The results of the hydrolysis of other 1,1,1-trifluoro-2,2-diarylethanes with alcoholic potassium hydroxide solution are summarized in Table I.

The hydrolysis of 1,1,1-trifluoro-2,2-diphenylethane and of 1,1,1-trifluorodi(*p*-chlorophenyl)ethane with sodium ethoxide in anhydrous ethanol, carried out as described above, gave only ethyl diphenylacetate, m.p. 58°, and ethyl di(*p*-chlorophenyl)acetate, m.p. 89°, respectively. With sodium methoxide in anhydrous methanol, methyl diphenylacetate, m.p. 60°, and methyl di(*p*-chlorophenyl)-acetate, b.p. 173°/2 mm., m.p. 35°, were obtained.

Di(p-chlorophenyl)ketene diethyl acetal. 1,1,1-Trifluoro-2,2-di(*p*-chlorophenyl)ethane (1.6 g.) was refluxed with 25 ml. of 1.5 *N* sodium ethoxide solution in anhydrous ethanol for 2 hours. The solvent then was evaporated under reduced pressure and the dry residue was extracted with anhydrous ether and isolated by evaporation of the solvent *in vacuo*. Thus, 1 g. of di(*p*-chlorophenyl)ketene diethyl acetal was obtained, which melted after recrystallization from ligroin at 102.5–103°. The substance was fluorine-free and decolorized a bromine solution.

Anal. Calc'd for $C_{18}H_{18}Cl_2O_2$: C, 64.1; H, 5.3. Found: C, 64.4; H, 5.3.

Acid hydrolysis of the ketene acetal. A solution of 0.4 g. of the ketene acetal in 3 ml. of 50% ethanol, to which 0.5 ml. of conc'd sulphuric acid had been added, was refluxed for 2 hours, and kept for 24 hours at 0°. The crystals that collected were filtered and extracted with petroleum ether. From the extract, 0.25 g. of ethyl di(*p*-chlorophenyl)acetate was isolated, while the petroleum ether-insoluble residue (0.025 g.) consisted of di(*p*-chlorophenyl)acetic acid.

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The Reduction of Nitrobenzene to Azoxybenzene by Sodium Borohydride[1]

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The versatility of sodium borohydride as a reducing agent has been demonstrated in recent publications.[2,3,4] The work of Brown and Subba Rao[3] and, Brown, Mead, and Subba Rao[4] has been valuable in extending the application of this reagent.

Brown, Mead, and Subba Rao[4] report a vigorous reaction with nitrobenzene if an equimolar amount of LiBr is added. They did not isolate any product. It has been found in this laboratory that nitrobenzene can be reduced to azoxybenzene by sodium borohydride if the reaction is conducted at 90–100° in the diglyme solvent (dimethyl ether of diethylene glycol) used in the work mentioned above.[3,4] Experiments conducted with 1-nitropropane under similar conditions have been unsuccessful.

EXPERIMENTAL

The diglyme solvent was purified by storage over NaOH pellets. Then it was refluxed over $NaBH_4$ and distilled. These operations were carried out in a nitrogen atmosphere.

Nitrobenzene (12 g.) was mixed with 20 ml. of the purified diglyme, and 2.0 g. of $NaBH_4$ were added. The reaction was heated under reflux at 90–100° for six hours. The reaction mixture then was diluted with water, acidified, and steam-distilled. The steam-distillate was discarded. The residue was extracted with *n*-hexane. Removal of the hexane yielded 5.5 g. (58%) of an orange product. Recrystallization yielded 5.2 g. (55%) of a yellow solid melting at 35°. Mixture melting point experiments conducted with Eastman Kodak azoxybenzene did not cause any depression of the melting point.

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[1] This work was conducted under a research grant provided by Metal Hydrides Inc. of Beverly, Mass.

[2] Kollonitsch, Fuchs, and Gabor, *Nature*, **173**, 125 (1954).

[3] Brown and Subba Rao, *J. Am. Chem. Soc.*, **77**, 3164 (1955).

