Additions of Phenyllithium and Phenyl Grignard Reagent to Dibenzoylacetylene[1]

ROBERT E. LUTZ, CHARLESWORTH L. DICKERSON,[2a] WILLIAM J. WELSTEAD, JR.,[2b] AND ROREBT G. BASS[2c]

Department of Chemistry, University of Virginia, Charlottesville, Virginia

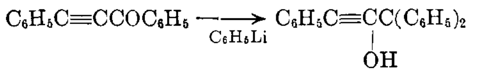
Received September 24, 1962

Phenyllithium adds 1,2 to the carbonyl group of phenylbenzoylacetylene and 1,2 to both carbonyl groups of dibenzoylacetylene, giving the acetylenic carbinol and 1,4-glycol, respectively. Phenyl Grignard reagent adds to dibenzoylacetylene twice 1,4 giving the di-enolate of dibenzoyldiphenylethane which upon hydrolysis undergoes competitive autoxidation to *cis*-dibenzoylstilbene, ketonization to *meso*-dibenzoyldiphenylethane, and dehydration to tetraphenylfuran. Synthetic applications are described, including a condensation approach to the diketones through copper-powder coupling of α-halo desoxybenzoins. The stereochemistry of the Grignard addition is discussed.

The present essentially preliminary study of dibenzoylacetylene was made in order to extend the comparison of the reactivities of the acetylenic analogs of chalcone and dibenzoylethylene. It is reported at this time because of its connection with other papers published[3-5] and in process.

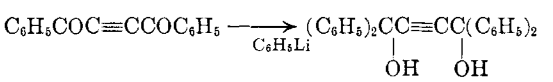
The following are pertinent reference facts. Phenyl Grignard reagent adds chiefly 1,4- to *cis*- and *trans*-chalcones[3] and to *cis*- and *trans*-dibenzoylethylenes.[4] Phenyllithium adds chiefly 1,2 to *trans*-chalcone[6] but largely 1,4 to *cis*-chalcone[7]; and it adds both 1,2 and 1,4 to the dibenzoylethylenes, the *trans* isomer adding 1,4 to a considerably greater extent than the *cis*.[4] Phenyl Grignard reagent reacts 1,2 with the carbonyl group of phenylbenzoylacetylene[8a] in which the β-carbon atom presumably is less electrophilic than in the chalcones, but it adds 1,4 to phenylmesitoylacetylene[4b] which can not react 1,2 at the carbonyl group because of prohibitive steric hindrance.

Phenyllithium is now found to add largely 1,2 to the carbonyl group of phenylbenzoylacetylene as it did to *trans*-chalcone, giving the carbinol II as the only isolated crystalline product.[9]



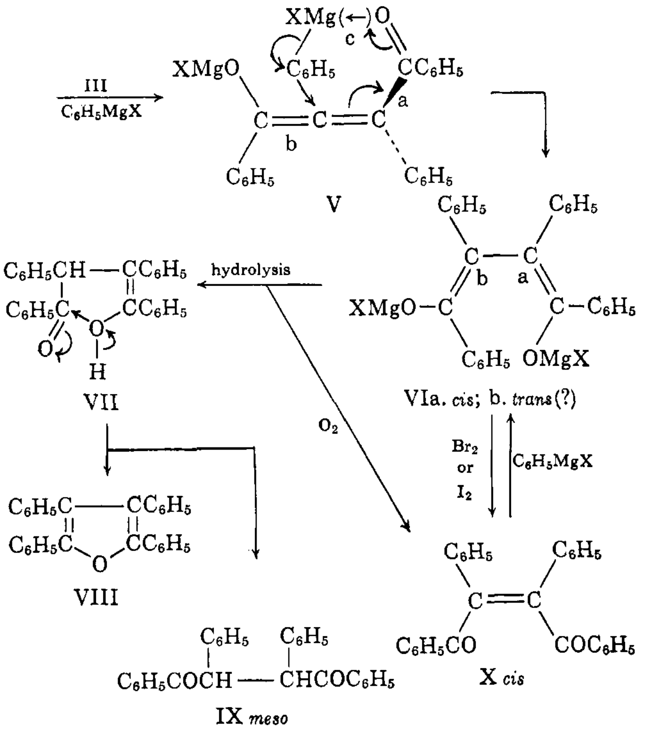
$$\underset{\text{I}}{C_6H_5C\equiv CCOC_6H_5} \xrightarrow[C_6H_5Li]{} \underset{\text{II}}{C_6H_5C\equiv C\underset{\displaystyle OH}{\underset{|}{C}}(C_6H_5)_2}$$

