 mole) *m*-chlorotoluene contained in a 2-liter three-necked flask there was added dropwise 256 g (1·60 mole) bromine while the flask at 140–160° was illuminated for 6 hr with a clear 375-watt tungsten lamp. After aspiration to remove hydrogen bromide, the crude *m*-chlorobenzyl bromide was added over 1 hr to a hot solution of 140 g potassium cyanide in 600 ml 1:1 water–ethanol. The stirred mixture was boiled for 6 hr, cooled and diluted with 1·5 l. water. Extraction with ether, drying over Drierite and distillation gave 76 g (0·50 mole, 32%) m-*chlorobenzyl cyanide*, b.p. 131–132°/9 mm $n_D^{28·5}$ 1·5540 (reported[27] b.p. 134–136°/10 mm), 127°/7 mm.

Ethyl m-*chlorophenylcyanoacetate*. The preparation was similar to that of the *p*-isomer (see above): the reaction of 62 g (0·41 mole) *m*-chlorobenzyl cyanide with 10 g (0·42 mole) sodium hydride and 48·3 g (0·41 mole) freshly distilled diethyl carbonate. The only modification was that the reaction mixture was stirred for 12 hr under reflux before work-up. Distillation of the ethereal extract gave 54 g (0·241 mole, 58%) *ethyl* m-*chlorophenylcyanoacetate*, b.p. 150–152°/0·2 mm; an analytical sample had a b.p. 151·5°/0·2 mm n_D^{25} 1·5199. (Found: C, 58·81; H, 4·47. Calc. for $C_{11}H_{10}ClNO_2$: C, 59·06; H, 4·50%).

Diethyl m-*chlorophenylmalonate*. This was prepared, as described for the *p*-isomer, from 53 g (0·240 mole) ethyl *m*-chlorophenylcyanoacetate, ethanol and gaseous hydrogen chloride. Distillation gave 32·9 g (0·122 mole, 51%) crude *diethyl* m-*chlorophenylmalonate*, b.p. 145–155°/1·5 mm. An analytical sample b.p. 145°/1·2 mm, n_D^{25} 1·5003, was obtained on redistillation. (Found: C, 57·79; H, 5·45. Calc. for $C_{13}H_{15}ClO_4$: C, 57·67; H, 5·58%).

Malonic esters with iodonium salts

Dimethyl malonate with sodium methoxide and diphenyliodonium chloride in methanol. After 198 g (1·5 moles) dimethyl malonate had been added to a solution containing 1·5 moles sodium methoxide in 1·5 l. absolute methanol, the reaction mixture containing a colorless gel was stirred for 30 min. Following the portionwise addition of 316 g (1·0 mole) diphenyliodonium chloride over 1 hr, stirring was continued: 20°, 24 hr; under reflux 1 hr. The solution was diluted with 5 l. saturated NaCl aq,

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[27] G. S. Miara and J. S. Shukla, *J. Indian Chem. Soc.* **28**, 482 (1951).

acidified, and extracted repeatedly with ether. The aqueous phase gave a negative test for formaldehyde when tested with dimedone.

Distillation of the dried ethereal solution and collecting a fraction to b.p. 83° gave a 15% yield of benzene as determined by uv spectrophotometry. Nitration of a portion of this fraction gave *m*-dinitrobenzene, m.p. 90°; no depression on mixed m.p. with an authentic sample. Continued distillation gave a mixture of 156 g (0·77 mole, 77%) iodobenzene and 40 g (0·31 mole) recovered dimethyl malonate.

A fraction, 51·6 g, b.p. 160–180°/16 mm, n_D^{25} 1·4902, was next collected. Carbon, hydrogen and I.R. analysis indicated the presence of some hydroxyl groups, possibly incorporated in the compound dimethyl hydroxymethyl-phenylmalonate. Treatment of a portion of this fraction with acetyl chloride and pyridine in order to convert it to the acetate failed, giving instead dimethyl phenylmalonate, m.p. 50° (from pet. ether), reported[28] m.p. 50°. On standing, the liquid fraction, b.p. 160–180°/16 mm, solidified. Recrystallization from pet. ether gave 49·1 g (0·24 mole, 24% based on iodonium salt) of colorless dimethyl phenylmalonate, m.p. 49–50°. Saponification of this ester, followed by heating with conc. HCl gave phenylacetic acid, m.p. 76°; no depression on mixed m.p. with an authentic sample. (Found: C, 63·30; H, 5·70. Calc. for $C_{11}H_{12}O_4$: C, 63·46; H, 5·81%).

A small final fraction, b.p. 124–164°/0·1 mm, was collected, which on redistillation gave a main cut at 146°/0·1 mm, n_D^{28} 1·4672. Elemental analysis indicated C and H values of 53·35 and 6·06% respectively, but the compound was not dientified further.

