which gave no depression in melting point upon admixture with an authentic sample[21] of **quinolizidine picrate.**

Further Reactions of $\Delta^{5(10)}$-Dehydroquinolizidinium Perchlorate. (a) **With *p*-Thiocresol, Potassium Salt.**—To a solution of 0.66 g. (0.018 mole) of potassium hydroxide and 1.46 g. (0.018 mole) of *p*-thiocresol in 35 ml. of methanol was added 2.80 g. (0.018 mole) of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate dissolved in 50 ml. of methanol. The potassium perchlorate formed was removed by filtration, and the filtrate was evaporated to dryness *in vacuo*. The 10-(*p*-thiocresyl)-quinolizidine was recrystallized from anhydrous ether using a Dry Ice-acetone-bath, colorless crystals, m.p. 61–63°.

Anal. Calcd. for $C_{16}H_{23}NS$: C, 73.31; H, 8.87; S, 12.27. Found: C, 74.09; H, 8.70; S, 12.11.

The material darkened rapidly on exposure to air and was decomposed to its component parts by dilute acid. The compound was also prepared by mixing equivalent parts of *p*-thiocresol and $\Delta^{1(10)}$-dehydroquinolizidine in ether.

(b) **With α-Naphthylmethyl Mercaptan, Potassium Salt.** Similar conditions resulted in the preparation of 10-(α-naphthylmethylmercapto)-quinolizidine from α-naphthylmethyl mercaptan; colorless needles, m.p. 98–99°.

Anal. Calcd. for $C_{20}H_{25}NS$: C, 77.11; H, 8.09; N, 4.50; S, 10.30. Found: C, 77.09; H, 8.14; N, 4.72; S, 10.06.

The compound darkened slowly on exposure to air. It was also prepared by mixing equivalent parts of α-naphthylmethyl mercaptan and $\Delta^{1(10)}$-dehydroquinolizidine in ether. The infrared spectrum in chloroform showed C=C absorption at 1655 cm.$^{-1}$ (reversal), but the band was absent when the spectrum was taken in Nujol mull.

The products resulting from the combination of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate and the potassium salts of *n*-propyl mercaptan and benzyl mercaptan were unstable and liberated mercaptan readily.

(c) **With Potassium Alkoxides or Phenoxides.**—The combination of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate with a mole equivalent of potassium methoxide or phenoxide in methanol caused the precipitation of potassium perchlorate. The evaporation of the filtrate in each case left a colorless oil which darkened rapidly on standing and decomposed on attempted distillation to $\Delta^{1(10)}$-dehydroquinolizidine. When the potassium salt of 4-hydroxybiphenyl was used, a solid of m.p. *ca.* 65° was obtained at the evaporation stage, but this darkened quickly and could not be purified by recrystallization.

Under similar conditions, potassium hydroxide, potassium thiocyanate, potassium benzoate, potassium fluoride, potassium *p*-toluenesulfonate and the potassium salt of malonic ester failed to yield stable products.

Reaction of $\Delta^{4(9)}$-Hexahydropyrrocolinium Perchlorate with Potassium Cyanide. 9-Cyanoöctahydropyrrocoline.—A solution of 6.71 g. (0.03 mole) of $\Delta^{4(9)}$-hexahydropyrrocolinium perchlorate[19] in water was added to an aqueous solution containing 1.96 g. (0.03 mole) of potassium cyanide. Sodium carbonate was added and the mixture was extracted with ether. The residue left after drying the ether extracts and removing the ether was distilled at 98° (14 mm.), $n^{28.5}$D 1.4790, yield 4.21 g., 96%.

Anal. Calcd. for $C_9H_{14}N_2$: C, 71.96; H, 9.39. Found: C, 72.50; H, 9.20.

The compound reverted to hexahydropyrrocoline on treatment with acids.

Reaction of 9-Cyanoöctahydropyrrocoline with Iodine. $\Delta^{4(9)}$-Hexahydropyrrocolinium Periodide.—To a solution of iodine (5 g.) in anhydrous ether was added 1.47 g. (0.01 mole) of 9-cyanoöctahydropyrrocoline. The brown precipitate which resulted was recrystallized from ethanol as brown-purple needles, m.p. 90–91°, yield 3.11 g. (63%), infrared maximum at 1678 cm.$^{-1}$ (Nujol mull).

Anal. Calcd. for $C_8H_{14}I_3N$: I, 75.42. Found: I, 75.57.

Reaction of 9-Cyanoöctahydropyrrocoline with Methylmagnesium Iodide. 9-Methyloctahydropyrrocoline.—The reaction with the Grignard reagent was carried out as in the case of 10-cyanoquinolizidine. The product was distilled at 68° (18 mm.), n^{28}D 1.4753.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31. Found: C, 77.25; H, 12.26.

9-Methyloctahydropyrrocoline picrate crystallized from ethanol as yellow plates, m.p. 274° dec.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47; N, 15.21. Found: C, 48.89; H, 5.35; N, 15.59.

9-Methyloctahydropyrrocoline hydriodide was prepared in the usual manner and recrystallized from ethanol–ether, m.p. 256.5–257.5° dec.

Anal. Calcd. for $C_9H_{18}IN$: C, 40.46; H, 6.79; N, 5.24. Found: C, 40.46; H, 6.61; N, 5.36.

2-Methylpyrrocolinium Perchlorate.—To an ethanol solution of 2-methylpyrrocoline, prepared according to the directions of Tschitschibabin,[22] was added 68% perchloric acid until the solution was acid to congo red paper. The precipitated salt was recrystallized from ethanol, m.p. 95.5–96°, infrared maxima at 1638, 2020 and 3100 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{10}ClNO_4$: C, 46.66; H, 4.35; N, 6.05. Found: C, 46.82; H, 4.45; N, 5.90.