Phenyllithium in reacting with dibenzoylacetylene (III) shows the expected preference for 1,2-addition to carbonyl groups by converting it into the known[10] acetylene glycol IV.



$$\underset{\text{III}}{C_6H_5COC\equiv CCOC_6H_5} \xrightarrow[C_6H_5Li]{} \underset{\text{IV}^{10}}{(C_6H_5)_2\underset{\displaystyle OH}{\underset{|}{C}}C\equiv C\underset{\displaystyle OH}{\underset{|}{C}}(C_6H_5)_2}$$

None of the easily crystallizable 1,4-addition products was isolated. The preference for 1,2- over 1,4-addition may be explained in terms of low polarizability of the acetylenic bond, high energy of the intermediate allenolate of 1,4-addition (V), and high reactivity of the reagent toward carbonyl groups.



The phenyl Grignard reagent, which adds chiefly 1,2 to phenylbenzoylacetylene,[8] has four reaction choices in the case of dibenzoylacetylene (III): two successive 1,2-additions, two successive 1,4-additions, and a combination of 1,2- and 1,4-additions in either of the two possible sequences. Actually the identifiable course of the reaction was shown to be two successive 1,4-additions by isolation of the following compounds (and only these compounds) upon hydrolysis of the reaction mixture: tetraphenylfuran (VIII), *meso*-dibenzoyldiphenylethane ("bidesyl," IX), the thermodynamically labile *cis*-dibenzoylstilbene (X), and, in only one of the numerous runs, a very small amount of *trans*-dibenzoylstilbene. The first 1,4-addition must have produced the highly active allenolate V which is itself an α,β-unsaturated ketone with a sterically unimpeded β-carbon. This in turn must undergo the second 1,4-addition to give the saturated diketone dienolate VI. Subsequent hydrolysis to the dienol would be followed on the one hand by competing autoxidation to the unsaturated diketone X, and on the other by monoketonization to the monoenol VII and then competing furanization to VIII and completion of ketonization to the saturated diketone IX. Actually *cis*-dibenzoylstilbene (X) became the major isolated

---

[1] This work was supported in part by a contract with the Office of Ordnance Research, U. S. Army, and in part by a grant from the National Science Foundation (G9494).

[2] Ph.D. dissertations, University of Virginia. (a) C. L. Dickerson, 1954; (b) W. J. Welstead, Jr., 1961; (c) R. G. Bass, 1961; (d) M. G. Reese, 1957; (e) J. I. Dale, 1962.

[3] R. E. Lutz, W. J. Welstead, Jr., R. G. Bass, and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962).

[4] R. E. Lutz and C. L. Dickerson, *ibid.*, 2040 (1962).

[5] R. E. Lutz and W. J. Welstead, Jr., (a) *ibid.*, 2763 (1962); (b) *J. Am. Chem. Soc.*, **85**, in press.

[6] H. Gilman and R. H. Kirby, *ibid.*, **63**, 2046 (1941).

[7] R. E. Lutz and J. O. Weiss, *ibid.*, **67**, 1814 (1945).

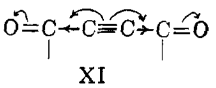
[8] (a) E. P. Kohler, *Am. Chem. J.*, **38**, 511 (1907); (b) R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

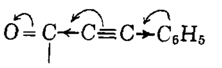
[9] Experiment performed by John I. Dale.