[4] Brown, Mead, and Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

1,4-Dibenzoyl-2,3-diphenyl-1,3-butadiene[1]

Howard W. Bost and Philip S. Bailey[2]

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During the course of another study it was thought advisable to prepare 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene (III). Although the substance is unequivocally listed by Bielstein's *Handbuch*, a study of the original literature showed that an element of doubt still exists concerning its structure. In 1898 Wislicenus and and Lehmann[3] reported the condensation of benzil (I) with acetophenone to give *cis*-1,2-dibenzoyl-1-phenylethylene[4] (II) and/or a dibenzoyldiphenylbutadiene which, in view of its preparative method, could be either 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene (III) or 1,4-dibenzoyl-1,3-diphenyl-1,3-butadiene (IV). This is especially true since the authors also obtained it by the condensation of the dibenzoylphenylethylene (II) with acetophenone. The authors made no attempt to distinguish between the two possibilities, although they favored structure III because one of the several products of chemical reduction was a substance

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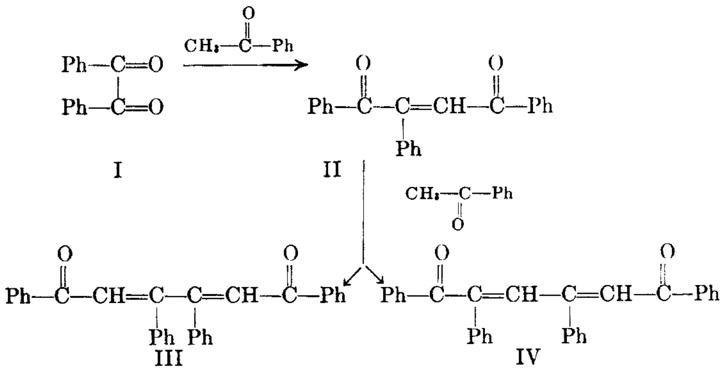
[1] Taken from a portion of the Ph.D. dissertation of H. W. B., January, 1955. This work was supported in part by a grant from The University of Texas Research Institute.

[2] To whom requests for reprints should be directed.

[3] Wislicenus and Lehmann, *Ann.*, **302**, 195 (1898).

[4] Prepared earlier in a similar manner by Japp and Miller, *J. Chem. Soc.*, **47**, 35 (1885). Configuration assigned by Japp and Wood, *J. Chem. Soc.*, **87**, 707 (1905).

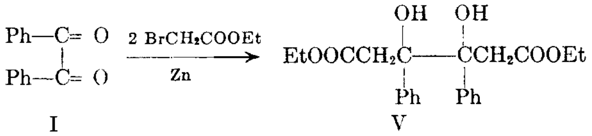


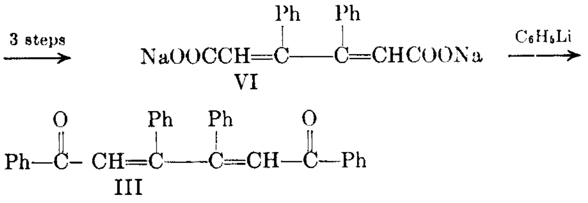
which they thought might be 1,2,4,5-tetraphenylbenzene.[5]

Another product of the chemical reduction of the dibenzoyldiphenylbutadiene[3] was identified by Japp and Mitchie[6] as 2,3,5-triphenylfuran. This substance could be produced from either III or IV, however, through hydrolysis to 1,2-dibenzoyl-1-phenylethylene (II) and acetophenone, followed by the reductive cyclization of II. Still another chemical reduction product, in very low yield, was a substance melting at 266–267° which was, probably, the high-melting isomer of 1,4-dibenzoyl-2,3-diphenylbutane obtained earlier by Harries and Hübner.[7] This was neither proved nor recognized by Wislicenus and Lehmann,[3] however, and thus the structure of their dibenzoyldiphenylbutadiene remains in doubt.

Proof of structure by oxidative degradation is not possible since the two substances in question (III and IV) should give the same products, benzil and phenylglyoxalic acid (or phenylglyoxal). It was not feasible to repeat Wislicenus and Lehmann's chemical reductions in hopes of identifying the supposed 1,6-dibenzoyl-2,3-diphenylbutane, because of the complexity of the mixture of products obtained.[3] Catalytic hydrogenation of the dibenzoyldiphenylbutadiene failed because of the apparent unreactivity of the highly substituted butadiene system.

The remaining course was an unambiguous synthesis and this was accomplished as outlined in the following diagram.