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[21] N. J. Leonard and W. C. Wildman, THIS JOURNAL, **71**, 3100 (1949).

[22] A. E. Tschitschibabin, *Ber.*, **60**, 1607 (1927).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Synthesis and Reactions of 1,1,2-Tribenzoylethylene and Related Compounds[1]

BY CHI-KANG DIEN[2] AND ROBERT E. LUTZ

RECEIVED OCTOBER 15, 1955

1,1,2-Tribenzoylethylene has been prepared from 3-benzoyl-2,5-diphenylfuran by nitric acid oxidation. It is reduced to the saturated triketone or to the furan, and undergoes typical addition–cyclizations to the chloro and acetoxy furans. In the additions of hydrogen halide and morpholine, the halide and morpholinyl groups go to the 2-position as shown by subsequent furanizations of the addition compounds and oxidations of the furans to the chloro and morpholinyl unsaturated triketones. Chlorinations of both the saturated and unsaturated triketones appear to be straightforward. Bromination of 1,1,2-tribenzoylethane is at the 1-position but is followed by facile rearrangement to the 2-bromo compound. Bromination of the unsaturated triketone involves reduction of the 1-bromine of the dibromide and furanization. Prohibitive steric hindrance to halogenation in the 1-position of 1,2-tribenzoylethane is offered by a previously substituted halogen in the 2-position.

This paper is the first of a series dealing with the broad study of the conjugation of the 1,1,2-tribenzoylethylene type (II and VI) and it includes investigation of the parent compound and the related saturated triketones and furans.

3-Benzoyl-2,5-diphenylfuran (IV),[3] an important intermediate for synthesis of the compounds in this

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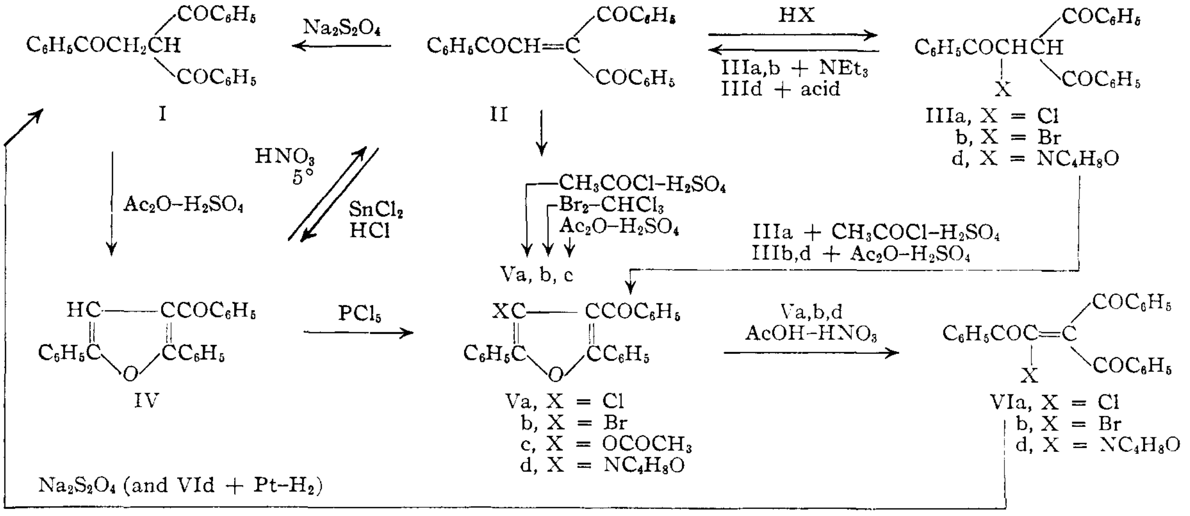
[1] This work was supported by a contract with the Office of Ordnance Research and a grant-in-aid from the National Science Foundation.

[2] Postdoctoral Fellow.

[3] (a) E. P. Kohler and W. N. Jones, THIS JOURNAL, **41**, 1249 (1919); (b) R. E. Lutz and J. M. Smith, *ibid.*, **63**, 1148 (1941); (c) H. Kleinfeller and H. Trommsdorff, *Ber.*, **71**, 2448 (1938).



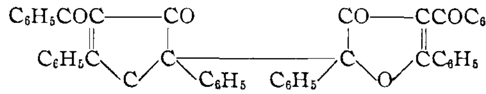
field, has been made in a new and practical way by the stannic chloride-catalyzed Friedel–Crafts reaction between benzoyl chloride and diphenylfuran.[4] Nitric acid oxidation of the furan (IV), although unsuccessful in previous attempts,[3b] proceeded in good yield at 5° and gave 1,1,2-tribenzoylethylene (II).

Tribenzoylethylene (II) has the expected high ultraviolet absorptivity (at 252.5 mμ). It is reductively furanized (to IV) by the action of stannous chloride in hydrochloric and acetic acids. Reduction by sodium hydrosulfite in dilute ethanol converted it into 1,1,2-tribenzoylethane (I) which could then be furanized (to IV) under the usual and stronger dehydrating conditions. These reactions are in accord with present concepts of conjugate reduction of the unsaturated diketone system.[5]

Addition–cyclizations of tribenzoylethylene (II) proceeded smoothly in acetyl chloride and sulfuric acid with the formation of 4-chloro-3-benzoyl-2,5-diphenylfuran (Va). This furan was obtained in another way by chlorination of 3-benzoyl-2,5-diphenylfuran (IV) with phosphorus pentachloride. Nitric acid oxidation of the chlorofuran Va gave the known 2-chloro-1,1,2-tribenzoylethylene[3c] (VIa) which was reduced by sodium hydrosulfite to the saturated triketone I.