[10] G. du Pont, *Ann. Chim. Phys.*, (8) **30**, 498 (1913).

product (25–30%) when the dienolate VI was oxidized by an excess of bromine or iodine prior to hydrolysis; and this product was favored when hydrolysis took place under effective contact with air. The formation of *cis*-dibenzoylstilbene could be minimized by operating under a nitrogen atmosphere.

The contrast between the 1,4-addition of phenyl Grignard reagent to the acetylenic ketone system of dibenzoylacetylene (III) and the 1,2-addition of this reagent to the carbonyl group of phenylbenzoylacetylene (I) would be difficult to account for on steric grounds. The following explanation is offered. Two acetylenic carbon atoms of dibenzoylacetylene can participate in 1,4-reactions, and in each case the electrophilic activity at these carbons is greatly increased by the strong inductive effect of the attached benzoyl group. Phenylbenzoylacetylene on the other hand has only the one acetylenic carbon atom β to the carbonyl group which, although capable of serving as the electrophilic center for 1,4-reaction, is only weakly influenced by inductive electron withdrawal by the attached β-phenyl group, whereas the electrophilicity of this β-carbon is in some degree actually diminished by the opposed electron donating power of the β-phenyl group. The following formulates the markedly different electron displacements in the two systems.


XI

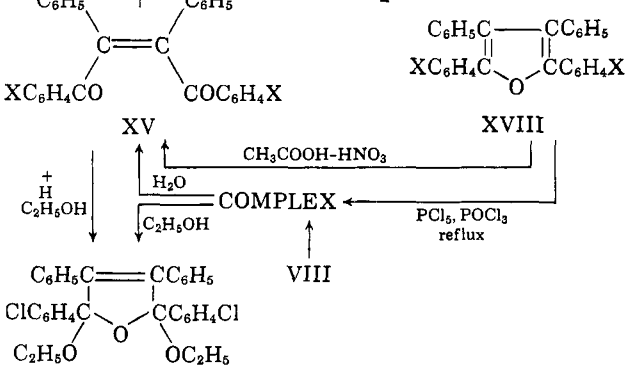


XII

The sterochemistry of the reaction steps in the addition of phenyl Grignard reagent to dibenzoylacetylene, III → V → VI, is of interest because the intermediate allenolate V lacks *cis–trans* type configurational possibilities, and because both enolate configurations of the final dienolate must develop simultaneously upon introduction of the second phenyl group at the middle allenic carbon atom in the second addition step V → VI. The ready and spontaneous furanization which occurs upon hydrolysis of the reaction mixture indicates that at least one of the two enolate groups of the dienolate VI is *cis* with respect to its two substituent phenyl groups. It is suggested that in the reaction at the central allene carbon atom of V, the incoming (second) phenyl group—possibly through transfer from the magnesium atom of an intermediate carbonyl–oxygen complex such as is pictured in Vac—will be guided sterically into a position *cis* relative to the benzoyl phenyl group. Thus this reaction would give rise to the *cis*-diphenylmonoenolate configuration VIa. The second monoenolate group may develop simultaneously but dependently. Should the latter step take place in the opposite steric sense, Vb → VIb producing the *cis–trans*-dienolate VI, subsequent ketonization presumably occurs faster at the *trans*-monoenolate group VIb than at the *cis* VIa. However, only this much can be said with confidence at the moment: Whether the dienolate is *cis–trans* or *cis–cis*, monoketonization must give as the first and moderarely persistent monoenol that of the *cis* configuration VII which then undergoes competitive ketonization to the saturated diketone IX or furanization to VIII.

It should be noted that a dienolate is formed also[2a,c] in the phenyl Grignard 1,4-addition to the *cis*- and *trans*-dibenzoylstyrenes and enolizations of *meso*-bidesyl IX. Each reaction mixture upon hydrolysis gave comparable quantities of products, VIII, IX and X. To the extent of furanization in all of these cases, the dienolates presumably have either the *cis-trans* (VI) or *cis–cis* configuration, but not the nonfuranizable *trans–trans* configuration.