The disodium β,β'-diphenylmuconate (VI) was made, as shown, essentially by the method of Beschke.[8] Van Dorp and Arens[9] have converted an acid directly to a methyl ketone by treatment with methyllithium. The lithium salts of the *gem*-hydroxy intermediates are sufficiently stable so that the products (ketones) are not formed until these intermediates are hydrolyzed, thus preventing further reaction.[10] Similarly, disodium β,β'-diphenylmuconate (VI) reacted with phenyllithium to yield 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene (III). This proved to be identical with the dibenzoyldiphenylbutadiene of Wislicenus and Lehmann,[3] thus establishing the identity of their compound.

EXPERIMENTAL

Attempted hydrogenation of 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene (III),[11] prepared by the method of Wislicenus and Lehmann,[3] in ethanol, or acetic acid solution at atmospheric pressure, using Adam's[12] catalyst, failed. The only hydrogen absorbed was that by the catalyst; a 95% recovery of starting material was made. Similar results were obtained in several experiments.

Disodium β,β'-diphenylmuconate (VI). Following the direction of Beschke[8a] diethyl β,β'-dihydroxy-β,β'-diphenyladipic acid (V) was obtained in 71% yield. The meso and racemic esters were separated and the racemic ester was converted to the dilactone (m.p. 194–195°) in 46% yield by treatment with phosphorus trichloride in benzene solution.[13] The dilactone was converted to the mono-

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[5] This substance has since been synthesized by Dilthey and Hurtig, *Ber.*, **67**, 2004 (1934). These authors believe their compound to be different from that of Wislicenus and Lehmann.[3]

[6] Japp and Mitchie, *J. Chem. Soc.*, **79**, 1010 (1901).

[7] Harries and Hübner, *Ann.*, **296**, 327 (1897).

[8] (a) Beschke, *Ann.*, **384**, 152 (1911). (b) Beschke, *Ann.*, **391**, 127 (1912).

[9] van Dorp and Arens, *Rec. trav. chim.*, **65**, 338 (1946).

[10] Gilman and Van Ess, *J. Am. Chem. Soc.*, **55**, 1258 (1933).

[11] This experiment was performed by John C. Smith.

[12] Adams, Voorhees, and Shriner in Gilman and Blatt, *Org. Syntheses*, Coll. Vol. 1, 2nd Ed., 463 (1941).

[13] Method of Farmer and Duffin, *J. Chem. Soc.*, 406 (1927). However, as stated, the dilactone was obtained instead of the diethyl β,β'-diphenylmuconate reported by these authors.

lactone (m.p. 179–180°) in 80% yield by the method of Beschke.[8b] Upon treatment of the monolactone with alcoholic sodium hydroxide as described by Beschke[8b] for its ethyl ester, disodium β,β'-diphenylmuconate was obtained.

1,4-Dibenzoyl-2,3-diphenyl-1,3-butadiene (III). Phenyllithium was prepared from 1.7 g. (0.011 mole) of bromobenzene and 0.16 g. (0.023 mole) of lithium in 30 ml. of dry ether by the procedure of Evans and Allen.[14] To this solution was added 1 g. (0.003 mole) of disodium β,β'-diphenylmuconate (VI) and the resulting mixture was refluxed, with stirring, for 5 hours, after which time it was poured onto ice. The resulting mixture was extracted with ether, and the ether extract was dried and evaporated to 10 ml. The precipitated product weighed 0.2 g. (16% yield) and melted at 190–191°. It showed no melting point depression in admixture with the dibenzoyldiphenylbutadiene of Wislicenus and Lehmann.[3]

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(14) Evans and Allen in Blatt, *Org. Syntheses*, Coll. Vol. 2, 517 (1943).

Derivatives of 3,4,5-Trimethoxybenzamide[1]

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In the course of an investigation, involving the evaluation of qualitative and quantitative effects of certain radicals and functional groups upon the pharmacological action of mescaline, we have prepared several arylalkylamides of 3,4,5-trimethoxybenzoic acid. The pharmacological evaluation of these compounds is in progress.