Hydrogen bromide in acetic acid failed to convert the unsaturated triketone into the known bromofuran (Vb[3b]).

Conversion of tribenzoylethylene(II) into 4-acetoxy-3-benzoyl-2,5-diphenylfuran (Vc) was brought about in good yield by treatment with acetic anhydride and sulfuric acid. The action of phosphorus pentachloride did not convert this acetoxyfuran Vc into the chlorofuran Va but it gave a small yield of a high-melting compound which analysis showed to be 2,2′-bis-(4-benzoyl-2,5-diphenylfuranone-3) (VII), the result of a dimolecular oxidation analogous to the oxidation of the β-hydroxyfurans.[6] The structure of the bisfuranone VII is supported by its ultraviolet absorption spectrum which shows two distinctive bands at 255 and 302 mμ with molar absorptivities of 24,400 and 15,000, respectively. This absorption spectrum with respect to the wave lengths of the principal bands is very similar to that of *cis*-chalcone [$C_6H_5COCH{=}CHC_6H_5$; λ_{max} 250 and 292.5 mμ, ε 13,700 and 8,800[7]]; the absorptivities are about twice as great and correspond to two *cis*-chalcone groups. The slight bathochromic shifts shown here, relative to the absorptivities of *cis*-chalcone, are doubtless due to the presence of the 3-carbonyl group in cross conjugation with each *cis*-chalcone system.



VII

Additions of hydrogen chloride and hydrogen bromide to tribenzoylethylene (II) in ether solution gave corresponding halogeno saturated triketones (IIIa and b). Their structures, and the mode of addition which was in the expected direction, were shown by furanizations to the 4-halogeno-3-benzoyl-2,5-diphenylfurans (Va and b). These halo triketones (IIIa and b) were readily dehydrohalogenated back to the unsaturated triketone II by triethylamine.

Morpholine reacted with 1,1,2-tribenzoylethylene (II) to give the 2-addition compound IIId which was also obtained by the action of morpholine on the chloro or bromotriketone (IIIa or b). The later reactions could proceed either through dehydrohalogenation and then addition or by simple substitution.[8] The fact that the morpholine addition compound could be dehydrated to the morpholinylfuran Vd proved that it was actually IIId and not the 1-morpholinyl isomer. Treatment of IIId with hydrochloric acid regenerated the unsaturated triketone II.

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[4] *Cf.* R. E. Lutz and R. J. Rowlett, THIS JOURNAL, **70**, 1359 (1948).

[5] (a) R. E. Lutz, *ibid.*, **51**, 3008 (1929); (b) R. E. Lutz and R. J. Taylor, *ibid.*, **55**, 1593 (1933); (c) R. E. Lutz and W. G. Reveley, *ibid.*, **61**, 1854 (1939); (d) R. E. Lutz and C. R. Bauer, *ibid.*, **73**, 3456 (1951).

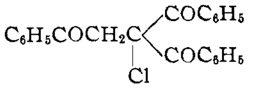
[6] (a) E. P. Kohler, F. H. Westheimer and M. Tishler, *ibid.*, **58**, 264 (1936); (b) R. E. Lutz, C. E. McGinn and P. S. Bailey, *ibid.*, **65**, 843 (1943); (c) R. E. Lutz and C. E. McGinn, *ibid.*, **65**, 849 (1943).

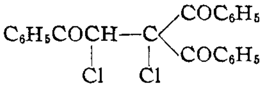
[7] W. B. Black and R. E. Lutz, *ibid.*, **75**, 5990 (1953).

[8] *Cf.* R. E. Lutz and W. R. Smithey, *J. Org. Chem.*, **16**, 51 (1950).

Oxidation of the morpholinylfuran Vd gave 2-morpholinyl-1,1,2-tribenzoylethylene (VId) which was also obtained from 2-chloro-1,1,2-tribenzoylethylene (VIa) by treatment with morpholine. The structures of both Vd and VId follow from analyses and ultraviolet absorption, and from the synthetic relationships. The morpholinyl unsaturated triketone VId (in contrast with IIId) was stable toward acid under mild conditions but was converted into non-crystalline products when heated with acids. Reduction by sodium hydrosulfide or by catalytic hydrogen caused elimination of the morpholinyl group and gave tribenzoylethane (I).

Chlorination of 1,1,2-tribenzoylethane (I) with one molar equivalent of chlorine in chloroform gave 27% of unchanged triketone and an oil. This oil was converted by the action of morpholine into a mixture of 2-morpholinyl-1,1,2-tribenzoylethane and ethylene (IIId and VId) in 30 and 22% yields, respectively; and on treatment with triethylamine it gave tribenzoylethylene (II). It evidently consisted of a mixture of the saturated 1-chloro and 1,2-dichloro-1,1,2-tribenzoylethanes (VIII and IX) and it contained little if any of the 2-chlorotribenzoylethane (IIIa) (the latter compound crystallizes easily and would have been isolated if present in significant amount, and if formed it would not have undergone further chlorination easily as was shown in subsequent experiments).


VIII (not isolated)


IX

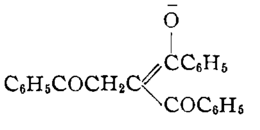
Excess chlorine in chloroform converted tribenzoylethane (I) into an oil which gave no solid product upon treatment with triethylamine but which reacted with morpholine to give 2-morpholinyltribenzoylethylene (VId) as the only crystalline product. Kleinfeller and Trommsdorff[3c] reported isolation of chlorotribenzoylethylene (VIa) as a chlorination product of tribenzoylethane (I), but their use of potassium hydroxide as a drying agent may have been responsible for the result. Doubtless VIa was formed to some extent under our conditions but we were unable to isolate it.