Synthetic Applications.—The two successive 1,4-additions of phenyl Grignard reagent to dibenzoylacetylene, although generally giving poor yields, have proved nevertheless to be of value in synthesis for structural proofs and for special uses.[2b] *cis*-Di-*p*-chlorobenzoylstilbene (XVa) had been obtained by phosphorus pentachloride–oxychloride oxidation of either tetraphenylfuran (VIII)[11,5b] or its 2,5-di-*p*-chloro analog XVIIIa.[2d] The reactions XIII → XIV → XVI ← XV → XVII, and the relation to the furans VIII and XVIII, confirmed the formulations assigned. There is here revealed, however, an interesting but disconcerting point. The *trans* rather than *cis* di-*p*-chlorobenzoylstilbene was the stereoisomer isolated from the dienolate oxidation, although the *cis* isomer was undoubtedly also formed to a considerable extent. This is to be contrasted to the oxidation of both bidesyl dienolate itself (VI) and the 1,4-di-*p*-bromo analog almost entirely to the *cis* forms of the respective unsaturated diketones.

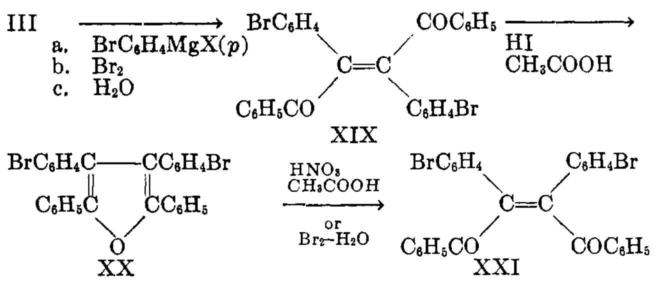


XVII *cis* and *trans* a. X = *para*-Cl; b. X = *para*-Br

The *cis* and *trans* *para*-phenyl-labeled compounds, the di-*p*-bromobenzoylstilbenes (XVb, XVIb) and the dibenzoyl-di-*p*-bromostilbenes (XIX, XXI), and the corresponding 2,5- and 3,4-di-*p*-bromotetraphenylfurans (XVIIIb and XX)[3], were made through addition of phenyl and *p*-bromophenyl Grignard reagents, respectively, to di-*p*-bromobenzoylacetylene and dibenzoylacetylene (XIVb and III). The structures and configurations were proved by the formulated relationships XIII–XXI.

---

(11) R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, **81**, 3397 (1959).



In a partially successful alternative approach to the synthesis of *para*-halogen-labeled dibenzoylstilbenes, copper powder converted α,α-dibromodesoxybenzoin, $C_6H_5COCBr_2C_6H_5$, into *cis*- and *trans*-dibenzoylstilbenes in yields of 35% and 5% respectively. This approach was suggested by the recent synthesis of tetracyanoethylene by the copper powder coupling of dicyanomethylene dibromide.[12] In limited attempts to prepare dibenzoyl-p,p'-dibromostilbene (XIX) in this way, however, we obtained from p-bromobenzyl phenyl ketone (XXII) only the α-monobromo derivative XXIII. This reacted with copper powder but gave a mixture of the diastereoisomeric dibenzoyl-di-p-bromophenylethanes (XXIV), which was then converted by hydriodic acid to the corresponding furan XX and subsequently oxidized with bromine to the *cis* unsaturated diketone XXI.

$$\underset{\text{XXII}}{\underset{(para)}{C_6H_5COCH_2C_6H_4Br}} \xrightarrow[Br_2]{} \underset{\text{XXIII}}{C_6H_5COCHBrC_6H_4Br} \xrightarrow[Cu]{}$$

$$\underset{\text{XXIV} \quad racemic \text{ and } meso}{C_6H_5COCH(C_6H_4Br)CH(C_6H_4Br)COC_6H_5} \xrightarrow[HI]{} \text{XX} \xrightarrow[\substack{Br_2\\ \text{ether}\\ H_2O}]{} \text{XXI}$$

