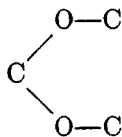


OBSERVATIONS ON 2-(*p*-BIPHENYLOYL)BENZOIC ACIDERNST D. BERGMANN AND S. PINCHAS<sup>1</sup>*Received March 16, 1950*

Scholl and Neovius (1) have shown that 4-phenylbenzophenone-2'-carboxylic acid (I) is reduced to the corresponding diphenylmethane derivative by very prolonged treatment with copper-activated zinc dust and ammonia. In an investigation of the reducibility of certain *o*-aroylbenzoic acids, I was subjected to the usual procedures of the Wolff-Kishner and the Clemmensen reduction, respectively. In the former case, in which the method of Huang-Minlon (2) was applied, the reaction proceeded only to the stage of 3-keto-4,5-benzo-6-(*p*-biphenyl)-2,3-dihydropyridazine (II) which was not further reducible, and in the latter, the reduction stopped at the stage of the secondary carbinol which was withdrawn from the further influence of the reducing agent by ring-closure to the lactone (III). Both heterocyclic systems showed remarkable stability. These observations are in accord with the fact that I—like many other *o*-acylbenzoic acids (3)—reacts with phenylmagnesium bromide to give the lactone (IV) corresponding to the normal triarylcarbinol expected (4). The "methyl ester" of I did not react at all with phenylmagnesium bromide; with benzylmagnesium chloride, however, reaction in the ratio of 1:1 took place, and the reaction product lost spontaneously 1 mole of water. The "normal" formula (V) of  $\alpha$ -phenyl- $\beta$ -(*o*-carbomethoxyphenyl)- $\beta$ -(*p*-biphenyl)ethylene is excluded by the resistance of the product to boiling alcoholic potash solution; one will assume following Fieser (3), that the methyl ester does not correspond in structure to the acid (I), but has the lactol form (VI) from which by interaction with benzylmagnesium chloride and dehydration, 2-benzylidene-5-methoxy-5-(*p*-biphenyl)-2,5-dihydro-3,4-benzisofuran (VII) is formed. Formula VI explains also the observation, that the methyl ester does not respond to the Reformatsky reaction with zinc and ethyl bromoacetate: only true carbonyl groups undergo this reaction. Formula VII was established by the results of the investigation of the infrared spectrum. This (Fig. 1) showed three bands, at 1071, 1109, and 1160  $\text{cm}^{-1}$ , respectively. It has been observed in this laboratory (4) that all acetals and ketals exhibit a triplet of bands with the wave lengths given, *i.e.*, this triplet is characteristic for the group



which, indeed is present in VII. This evidence supplements the spectrochemical work carried out by von Auwers and Heinze (5), and the ultraviolet absorption study undertaken by Hantzsch and Schwiete (6) on the esters of acids of type I.

<sup>1</sup> Part of a thesis presented by S. Pinchas to the Hebrew University in partial fulfillment of the requirements for the degree of Ph.D.

No systematic work appears to have been done on the Wolff-Kishner reduction of *o*-aroylbenzoic acids; Martin, in a recent review (7), indicates, without any references, that for this reaction the usual reduction by means of zinc dust and alkali appears preferable. The formation of a carbinol (as III) in the Clemmensen reduction is definitely in contradiction with current ideas on the mechanism of this reaction—although the formation of (“dimolecular”) pinacols (8) or

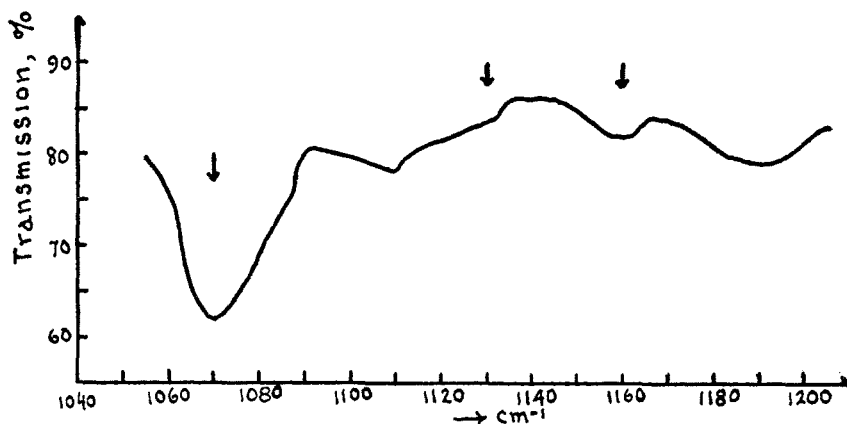
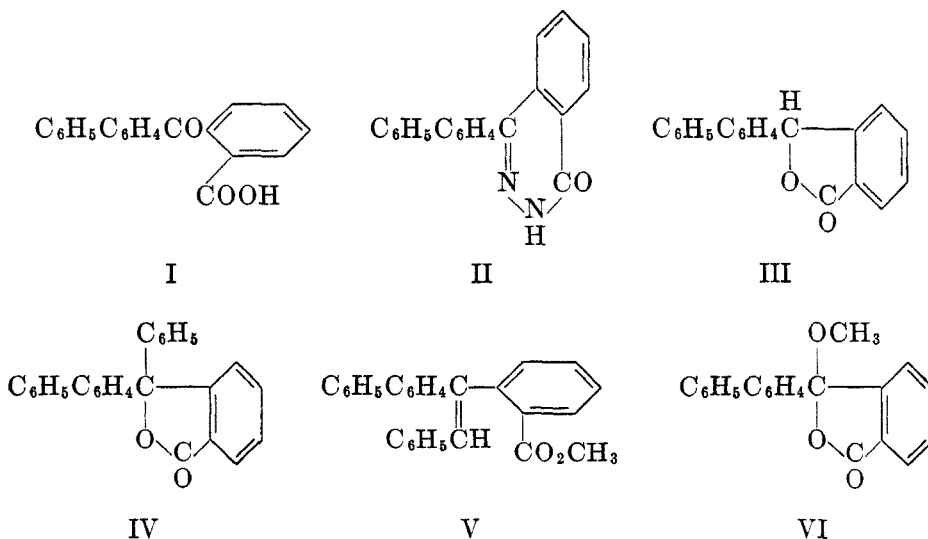
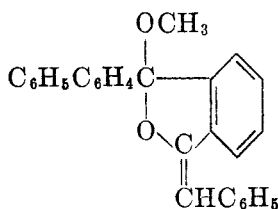