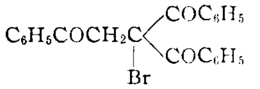
2-Chloro-1,1,2-tribenzoylethane (IIIa) reacted very slowly with chlorine under the conditions of the above experiments and was largely recovered unchanged. It would seem that the 1,2-dichloro compound IX can and does exist but that chlorination at the 1-position of tribenzoylethane (I) must precede substitution of chlorine at the 2-position.

The action of chlorine on tribenzoylethylene (II) gave some chlorotribenzoylethylene (VIa) but the major product was an oil, presumably the dichloride IX, which could be converted into morpholinyltribenzoylethylene (VId) in good yield by the action of morpholine.

It is evident that chlorination of tribenzoylethane (I) occurs first at the tertiary hydrogen to give 1-chloro-1,1,2-tribenzoylethane (VIII) and proceeds further with considerable rapidity at the secondary methylene position of VIII to give dichlorotribenzoylethane (IX), with subsequent partial dehydrohalogenation to chlorotribenzoylethylene (VIa); and that primary attack at the secondary 2-carbon (of I) does not occur to any significant degree. Both dichlorotribenzoylethane (IX) and chlorotribenzoylethylene (VIa) are logical precursors of morpholinyltribenzoylethylene (VId).

Bromination of tribenzoylethane (I) in chloroform gave in good yield 2-bromo-1,1,2-tribenzoylethane (IIIb) which, as was confirmed in separate experiment, resists further bromination. There was no evidence of the presence of 1-bromo-1,1,2-tribenzoylethane (XI) which was subsequently made and characterized and which would have been isolated if it had been formed in significant amounts. It is logical to suppose that as in chlorination (above), the primary attack is at the more active tertiary CH-group of the β-diketone system to give the 1-bromo compound XI but that the reaction is followed by rearrangement of the very "positive" 1-bromine under catalysis by the hydrogen bromide necessarily present, to the more stable 2-bromo compound IIIb. The difference between chloride and bromide reactivities and mobilities, involving reversibility of the 1-bromination under the reaction conditions, would adequately account for these results.[9]


X


XI

It was possible to demonstrate that the bromination of tribenzoylethane (I) proceeds through the 1-bromo compound XI as suggested above by carrying out the reaction in methanol containing sufficient sodium hydroxide to enolize the triketone (to X) and to neutralize the hydrogen bromide formed, and by these means, and by the solvent effect, to diminish the speed of rearrangement of the 1-bromide XI to the 2-bromo compound IIIb. The 1-bromide was isolated. As predicted it proved to be relatively very unstable. It underwent rearrangement to the more stable 2-bromotribenzoylethane (IIIb) in chloroform containing an amount of hydrogen bromide corresponding to that produced in brominations in that solvent, and also in refluxing benzene without added hydrogen bromide. It was easily dehydrohalogenated by triethylamine to the tribenzoylethylene (II), and it reacted with morpholine to give the 2-morpholinyltribenzoylethane (IIId). It was converted by acetic anhydride and sulfuric acid into 4-acetoxy-3-benzoyl-2,5-diphenylfuran (Vc). This last reaction is of particular interest because the 1-bromo compound XI is incapable of going directly to a furan and must first undergo intermediate dehydrohalogenation; the 1-bromo compound XI cannot have undergone rearrangement first to the 2-bromo compound IIIb, because the latter compound furanizes directly to the 4-bromo-3-benzoyl-2,5-diphenylfuran (Vb) under these conditions. Incidentally, these facts validate the use of the direct furani-

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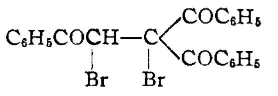
[9] *Cf.* (a) R. E. Lutz and A. H. Stuart, THIS JOURNAL, **59**, 2324 (1937); (b) R. Altschul and P. D. Bartlett, *J. Org. Chem.*, **5**, 623 (1940); (c) M. Couper and R. E. Lutz, *ibid.*, **7**, 86 (1942).

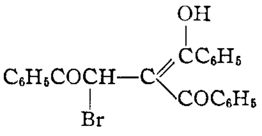
zation of the 2-bromo compound IIIb (above) as a proof of the structure of the latter.

It will be noted that in the 2-bromo compound IIIb as in the 2-chloro compound IIIa, 2-halogen suppresses the normally facile halogenation at the tertiary CH-position of the triketone I. No attempt was made to determine whether or not the 1-bromo compound XI would undergo halogenation at the 2-CH_2 group (like the chlorination of the 1-chloro compound VIII) because of the great facility of rearrangement of the bromine in this compound.

The action of bromine on tribenzoylethylene (II) gave chiefly 4-bromo-3-benzoyl-2,5-diphenylfuran (Vb) and a small amount of oil. The oil upon treatment with morpholine gave morpholinyltribenzoylethylene (VId), a result which indicated the presence of some dibromide XII or the bromotribenzoylethylene (VIb). The principal and final product, the bromofuran Vb, is at a level of reduction one stage below that of the dibromide XII and corresponding to that of 2-bromotribenzoylethane (IIIb) which would be a logical precursor of the bromofuran Vb. The latter compound IIIb was shown not to furanize under the experimental conditions involved, however, and is therefore excluded as a possible intermediate. The formation of the bromofuran Vb can be accounted for satisfactorily in terms of the formation of the dibromide XII, release of hydrogen bromide in small amounts, hydrogen bromide-catalyzed reduction of the more active and very "positive" 1-bromine (of XII) to the metastable non-chelated *trans*-enol XIII, and subsequent furanization of this in successful competition with ketonization, dehydrohalogenation and further bromination.