Experimental[13]

Addition of Phenyllithium to Benzoylphenylacetylene (I).[9]—Phenyllithium was prepared from 2.28 g. (0.326 mole) of lithium and 22.8 g. (0.145 mole) of bromobenzene in 100 ml. of ether, diluted with 100 ml. of ether and cooled to −10°. The acetylenic ketone I, 10 g. (0.048 mole), was added portionwise over 2 min. under stirring (washed in with 30 ml. of ether). After 5 min. of stirring the reaction mixture was quenched in ice–ammonium chloride. After evaporation of the ether extract the residue was crystallized twice from petroleum–hexane; yield of the carbinol II, 11.8 g. (76%); m.p. 82–82° (lit.,[14] 82°).

Anal. Calcd. for $C_{21}H_{16}O$: C, 89.12; H, 5.44. Found: C, 88.98; H, 5.84. Infrared band (hydroxyl), 2.89 μ (none at *ca.* 6 μ).

Addition of Phenyllithium to Dibenzoylacetylene (III).—In small portions, 1.0 g. of dibenzoylacetylene[15] was added to a 100 ml. ether solution of 0.2 mole of phenyllithium (made in the usual way). Upon immediate quenching with ice–water, the ether extract was evaporated and the glycol IV was crystallized from petroleum–hexane; 0.89 g. (54%), m.p. 193°, (lit.,[10] 193°).[13a]

Addition of Phenyl Grignard Reagent to Dibenzoylacetylene (III).—Over 3–5 min., 5.0 g. of dibenzoylacetylene[14] were added portionwise to a stirred ether solution of 2.5 equivalents of phenyl Grignard reagent made in the usual way and used without exclusion of air. The reaction mixture was immediately quenched in ice with (A) or without (B) sodium hydroxide present, followed by acidification. The ether extract was dried over sodium sulfate and concentrated and the crystalline precipitate was filtered. Leaching with ether removed the more soluble component, nearly pure tetraphenylfuran [VIII, crystallized from glacial acetic acid, (A) 11%, (B) 7%, m.p. 174–176°, identified]. Further leaching with chloroform removed crude *cis*-dibenzoylstilbene (X, crystallized from glacial acetic acid, 7%, 11%, m.p. 211°, identified). In two other runs, instead of obtaining the furan, there remained after these extractions a nearly pure sample of bidesyl (IX, *meso*, 11%). When the reaction was run on a larger scale (7–10-fold) and using just 2 equivalents of Grignard reagent, the resulting mixture before hydrolysis was treated dropwise with 2 atom-equivalents of bromine and followed by quenching in ice–hydrochloric acid mixture; only the *cis* unsaturated diketone X was obtained (25–30%), but in the second of these runs a small yield (1%) of *trans*-dibenzoylstilbene was isolated and identified by analysis and mixture m.p. The residues from all of the above runs were intractable resins from which column chromatography failed to yield a crystalline product. Were IV present in significant amounts it would have been detected. The total yields of crystalline products ranged from 18–31%.

Di-(p-chlorobenzoyl)acetylene (1,4-Di-p-chlorophenylbutyne-1,4-dione) (XIVa).[15] The dibromide stereoisomer mixture from *trans*-di-p-chlorobenzoylethylene (XIIIa) was made by dropwise addition of 9.0 g. of bromine to a suspension of 15.3 g. of the unsaturated diketone in 150 ml. of glacial acetic acid (yield 23 g.). After stirring for a half hour the *meso* dibromide was filtered; it was nearly pure, m.p. 197–203° (lit.,[16] 201°), yield *ca.* 82%; and the second crop from the filtrate presumably consisted largely of the *racemic* dibromide (m.p. 121–128°, *ca.* 11%).