When the same reaction was carried out with diethyl malonate in excess methanol with sodium methoxide, the results were found to be essentially the same, with 13% of benzene and 21% of dimethyl phenylmalonate as products.

Diethyl malonate with sodium ethoxide and diphenyliodonium chloride in ethanol. After 240 g (1·5 mole) ethyl malonate had been added to a solution of 34·5 g (1·5 g-atom) sodium in 1·5 l. abs. ethanol and 316 g (1·0 mole) diphenyliodonium chloride had been added in 10 portions at 15° over 1 hr, stirring was continued: 20°, 18 hr; 55°, 1 hr.

The cooled reaction mixture was diluted with 5 l. water and acidified (congo red). After cooling, a mixture of diphenyliodonium chloride and iodide weighing 162 g was filtered from the aqueous solution. Treatment of a small portion of this solid with hydrogen peroxide in acid solution gave a positive starch-iodide test. Fractional crystallization of this mixture gave 24 g (0·075 mole) recovered diphenyliodonium chloride, m.p. 228°, and 136 g (0·334 mole) of the less soluble diphenyliodonium iodide, m.p. 173°; admixture with authentic salts gave no depression in m.p.

The above aqueous solution was then saturated with sodium chloride and repeatedly extracted with ether. Distillation of the dried extract gave a first fraction of b.p. to 83° which contained 21·3 g (0·272 mole, 46% based on unrecovered iodonium salt) benzene, as determined by U.V. spectrophotometry.

Continued distillation gave 146·5 g (0·423 mole, 72%, based on unrecovered iodonium salt) ethylidene-bis-malonic ester, b.p. 137–153°/0·1 mm, n_D^{25} 1·4422. An analytical sample, b.p. 125°/0·03 mm, n_D^{25} 1·4406, was prepared; its I.R. spectrum was found to be completely superimposable on that of authentic ethylidene-bis-malonic ester.[29] (Found: C, 55·71; H, 7·52. Calc. for $C_{16}H_{26}O_8$: C, 55.48; H, 7·57%).

When diphenyliodonium bromide was used, a 69% yield of ethylidene-bis-malonic ester was obtained.

Ethyl malonate with sodium isopropoxide and diphenyliodonium chloride in isopropyl alcohol. To a solution containing 1·5 l. dry isopropyl alcohol there was added with stirring 240 g (1·5 moles) of diethyl malonate. After stirring for 30 min, 316 g (1·0 mole) diphenyliodonium chloride was added over 1 hr, with the temp rising to 65°, held there for 1 hr and increased to reflux for 2 hr. The cooled reaction mixture was diluted with 5 l. saturated sodium chloride solution, acidified and extracted with ether. Treatment of a measured volume of the aqueous phase with 2,4-dinitrophenylhydrazine gave a calculated total yield of 27% *acetone 2,4-dinitrophenylhydrazone*, based on diphenyliodonium chloride.

Distillation of the dried ethereal extract on a stream bath gave a fraction b.p. to 84° containing an 11% yield of benzene, as determined by u.v. spectrophotometry. Distillation of the residue gave 145 g (0·71 mole, 71%) iodobenzene and 180 g (1·125 moles) recovered diethyl malonate. Continued

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[28] M. Rising and J. Stieglitz, *J. Amer. Chem. Soc.* **40**, 728 (1918).

[29] F. E. Ray, *J. Amer. Chem. Soc.* **50**, 561 (1928).

distillation gave 10·3 g (51 mmoles, 14%, based on unrecovered diethyl malonate) *diethyl isopropylidenemalonate*, b.p. 114–115°/10 mm, n_D^{25} 1·4470. Comparison of the I.R. spectrum with that of authentic diethyl isopropylidenemalonate[30] showed the samples to be identical. (Found: C, 60·17; H, 7·89. Calc. for $C_{10}H_{16}O_4$: C, 59·98; H, 8·05%).

The residue was distilled further to give 8·5 g (36 mmoles, 10%, based on unrecovered diethyl malonate) of *ethyl phenylmalonate*, b.p. 160–161°/10 mm.

A final heavy yellow fraction, 6·2 g, was obtained from the tarry residue using a Hickman molecular still at 160° and 10^{-4} mm. Analysis gave 71·61% C and 6·59% H, but this product was not identified further. Distillation of material found in the traps (dry-ice-acetone mixture) gave 4·2 g (48 mmoles, 13%) of ethyl acetate, b.p. 77%, converted to acetamide, m.p. 81–82°.