XII

(not isolated)


XIII

In three experiments (above) it has been noted that when the 2-carbon of tribenzoylethane (I) carries a chlorine or bromine as a substituent, halogenation at the 1-position is difficult or does not occur. This phenomenon may be explained in terms of the probable mechanism of halogenation involving enolates of the types X and XIII, and the inordinately increased steric interferences brought about by the 2-substituton. Such effects are known in simpler β-diketone types.[10] Scalar models demonstrate this effect.

The ultraviolet absorptivities of many of the compounds described in this paper correspond closely to expectations on the basis of the structures assigned. Of particular interest is the effect of introduction of the 2-chlorine into 1,1,2-tribenzoylethylene (II), which produces a bathochromic shift of 8.5 mμ and an increase in absorptivity of 4,600. The morpholinyl compound VId has a broader peak of lower absorptivity in the middle wave length area, λ_{max} 253, but it has also a longer wave length band at 314 mμ, ϵ 12,200, which is comparable to the longer wave length band of secondary-aminodibenzoylethylenes.[11]

The several tribenzoylethanes and 3-benzoyl-2,5-diphenylfurans showed typical ultraviolet absorption spectra comparable with those of dibenzoylethanes and 2,5-diphenylfurans.[12]

Two phenomena of interest are to be noted. The absorptivity of 1-bromo-1,1,2-tribenzoylethane (XI) (λ_{max} 251.5, ϵ 27,800) is very considerably lower than that of tribenzoylethane itself (I) (λ_{max} 247.5, ϵ 40,200); this effect doubtless is due to the very great steric hindrance at the quaternary 1-carbon with the planarity of the individual 1-benzoyl groups, which is evident upon examination of scalar models. In the case of the 3-benzoyl-2,5-diphenylfurans, a 25 mμ hypsochromic shift of the long wave length band of the parent 2,5-diphenylfuran is observed, due presumably to the considerable interference with coplanarity of the cross-conjugated *cis*-chalcone and *trans-trans*-diphenylbutadiene systems caused by the mutual adjacency of the 2-phenyl and 3-benzoyl groups.

Experimental[13]

Preparation of 3-Benzoyl-2,5-diphenylfuran[3,4] (IV).—A solution of 13 g. of anhydrous stannic chloride in 20 ml. of dry benzene was added over a period of 20 min. at room temperature to a stirred mixture of 10 g. of 2,5-diphenylfuran, 7 g. of benzoyl chloride and 60 ml. of dry benzene. After stirring for an additional 30 min. at 50–60°, the mixture was hydrolyzed with ice and hydrochloric acid. The organic layer was separated, washed and evaporated; the residue was crystallized from benzene–petroleum ether; 13 g. (88%); m.p. 75–77°; λ_{max} 245, 299, ϵ 20,400, 26,700; shoulder, 255 mμ, ϵ 19,200; λ_{min} 237, 268, ϵ 19,800, 15,800 (*cf.* similar values[14]).

1,1,2-Tribenzoylethylene (II).—To an ice-cooled mixture of 8 g. of IV in 40 ml. of propionic acid was added slowly 8 g. of concd. nitric acid in 16 ml. of propionic acid. After standing at 0–5° for a total of 20 min. the yellowish-green solution was poured into ice-water and the resulting oil was extracted with ether. Evaporation of the ether and crystallization of the residue from methanol gave 6.7 g. (80%); m.p. after recrystallization from methanol, 101–102°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.13; H, 4.74. Found: C, 81.08; H, 4.70. λ_{max} 252.5, ϵ 25,200, with nearly linear drop to ϵ 3,200 at 315 mμ.

Reduction of 0.5 g. of II with 1 g. of stannous chloride in 2 ml. of concd. hydrochloric acid and 5 ml. of glacial acetic acid at reflux temperature for 10 min. gave 0.38 g. of IV (identified by mixture m.p.). Reduction with zinc dust in glacial acetic acid at reflux temperature for a few minutes gave only an oil.

1,1,2-Tribenzoylethane (I).—To a nearly boiling solution of 1 g. of II in 200 ml. of 50% ethanol was added 4 g. of sodium hydrosulfite; the mixture was refluxed for 20 min. On dilution with ice-water the product coagulated, and was filtered and recrystallized from ethanol containing a little benzene; 0.78 g., m.p. 156–157° (K. and T.[3c] 155°); λ_{max} 247.5, ϵ 40,200. It gave no color test with ethanolic ferric chloride.

Furanization to IV occurred in 66% yield when a mixture of 0.5 g. of I, 5 ml. of acetic anhydride and three drops of concd. sulfuric acid was allowed to stand at 25° for one hour (identified by mixture m.p.).

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(10) P. D. Bartlett and S. G. Cohn, *J. Org. Chem.*, **4**, 88 (1939).

(11) R. E. Lutz, T. Amacker, S. M. King and N. H. Shearer, *ibid.*, **15**, 181 (1950).

(12) *Cf.* L. P. Kuhn, R. E. Lutz and C. R. Bauer, THIS JOURNAL, **72**, 5058 (1950); S. M. King, C. R. Bauer and R. E. Lutz, *ibid.*, **73**, 2253 (1951).

(13) (a) Microanalyses were by Misses P. L. Paynter, M. Lai and B. G. Williamson; (b) melting points are "corrected"; (c) ultraviolet absorptions were obtained using a Beckman DU quartz spectrophotometer, in 0.00005 *M* absolute ethanol.