Following the general procedure for III,[15] a solution of 9.0 g. (0.019 mole) of the *meso*-dibromide in 75 ml. of benzene and 3.85 g. (0.038 mole) of triethylamine was refluxed for 2.5 hr. and the precipitated triethylamine hydrobromide was removed by filtration. Evaporation and cooling gave two crops of crystals (4.95 g., XIVa); it was recrystallized (Darco treatment) from absolute ethanol containing a little benzene; yield 3.7 g. (65%); m.p. 165.5–166.5° after further crystallization from ethanol.

Anal. Calcd. for $C_{16}H_8Cl_2O_2$: C, 63.39; H, 2.66. Found: C, 63.22; H, 2.84. Absorption maxima: in ethanol, 262.5 mμ, ϵ 27,490; 6.00 μ[13] (aromatic carbonyl).

***trans*-Di(p-chlorobenzoyl)stilbene [1,4-Di(4-chlorophenyl)-1,2-diphenyl-2-butene-1,4-dione] (XVI).**—To a 50-ml. ether solution of phenyl Grignard reagent made from 0.013 g.-atom of magnesium was added 1.0 g. (0.003 mole) of the acetylenic diketone XIVa. A slight excess of bromine was then added to oxidize the dienolate, and the bright orange solution was then hydrolyzed with ice–hydrochloric acid mixture. The ether extract was dried and evaporated, and the product (XVI) was crystallized (after charcoal treatment) from ethanol; yield 0.16 g. (11%); m.p. 234–239°. The analytical sample melted at 237.5–239°. A considerable amount (*ca.* 0.9 g.) of a crude mixture, evidently containing *cis* isomer, was obtained also.

Anal. Calcd. for $C_{28}H_{18}Cl_2O_2$: C, 73.52; H, 3.97. Found: C, 73.21; H, 4.02. Absorption maxima: in ethanol, 262.5 mμ, ϵ 40,260; 6.00 μ (aromatic carbonyl).

For preparation of the *cis* isomer (XVa) and its stereoisomerization to XVI by alcoholic potassium hydroxide, see ref. 5.

Action of Copper Powder on α,α-Dibromodesoxybenzoin.—A mixture of 2.0 g. (prepared by the procedure of Zinin[17]), 4 g. of copper powder, and 30 ml. of dry benzene was refluxed for 8 hr. (an additional 4 g. of copper powder was added after 4 hr.). Upon filtering, evaporating to small volume, and standing, 0.05 g. (5%) of *trans*-dibenzoylstilbene precipitated.[13b] The residue from evaporation of the filtrate was crystallized from absolute ethanol–benzene mixture; 0.35 g. (35%), m.p. 212–214°, identified as *cis*-dibenzoylstilbene (X) by infrared spectra.

α-Bromo-p-bromobenzyl Phenyl Ketone (XXII).—A suspension of 30 g. of p-bromobenzyl phenyl ketone (XXIV)[18] in 40 g. of bromine and 300 ml. of ether after stirring at room temperature for 45 min., suddenly began to react, and after 10 min. the solid became an oil. Evaporation and crystallization from ethanol gave the α-bromo ketone XXIII, 30 g. (79%), m.p. 78–80°.

Anal. Calcd. for $C_{14}H_{10}Br_2O$: C, 47.49; H, 2.85. Found: C, 47.31; H, 2.79. Infrared absorption band: 5.92 μ.

***meso*- and *racemic*-2,3-p-Bromophenyl-1,4-diphenylbutane-1,4-dione (XXIV).**—A suspension of 12 g. of the above α-bromo ketone XXIII and 20 g. of copper powder in 150 ml. of dry benzene was refluxed for 72 hr. (with addition of an additional 2 g. of copper after 24 hr.). Filtering and evaporating the solution to

---

(12) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(13) Melting points are corrected. Infrared absorptions were determined in potassium bromide pellets, using Perkin–Elmer Infracord. Ultraviolet absorptions in 5 × 10^{-6} M absolute ethanol using Perkin–Elmer Spectracord 4000 A. Identifications were by (a) mixture m.p. and (b) infrared absorption spectra, comparing with an authentic sample.

(14) J. V. Nef, *Ann.*, **308**, 282 (1899).