Diethyl malonate with potassium t-butoxide and diphenyliodonium chloride in t-butyl alcohol. After 120 g (0·75 mole) diethyl malonate had been added to a solution containing 0·75 mole potassium t-butoxide in 1·2 l. dry t-butyl alcohol, the reaction mixture containing a colorless gel was stirred for 30 min. Diphenyliodonium chloride (237·7 g, 0·75 mole) was added over 30 min at 15°. Removal of the ice bath allowed the temp of the reaction to rise to 45°, where it was held by cooling. Stirring was continued for 24 hr at room temp and for 30 hr under reflux.

The 800 ml solvent obtained by distillation of the reaction mixture contained, by vapor phase chromatographic analysis, 20·4 g (0·35 mole, 46%, based on iodonium salt) acetone and 11 g (0·14 mole, 19%) benzene. Acetone was also identified as the 2,4-dinitrophenylhydrazone. Benzene was isolated as such by first forming the ternary azeotrope (water, benzene, t-butyl alcohol, b.p. 67°), drying over calcium chloride and distilling over sodium. This gave benzene b.p. 80°, n_D^{25} 1·5002, with an I.R. spectrum identical to that of pure benzene.

The reaction mixture was then diluted with 3 l. water, acidified, and extracted with ether. Distillation of the dried extract gave 91·4 g (0·45 mole, 60%) iodiobenzene and 31·1 g (0·193 mole) recovered diethyl malonate. Continued distillation gave 7·8 g (33 mmoles, 6%) *diethyl phenylmalonate*, b.p. 161–163°/10 mm, with an I.R. spectrum identical to that of an authentic sample.

The next fraction gave 18·1 g (58 mmoles, 20%) *diethyl diphenylmalonate*, b.p. 150–159°/0·1 mm, m.p. 58°. (Found: C, 72·78; H, 6·63. Calc. for $C_{19}H_{20}O_4$: C, 73·04; H, 6·45%).

Heating diethyl diphenylmalonate with excess aniline under reflux gave diphenylmalonanilide, m.p. 187–188°, reported[31] m.p. 187–188°. Also saponification of this ester and decarboxylation gave diphenylacetic acid, neutralization equivalent 212·2, m.p. 145–146°, reported[32] m.p. 145°.

A final fraction of 4·2 g viscous oil, b.p. 190–225° at 0·3–0·4 mm, was collected. Dissolving this oil in a small amount of benzene followed by the addition of pet. ether gave 3·1 g (7 mmoles, 3%) white clusters of an ester, possibly *t-butyl diethyl* 1,2-*diphenylethane*-1,1,2-*tricarboxylate*, m.p. 121–122°. Elemental and I.R. analysis (bands for phenyl, ester and t-butyl groups) indicate a structure of this general type. (Found: C, 70·42; H, 6·69. Calc, for $C_{25}H_{30}O_6$: C, 70·40; H, 7·09%).

The I.R. spectrum of this compound was found to be identical with that of the small amount of material obtained from the reaction of diethyl phenylmalonate with diphenyliodonium chloride in t-butyl alcohol.[2]

An earlier experiment gave a crude fraction, b.p. 110–158°/3 mm, which with excess aniline at reflux temp for 2 hr yielded (after boiling in hot ethanol) 3·6 (7 mmoles, 3%) of very insoluble 1,1,2,2-ethanetetracarboxanilide m.p. 280°. (Found: C, 71·13; H, 5·82. Calc. for $C_{30}H_{26}O_4N_4$: C, 71·13; H, 5·17%).

Diethyl malonate with 4,4′-*dichlorodiphenyliodonium chloride* (*attempted arylation in ethanol*). After 74 g (0·44 mole) diethyl malonate had been added to a solution of 1·5 l. of abs. ethanol containing 0·44 mole sodium ethoxide, 85·1 g (0·22 mole) 4,4′-dichlorodiphenyliodonium chloride was added over ½ hr. During the addition the temp rose to 60°, where it was held by cooling. The mixture was stirred at 70° for ½ hr and then at room temp for an additional 14 hr. Removal of 1 l. solvent by distillation was followed by dilution with 3 l. water, acidification and extraction with ether. The aqueous phase was filtered to give 5·2 g (11 mmoles, 5%) 4,4′-*dichlorodiphenyliodonium iodide*, m.p. 159° from methanol; undepressed by admixture with an authentic sample.

Distillation of the dried ethereal extract gave 14·4 g (128 mmoles, 59%) chlorobenzene and 19·7 g crude 4-*chloroiodobenzene*. Recrystallization from ethanol gave 14·5 g (61 mmoles, 28%) pure

[30] A. C. Cope and E. M. Hancock, *J. Amer. Chem. Soc.* **60**, 2645 (1938).

[31] H. Standinger, O. Gohring and M. Scholler, *Ber. Dtsch. Chem. Ges.* **47**, 43 (1914).