(14) H. Schmid, M. Hochweber and H. V. Halban, *Helv. Chim. Acta*, **30**, 426 (1947).

4-Chloro-3-benzoyl-2,5-diphenylfuran (Va). (a).—A solution of 1 g. of II in 10 ml. of redistilled acetyl chloride and one drop of concd. sulfuric acid at 0°, after standing at 0° for 8 min., was hydrolyzed by ice-water and worked up in the usual way. Several crystallizations from ethanol gave 0.85 g. (81%) of colorless needles, m.p. 118–119°.

(b).—A mixture of 1 g. of furan (IV) and 3 g. of phosphorus pentachloride was heated at 100° for 40 min. The brown solution obtained was treated with cold water and the resulting precipitate Va was filtered and crystallized from ethanol; 0.52 g. (47%), m.p. 117–119°.

Anal. Calcd. for $C_{23}H_{15}ClO_2$: C, 76.99; H, 4.21. Found: C, 76.87; H, 4.15. λ_{max} 255, 305, ϵ 19,200, 25,200; λ_{min} 241, 274, ϵ 18,500, 14,000.

2-Chloro-1,1,2-tribenzoylethylene[3c] (VIa) was prepared by oxidation of Va with nitric acid in propionic acid (at 0–5° for 15 min.); colorless needles from ethanol; m.p. 90–91° (as reported[3c]); λ_{max} 261, ϵ 29,800.

Reduction of VIa with sodium hydrosulfite in 70% ethanol in the usual way gave I in nearly quantitative yield.

Reaction of tribenzoylethylene (II) with hydrogen bromide (1 g. in 25 ml. of 20% hydrogen bromide–glacial acetic acid) at room temperature (30 min.) gave only non-crystalline material.

4-Acetoxy-3-benzoyl-2,5-diphenylfuran (Vc).—A solution of 2 g. of II, 20 ml. of acetic anhydride and one drop of concd. sulfuric acid was allowed to stand at 0–5° for 7 min. Hydrolysis with ice-water, filtration and crystallization from ethanol gave 2 g. (89%); recrystallized from ethanol; m.p. 135–136°.

Anal. Calcd. for $C_{25}H_{18}O_4$: C, 78.52; H, 4.74. Found: C, 78.69; H, 4.70. λ_{max} 242, 298, ϵ 21,100, 29,400; λ_{min} 237, 270, ϵ 20,800, 17,700; shoulder, 355 mμ, ϵ 20,200.

2,2'-Bis-(4-benzoyl-2,5-diphenylfuranone-3) (VII).—Treatment of Vc with phosphorus pentachloride (heated) gave mainly oil and a small amount of halogen-free product which crystallized from benzene–ethanol mixture; m.p. 260–262°.

Anal. Calcd. for $C_{46}H_{32}O_6$: C, 81.13; H, 4.74. Found: C, 81.27; H, 4.61. λ_{max} 255, 302, ϵ 24,400, 15,000; λ_{min} 233, 280, ϵ 13,400, 12,900.

2-Morpholinyl-1,1,2-tribenzoylethane (IIId).—Addition of 5 ml. of morpholine to a solution of 1 g. of II in 30 ml. of ether caused gradual precipitation of the addition product. Standing at room temperature for 20 min., filtering and recrystallizing from ethanol gave 0.98 g. (78%); m.p. 162–163°.

Anal. Calcd. for $C_{27}H_{25}O_4N$: C, 75.86; H, 5.90. Found: C, 75.76; H, 5.81. λ_{max} 249, ϵ 35,200.

The compound was soluble in dilute hydrochloric acid and gave no ferric chloride color test. It was converted back to tribenzoylethylene (II) by heating a solution in acetic acid or dilute hydrochloric acid for a few minutes. Attempted dehydration of IIId with acetyl chloride and concd. sulfuric acid gave only tribenzoylethylene (II).

4-Morpholinyl-3-benzoyl-2,5-diphenylfuran (Vd).—To a mixture of 3 g. of morpholinyltribenzoylethane (IIId) in 30 ml. of acetic anhydride was added dropwise 2 ml. of concd. sulfuric acid. After standing at room temperature for 2 hr. the mixture was hydrolyzed in ice-water and worked up in the usual way, 2.42 g. (84%); recrystallized from isopropyl alcohol and from methanol; m.p. 146–148°.

Anal. Calcd. for $C_{27}H_{23}O_3N$: C, 79.19; H, 5.66; N, 3.42. Found: C, 78.89; H, 5.73; N, 3.60. λ_{max} 258, 315, ϵ 21,300, 21,160; λ_{min} 281, ϵ 15,200.

The product was slightly soluble in dilute hydrochloric acid.

2-Morpholinyl-1,1,2-tribenzoylethylene (VId). (a).—Oxidation of the morpholinylfuran Vd in propionic acid in the usual way with nitric acid at room temperature for 20 min. gave the deep-yellow product in 75% yield; recrystallized from ethyl acetate and methanol mixture; m.p. 194–195°.

Anal. Calcd. for $C_{27}H_{23}O_4N$: C, 76.22; H, 5.45; N, 3.29. Found: C, 76.01; H, 5.57; N, 3.59. λ_{max} 253, 314; ϵ 21,250; 12,200; λ_{min} 222, 295; ϵ 17,200; 11,400.

(b).—Treatment of 2-chloro-1,1,2-tribenzoylethylene (VIa) with morpholine in ether solution caused rapid color changes to deep yellow, and precipitation. After standing at room temperature for 3 hr., evaporation to dryness, and washing with water, the residue was crystallized from ethyl acetate and methanol mixture; yield nearly quantitative, m.p. 189–192° (identified by mixture m.p. with a).