(15) R. E. Lutz and W. R. Smithey, *J. Org. Chem.*, **16**, 51 (1951).

(16) J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **47**, 886 (1925).

(17) N. Zinin, *Ann.*, **126**, 221 (1863).

(18) E. J. Corey and J. P. Schaefer, *J. Am. Chem. Soc.*, **82**, 9181 (1960).

small volume gave 6.6 g. (70%) of the isomer mixture XXIV. A small portion upon fractional crystallization from glacial acetic acid gave analytical samples of the pure stereoisomers.

Anal. Calcd. for $C_{28}H_{25}Br_2O_2$: C, 61.33; H, 3.68. Found: Higher melting isomer, presumed to be *meso*, m.p. 275–277°: C, 61.61; H, 3.87. Lower melting isomer, presumably *racemic*, m.p. 238–240°; ϵ, 61.62; H, 3.95. Infrared carbonyl absorption bands: 5.99 and 6.04 μ, respectively.

3,4-Di-*p*-bromophenyl-2,5-diphenylfuran (**XX**). (**A**)—Furanization of the above stereoisomer mixture (XXIV) (10 g.) was effected in 200 ml. of boiling glacial acetic acid by 10 ml. of 47% hydriodic acid (5 min.). The furan (XX) was crystallized from ethanol (9.0 g., 93%) and identified by mixture m.p. with a sample prepared from dibenzoylacetylene (III) as described below.

(**B**) A solution of 0.40 g. of *trans*-dibenzoyl-*p*,*p*′-dibromostilbene (XIX) in 20 ml. of glacial acetic acid and 1 ml. of 47% hydriodic acid was refluxed for 1 hr. Cooling and crystallization of the resulting precipitate from ethanol gave the furan XX in near quantitative yield; m.p. 210.5–212°.

Anal. Calcd. for $C_{28}H_{18}Br_2O$: C, 63.42; H, 3.40. Found: C, 63.68; H, 3.55. Ultraviolet absorption maxima: 232.5, 259, 320 mμ, ϵ 25,800, 20,300, 18,400.

cis*-1,2-Dibenzoyl-*p*,*p*′-dibromostilbene** (cis*-2,3-Di-*p*-bromophenyl-1,4-diphenyl-2-butene-1,4-dione**) (**XXI**).—A suspension of 1.0 g. of the furan XX in a mixture of 1.5 g. of bromine, 100 ml. of ether and 50 ml. of water, was shaken for 30 min., separated, and the excess of bromine destroyed by sodium bisulfite solution. Evaporation of the ether solution and crystallization of the product from ethanol gave a 97% yield of the *cis*-diketone XXI, m.p. 228–230° (not raised by recrystallizations from absolute ethanol–benzene mixture).

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 61.56; H, 3.32. Found: C, 61.85; H, 3.36. Absorption maxima: 258 mμ, ϵ 22,700; 5.99 μ.

***trans*-1,2-Dibenzoyl-*p*,*p*′-dibromostilbene** (**2,3-Di-*p*-bromophenyl-1,4-diphenyl-2-butene-1,4-dione**) (**XIX**).—In oven-baked apparatus *p*-bromophenyl Grignard reagent was prepared under nitrogen from 20 g. (0.85 g.-atom) of magnesium and 195 g. (0.825 mole) of 1,4-dibromobenzene in 500 ml. of ether. At 0°, 50 g. (0.21 mole) of dibenzoylacetylene (III) was added portionwise over 5 min. and allowed to react. After standing for 40 min. the reaction mixture was treated portionwise with 200 g. of iodine (30 min. at 0°). Hydrolysis with aqueous sodium bisulfite solution, isolation of the crude product and crystallization from glacial acetic acid gave 1.5 g. (3%) of this *trans* diketone XIX, m.p. 220–222°.

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 61.56; H, 3.32. Found: C, 61.32; H, 3.14. Absorption maxima: 256 mμ, ϵ 26,700; 6.06 μ.