[32] C. D. Hurd, R. Christ and C. L. Thomas, *J. Amer. Chem. Soc.* **55**, 2592 (1933).

4-chloroiodobenzene, m.p. 56°. A final fraction of 52·3 g crude *ethylidene-bis-malonic ester* on redistillation gave 31·2 g (90 mmoles, 42%) pure ester, b.p. 154–155°/0·7 mm; the I.R. spectrum confirmed this structure.

Diethyl malonate with 4,4′-*dichlorodiphenyliodonium chloride* (*arylation in t-butyl alcohol*). To 1·3 l. dry t-butyl alcohol in which 23·5 g (0·6 g-atom) potassium metal had been dissolved, there was added 96 g (0·60 mole) diethyl malonate, followed by 112 g (0·29 mole) 4,4′-dichlorodiphenyliodonium chloride. After stirring for 2·5 days at room temp, there was no unreacted iodonium ion. About 800 ml solvent distilled from the reaction mixture and analyzed by vapor phase chromatography contained 1·7 g (30 mmoles, 10%) acetone; confirmed by formation of the 2,4-dinitrophenylhydrazone.

The residue after partial solvent removal was diluted with 3 l. water, acidified and extracted with ether. Distillation of the dried extract gave 2 g (18 mmoles, 6%) *chlorobenzene* and 43 g (181 mmoles, 63%) 4-*chloroiodobenzene*. A fraction (40·8 g) of b.p. 110–220° at 0·6–0·8 mm on refractionation gave 17·1 g (63 mmoles, 23%) *diethyl* 4-*chlorophenylmalonate*, b.p. 115–140° at 0·15 mm. Its purity and the absence of appreciable diethyl 3-chlorophenylmalonate was shown by comparison of its I.R. spectrum with the independently synthesized isomers. A redistilled sample, b.p. 121°/0·15 mm, n_D^{25} 1·5002, was submitted for analysis. (Found: C, 57·81; H, 5·49. Calc. for $C_{13}H_{15}ClO_4$: C, 57·67; H, 5·58%).

Continued distillation of the final crude fraction gave 21·1 g, (58 mmoles, 36%) of *diethyl bis*-(4-*chlorophenyl*)-*malonate* as a heavy yellow oil, b.p. 161–168°/0·2 mm, n_D^{25} 1·5408. (Found: C, 60·06; H, 4·72; Cl, 18·38. Calc. for $C_{19}H_{18}Cl_2O_4$: C, 59·85; H, 4·73; Cl, 18·61%).

Oxidation of diethyl bis-(4-*chlorophenyl*) malonate to 4,4′-*dichlorobenzophenone*. To 0·5 g of the above diethyl bis-4-(chlorophenyl) malonate in 80 ml water there were added 1 g potassium hydroxide and 6 g potassium permanganate. The solution was heated under reflux 4 hr, cooled and treated with dil. sulfuric acid and sodium bisulfite. The material which crystallized was recrystallized from ethanol, yielding first crop, m.p. 141–142°, and after partial evaporation of the solvent, second and third crops, m.p. 139–140°, and 135–137° respectively; the total yield of 4,4′-dichlorobenzophenone was 54%. Treatment of these chlorinated benzophenones with alcoholic 2,4-dinitrophenylhydrazine in sulfuric acid solution, gave hydrazones which recrystallized from pyridine m.p. 238–239° and mixed m.p. with the 2,4-*dinitrophenylhydrazone of* 4,4′-*dichloro-benzophenone*[33] gave no depression, thus indicating the isomeric purity of the diethyl bis-(4-chlorophenyl) malonate.

Hydrolysis of diethyl bis-(4-*chlorophenyl*)*malonate and decarboxylation*. The ester (0·5 g) was heated with Claisen's alkali (5 g potassium hydroxide in 20 ml methanol and 5 ml water) for 20 hr. After removal of methyl alcohol by distillation, the residue was extracted with ether, acidified and boiled under reflux for 2 hr. Cooling gave a tan precipitate, which was dissolved in ethanol–water and clarified with charcoal. The cold solution deposited colorless needles, which recrystallized from benzene to give *bis*-(4-*chlorophenyl*) *acetic acid*, m.p. 167–168°, reported[34] 163–164° and 166–168°. (Found: C, 59·61; H, 3·65. Calc. for $C_{14}H_{10}Cl_2O_2$: C, 59·84; H, 3·58%).

Acknowledgement—The support of this research by the Alfred P. Sloan Foundation is gratefully acknowledged.

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[34] J. Forrest, O. Stephenson and W. A. Waters, *J. Chem. Soc.* 1946, 339, K. Gatzi and O. Stammback, *Helv. Chim. Acta* 29, 659 (1946).