The product was only slightly soluble in dilute hydrochloric acid and it was recovered unchanged after heating a solution of it in acetic acid or methanolic hydrogen chloride for a few minutes. Prolonged heating with acid gave an oil which resisted crystallization.

Reduction of VId with sodium hydrosulfite in boiling 50% ethanol for several minutes, or by catalytic hydrogen, gave nearly quantitative yield of 1,1,2-tribenzoylethane (I).

2-Chloro-1,1,2-tribenzoylethane (IIIa).—Dry hydrogen chloride was absorbed in a solution of 5 g. of II in 200 ml. of ether. After standing at room temperature for 20 hr. and evaporation to dryness the residue was recrystallized from ethanol; yield 86%; m.p. 138–139°.

Anal. Calcd. for $C_{23}H_{17}O_3Cl$: C, 73.31; H, 4.55. Found: C, 73.18; H, 4.63. λ_{max} 253.5, ϵ 37,850.

2-Bromo-1,1,2-tribenzoylethane (IIIb).—A solution of 0.2 g. of II in 30 ml. of ether and 2 ml. of 20% hydrogen bromide in acetic acid, was allowed to stand at room temperature for 16 hr. and was worked up in the usual way. Repeated recrystallization of the product from ethyl acetate–methanol mixture gave 0.16 g. (64%); m.p. 129–130°.

Anal. Calcd. for $C_{23}H_{17}O_3Br$: C, 65.57; H, 4.07. Found: C, 65.64; H, 4.18. λ_{max} 255, ϵ 35,800.

It was not affected by 1 *M* hydrogen bromide–chloroform solution at room temperature for 14 hours.

Dehydrohalogenations of IIIa and b and XI, with excess triethylamine in ether solution (room temperature, 16 hr.) gave II, m.p. 98–100°, in 80, 70 and 70% yields, respectively.

Treatment with excess morpholine in ether solution (room temperature, 2 hr.) of both IIIa and b, and of XI, gave IIId, m.p. 160–162°; in the cases of IIIa and b in nearly quantitative yields, and from XI in 80% yield.

Dehydration of IIIa with acetyl chloride and sulfuric acid (room temperature, 20 min.) gave Va in 80% yield, m.p. 116–118°. IIIb was dehydrated with acetic anhydride and concd. sulfuric acid (room temperature, 16 hr.) giving Vb in 65% yield, m.p. 119–120°.

All of these products were identified by mixture m.p.

1-Bromo-1,1,2-tribenzoylethane (XI).—To a mixture of 3 g. of powdered I in 250 ml. of methanol was added 10 ml. of 5% potassium hydroxide in methanol solution with stirring at room temperature for a few minutes. A large portion of the triketone dissolved to give a pale yellow mixture; 30 ml. of 5% bromine in methanol solution was then added and the mixture was stirred at room temperature for 15 min. The unreacted triketone (0.31 g.) was filtered out and the filtrate was diluted with 250 ml. of water. The precipitated organic material was washed with water and recrystallized by dissolving in warm ethyl acetate and diluting with methanol; yield 1.1 g. (30%). Recrystallizations by the same method gave pure colorless product, m.p. 104–105°. The mixture m.p. with IIIb was 101–110°.

Anal. Calcd. for $C_{23}H_{17}O_3Br$: C, 65.57; H, 4.07. Found: C, 65.65; H, 4.16. λ_{max} 251.5, ϵ 27,800.

After heating XI at 105–110° for 3 min. no solid product could be recovered.

Isomerization of XI.—In an attempt to recrystallize the crude product XI from benzene, hydrogen bromide was evolved on heating and the product isomerized to IIIb in 51% yield. In another experiment XI was treated with a molar equivalent amount of hydrogen bromide in chloroform solution at room temperature for 1 hr. and gave IIIb in 75% yield, m.p. 125–128°.

Treatment of XI with acetic anhydride and concd. sulfuric acid at room temperature for 12 hr. gave Vc in 63% yield, m.p. 133–136°.

Reactions of halogen with 1,1,2-tribenzoylethane (I) and 1,1,2-tribenzoylethylene (II) (one molar equivalent unless otherwise stated).—The reactions were carried out in chloroform solution at room temperature (standing for several hours). The products were crystallized from methanol or ethyl acetate–methanol mixture, and were identified by mixture m.p.

(a).—The reaction between chlorine (generated from the calculated amount of potassium permanganate with excess hydrochloric acid) and 3 g. of I (3 hr.), gave 0.82 g. (27%) of unchanged material, m.p. 151–154°, and an oil which resisted crystallization. Treatment of the oil with excess morpholine in ether solution (room temperature, 2 hr.)

gave 0.84 g. (22%) of VId, m.p. 193–194°, and 1.1 g. (30%) of IIId. In a separate experiment, the oil when treated with excess triethylamine gave tribenzoylethylene (II) in 62% yield.

(b).—Excess chlorine reacted with I to give only oil which was converted by morpholine to VId in 55% yield, m.p. 190–193°. No solid derivative was obtained when the oil was treated with triethylamine (room temperature, 10 hr.).

(c).—When 1 g. of 2-chloro-1,1,2-tribenzoylethane (IIIa) was treated with chlorine (3 hr.) 0.62 g. of unchanged material was recovered. The residual oil reacted with morpholine to give 0.12 g. (10%) of VId, m.p. 190–194°.