EXPERIMENTAL

(All melting points are uncorrected. Microanalyses by Drs. G. Weiler and F. B. Strauss, Oxford, England. The compounds were obtained in their highest state of purity in 30 to 40% yields.)

dl-[N-(α-Methylbenzyl)-3,4,5-trimethoxybenzamide] (I). The 3,4,5-trimethoxybenzoyl chloride was prepared by using a modification of the Marsh and Stephen procedure.[2] To 12 g. (0.0565 mole) of 3,4,5-trimethoxybenzoic acid, dispersed in 200 ml. of anhydrous benzene, 67 g. (0.565 mole) of thionyl chloride was added. The resulting mixture was heated on the water-bath (50°) until a clear solution was obtained and the latter was refluxed for 30 minutes to 1 hour on the steam-bath. The excess thionyl chloride and the benzene were removed under reduced pressure (max. pot temp. 40°). The residual thionyl chloride was removed by azeotropic distillation under reduced pressure with two 100-ml. portions of anhydrous benzene. The residue was taken up in 400 ml. of anhydrous benzene and 35 g. (0.289 mole) of *dl*-(α-methylbenzylamine), in 100 ml. of anhydrous benzene, was added gradually. The contents of the reaction vessel were refluxed for 8 hours on the steam-bath. The reaction mixture was cooled to 20° and treated with cold 40% aqueous potassium hydroxide. The benzene layer was drawn off, dried over magnesium sulfate, filtered, and the benzene was removed under reduced pressure. The white crystalline residue was recrystallized thrice from benzene. The crystals melted at 177.5–178.0°.

Anal. Calc'd for $C_{18}H_{21}NO_4$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.74; H, 6.71; N, 4.40.

N-Phenethyl-3,4,5-trimethoxybenzamide (II). The acid chloride of 3,4,5-trimethoxybenzoic acid (12 g., 0.0565 mole) was prepared as above. To the acid chloride, dissolved in 400 ml. of anhydrous benzene, 35 g. (0.289 mole) of phenethylamine in 100 ml. of anhydrous benzene, was added gradually. The resulting mixture was heated for 3 hours on the water-bath (50°). The reaction mixture was cooled to 20° and the phenethylamine hydrochloride formed during the reaction was filtered off. The benzene solution was washed with cold 40% aqueous potassium hydroxide, dried over magnesium sulfate, filtered, and the benzene was removed under reduced pressure. The crystalline residue was three times recrystallized from benzene. The white crystals melted at 122.0–123.0°.

Anal. Calc'd for $C_{18}H_{21}NO_4$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.46; H, 6.71; N, 4.42.

N-(3,4-Dimethoxyphenethyl)-3,4,5-trimethoxybenzamide (III). The acid chloride of 3,4,5-trimethoxybenzoic acid (12 g., 0.0565 mole) was prepared as above. To the acid chloride, 12 g. (0.0665 mole) of 3,4-dimethoxyphenethylamine, dispersed in 200 ml. of 15% aqueous sodium hydroxide, was added. The reaction mixture was heated for 2 hours on the water-bath (50°), while applying vigorous stirring. The precipitate formed during the reaction was filtered off, washed with water, and the residual moisture was removed by azeotropic distillation under reduced pressure with two 300-ml. portions of anhydrous benzene. The product was three times recrystallized from benzene. The white crystals melted at 133.0–133.4°.

Anal. Calc'd for $C_{20}H_{25}NO_6$: C, 63.98; H, 6.71; N, 3.73. Found: C, 64.03; H, 6.74; N, 3.84.

N-(3,4,5-Trimethoxyphenethyl)-3,4,5-trimethoxybenzamide (IV). The acid chloride of 3,4,5-trimethoxybenzoic acid (4.5 g., 0.0212 mole) was prepared as above. To the acid chloride, 4.5 g. (0.0182 mole) of 3,4,5-trimethoxyphenethylamine hydrochloride, dispersed in 100 ml. of 15% aqueous sodium hydroxide, was added. The reaction mixture was heated for 4 hours on the water-bath (50°), while applying vigorous stirring. The precipitate formed during the reaction was filtered off and washed with water. The air-dried product was recrystallized thrice from a benzene-ethanol solvent system. The white crystals melted at 180.5–181.0°.

Anal. Calc'd for $C_{21}H_{27}NO_7$: C, 62.21; H, 6.71; N, 3.46. Found: C, 62.43; H, 6.76; N, 3.44.

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(1) This investigation is supported by grants from the Geschickter Foundation for Medical Research and the U. S. Public Health Service.

(2) J. T. Marsh and H. Stephen, *J. Chem. Soc.*, 127, 1635 (1925).

N-Benzylidenebenzylamine from Benzylamine and Butyl Nitrite

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When carefully dried benzylamine and butyl nitrite were mixed there was no apparent reaction, but in the presence of even a trace of water, a slow

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