***cis*-Di-*p*-bromobenzoylstilbene** (**XVb**) **and 2,5-Di-*p*-bromotetraphenylfuran** (**XVIIIb**).—For data see ref. 5b.

Acknowledgment.—The authors are indebted to John I. Dale for carrying out one important experiment.

Diaryliodonium Salts. XVIII. The Phenylation of Esters in *t*-Butyl Alcohol[1-3]

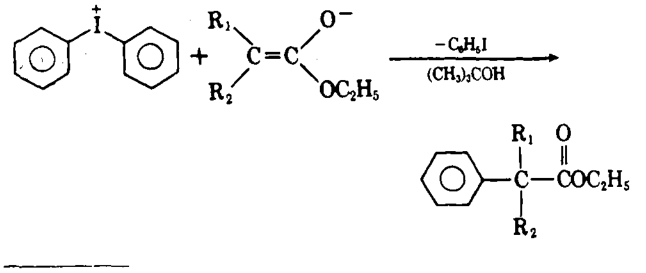
F. MARSHALL BERINGER AND PETER S. FORGIONE[4]

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

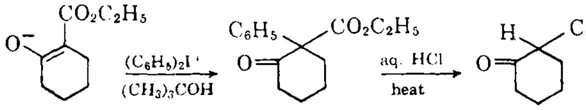
Received October 1, 1962

In *t*-butyl alcohol containing potassium *t*-butoxide substituted malonic and oxalacetic esters, ethyl cyclohexanone-2-carboxylate and ethyl diphenylacetate were converted by diphenyliodonium chloride to their phenyl derivatives, while in liquid ammonia containing sodamide ethyl phenylacetate gave a mixture of ethyl diphenylacetate and triphenylacetamide.

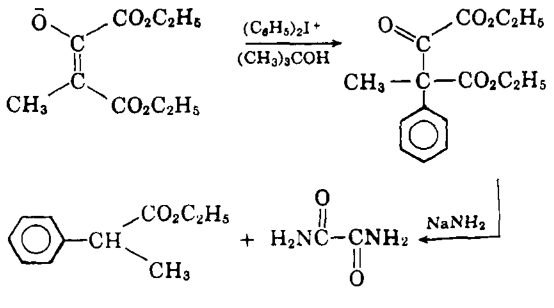
Before the completion of this research in 1959, there appeared a report on the phenylation of dimedone using a diphenyliodonium salt.[5] Since then there have been articles[2,6] on the phenylation of di- and triketones, the more recent[2] proposing a mechanism for the phenylation of carbanions by diphenyliodonium salts. The present work is concerned with the phenylation of esters in *t*-butyl alcohol containing potassium *t*-butoxide and was an exploration of the reaction's scope[3] and potential value in synthesis.



Ethyl Cyclohexanone-2-carboxylate.—A good yield (60%) of ethyl 2-phenylcyclohexanone-2-carboxylate was obtained when ethyl cyclohexanone-2-carboxylate was treated with diphenyliodonium chloride in *t*-butyl alcohol containing potassium *t*-butoxide. No O-phenylated product was found. Attempted saponification of this product with alcoholic potassium hydroxide failed, but after prolonged heating with concentrated hydrochloric acid 2-phenylcyclohexanone was isolated as the oxime.



Diethyl Methyloxalacetate.—While oxalacetic ester gave a mixture of products, including lactones, the



---

[1] This article is taken from the dissertation of P. S. F., submitted in 1959 in partial fulfillment of the degree of Doctor of Philosophy (chemistry).

[2] Preceding article: F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962).

[3] The reactions of dimethyl and diethyl malonate with diphenyl- and 4,4-dichlorodiphenyliodonium chloride in various alcohols containing sodium or potassium alkoxide will be reported separately: F. M. Beringer and P. S. Forgione, *Tetrahedron*, in press.

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

[5] O. Neiland, G. Ia. Vanag, and E. Iu. Gudrinietse, *J. Gen. Chem. USSR*, **28**, 1256 (1958) (in English).

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