(d).—Chlorination of 1.5 g. of II (6 hr.) gave 0.36 g. (22%) of VIa, m.p. 88–90°, 0.05 g. (3%) of IIIa, m.p. 134–136°, and an oil which upon treatment with morpholine gave 0.92 g. (49%) of VId, m.p. 190–193°.

(e).—Bromination of 1 g. of I proceeded smoothly at room temperature with rapid discharge of bromine color and evolution of hydrogen bromide to give 0.84 g. (68%) of IIIb, m.p. 129–130°. This product IIIb resisted further reaction with excess bromine (14 hr.).

(f).—Bromination of 1 g. of II (12 hr.) gave 0.42 g. (35%) of 4-bromo-3-benzoyl-2,5-diphenylfuran (Vb[8b]), m.p. 116–118°; purified, m.p. 119–120°; λ_{max} 227.5, 253, 305, ϵ 21,200, 20,200, 24,100; λ_{min} 242.5, 274, ϵ 18,900, 14,050. An oil obtained as by-product reacted with morpholine to give 0.22 g. (18%) of VId, m.p. 188–192°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Benzidine Rearrangement. VII. The Rearrangements of 3,3'-Dibromo-5,5'-dimethylhydrazobenzene in 2:1 Sulfuric Acid[1]

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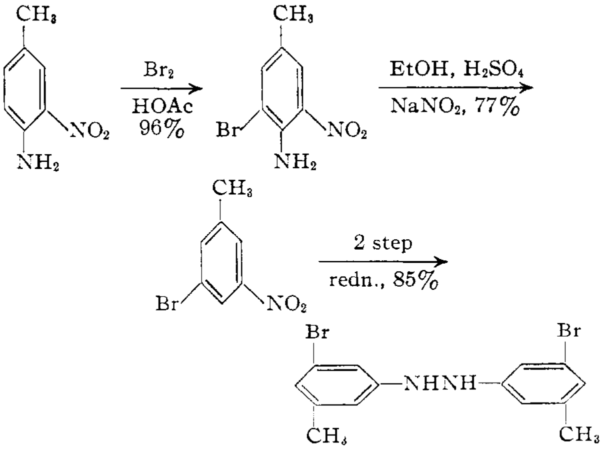
RECEIVED SEPTEMBER 30, 1955

Treatment of 3,3'-dibromo-5,5'-dimethylhydrazobenzene (I) with 2:1 sulfuric acid at 85–90° yielded a benzidine (II), dimorphic diphenylines (IIIa and IIIb), a 2,2'-diaminobiphenyl (IV), 5-bromo-3-toluidine (V), the azobenzene (VI) corresponding to I and a trace of a rearrangement product which may have been a semidine. The structures of the rearrangement products II–IV were established by catalytic reductive debromination to diaminodimethylbiphenyls which were synthesized by other means. Relatively more benzidine product and less diphenyline, 2,2'-diaminobiphenyl and disproportionation products are formed from I than from the related symmetrical compounds, 3,3',5,5'-tetrabromo- and -tetramethylhydrazobenzenes under similar conditions. Also, only one of two possible diphenyline structures and one of three possible 2,2'-diaminobiphenyls could be identified among the products. These observations make it clear that the relationship, deduced from previous investigations, between steric size of the four *meta* substituents and product ratios is valid only for those cases in which all four substituents are alike. The factor of polar symmetry affects the product ratios, and it also appears to have a decisive effect on the choice among the transition states leading to the several possible products. No mechanism thus far proposed for the benzidine rearrangement seems capable of yielding a satisfactory explanation of the behavior of I.

Previous investigations of the rearrangements of 3,3',5,5'-tetrasubstituted hydrazobenzenes in 2:1 sulfuric acid at 85–90° have led to results suggesting that benzidine : diphenyline : 2,2'-diaminobiphenyl product ratios are governed largely, though not entirely, by the steric size of the four substituents under the imposed conditions.[3] In all of the 3,3',5,5'-tetrasubstituted hydrazobenzenes thus far subjected to these conditions, the four substituents have been alike, and the question of the effects on the product ratios of introducing new elements of dissymmetry into the molecule arose. The choice of 3,3'-dibromo-5,5'-dimethylhydrazobenzene (I) as the first unsymmetrically tetrasubstituted hydrazobenzene to be investigated was based upon the fact that the two related symmetrical compounds, 3,3',5,5'-tetrabromo- and -tetramethylhydrazobenzenes already had been studied[4] and had been shown to give quite similar product ratios. Inasmuch as bromine and methyl have effectively identical van der Waals radii,[5] the steric character of I should not differ appreciably from those of its two related symmetrically substituted analogs; it follows that if steric size of the four substituents is the chief operative factor in determining product ratios, then compound I should behave like the tetrabromo and tetramethyl analogs in this respect. This article reports the products of the action of 2:1 sulfuric acid on I at 85–90°, their relative amounts, and the proof of their structures.

The dibromodimethylhydrazobenzene I was prepared by means of the synthetic scheme



The action of 2:1 sulfuric acid on I at 85–90° for a half-hour gave a mixture from which two disproportionation products and four rearrangement products were separated in 82% total yield. Of the remaining 18% of material, some survived the complex separation procedures as tarry residues and some was lost. The separation procedures, described in the Experimental part, involved countercurrent liquid–liquid extraction, steam distillation,

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(1) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(2) Institute Graduate Fellow in Organic Chemistry, 1951–1952.

(3) *Cf.* R. B. Carlin and S. A. Heininger, THIS JOURNAL, **77**, 2272 (1955).

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(5) W. A. Waters, "Physical Aspects of Organic Chemistry," 4th Ed., Van Nostrand, New York, N. Y., 1950, p. 58.