FIGURE 1. INFRARED SPECTRUM OF 2-BENZYLIDENE-5-METHOXY-5-(*p*-BIPHENYL)-2,5-DIHYDRO-3,4-BENZISOFURAN (VII) IN CARBON TETRACHLORIDE (0.060 g. per cc.; 0.1 mm.)

their lactones (9, 10) has been observed in specific cases. However, *o*-benzoylbenzoic acid was known to be reducible to the corresponding benzyl compound.





VII

## EXPERIMENTAL

*3-Keto-6-(p-biphenyl)-4,5-benzo-2,3-dihydropyridazine* (II). A mixture of the acid (I) (1) (3.0 g.), sodium hydroxide (0.8 g.), diethylene glycol (20 cc.), and hydrazine hydrate (1.5 cc.) was treated according to the procedure of Huang-Minlon (2). Dilute (5%) sulfuric acid gave a precipitate which was recrystallized repeatedly from alcohol (200 vols.) and formed white needles of m.p. 278°, insoluble in aqueous alkali and unchanged, when subjected anew to the same reduction process. Yield, almost quantitative.

*Anal.* Calc'd for  $C_{20}H_{14}N_2O$ : C, 80.5; H, 4.7.

Found: C, 80.6; H, 4.8.

*3-(p-Biphenyl)phthalide* (III). A solution of the acid (I) (2 g.) in glacial acetic acid (200 cc.) was reduced in the usual manner with activated zinc wool (5 g.) and repeated additions of concentrated hydrochloric acid. When the metal had dissolved, the solution was diluted with water and the solid product recrystallized from alcohol or benzene (250 vols.). Colorless prisms, m.p. 210°; yield, 1.6 g. The substance was insoluble in aqueous alkali, but dissolved in boiling alcoholic alkali (hydrolysis); acidification gave III again.

*Anal.* Calc'd for  $C_{20}H_{14}O_2$ : C, 83.9; H, 4.9.

Found: C, 83.9; H, 4.8.

The substance has been prepared before by Elbs (11) using zinc dust and aqueous ammonia as reducing agent.

*Lactone* (IV) of *4-phenyl-triphenylcarbinol-2'-carboxylic acid*. A suspension of the acid (I) (3 g.) in benzene (150 cc.) was treated (two hours at room temperature, 30 minutes reflux) with a Grignard solution, prepared from magnesium (0.8 g.) and bromobenzene (5.0 g.) in ether (20 cc.). The reaction product was decomposed with 5% hydrochloric acid and the unchanged starting material (2 g.) removed from the benzene layer with sodium carbonate solution. After evaporation of the solvent, there remained an oil which crystallized upon trituration with warm methanol. From methanol, microcrystalline powder, m.p. 86°. Yield, 0.5 g.

*Anal.* Calc'd for  $C_{26}H_{18}O_2$ : C, 86.2; H, 5.0.

Found: C, 85.6; H, 5.5.

From the mother-liquors, small quantities of a substance of m.p. 171° (leaflets from alcohol) were obtained; it was not further investigated.

*pseudo-Methyl 4-phenylbenzophenone-2'-carboxylate* (VI). A mixture of the acid (I) (57 g.), methanol (300 cc.), and concentrated sulfuric acid (7 cc.) was refluxed for four hours. Upon cooling, the ester crystallized in practically quantitative yield. After recrystallization from methyl alcohol, it had m.p. 103°.

*2-Benzylidene-5-methoxy-5-(p-biphenyl)-2,5-dihydro-3,4-benzisofuran* (VII). In small portions, the pseudo-methyl ester (VI) of I (12.5 g.) was added to the Grignard solution prepared from benzyl chloride (5 g.) and magnesium turnings (1 g.) in ether (25 cc.). When the spontaneous reaction subsided, the solution was stirred vigorously for three hours and decomposed with dilute sulfuric acid (150 cc.). The ethereal solution left, after drying and

<sup>2</sup> Kaiser (12) gives m.p. 85–90° for this substance; this corresponds to an impure preparation.

evaporation, an oil which was triturated at 0° with a mixture of isopropanol and acetone. From this solvent mixture, the product formed colorless crystals of m.p. 143°, easily soluble in most organic solvents. The yield was only about 1 g.

*Anal.* Calc'd for  $C_{22}H_{22}O_2$ : C, 86.1; H, 5.6.

Found: C, 85.9; H, 5.9.

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