2,3,6,7-Naphthalenetetracarboxylic Dianhydride.—2,3-6,7-Naphthalenetetracarboxylic acid (0.50 g., 0.0017 mole) was dissolved in 100 ml. of acetic anhydride. The mixture was heated under reflux for 1 hr., and then most of the acetic anhydride was removed by evaporation. The solid that formed on cooling was recrystallized from acetic anhydride to give 0.12 g. of naphthalene dianhydride. The anhydride darkens on heating to 400° but does not melt.

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.70; H, 1.50; neut. equiv., 67.1. Found: C, 63.21; H, 1.71; neut. equiv., 65.0.

Ultraviolet absorption of water solutions of the anhydride: λ_{max} 252 mμ (ϵ 6.56 $\times 10^4$), 285 mμ (ϵ 8.56 $\times 10^3$), 346 mμ (ϵ 2.41 $\times 10^3$). Infrared absorption: 3085 and 3040 cm.$^{-1}$ (aromatic CH), and multiple absorption at the 1820-cm.$^{-1}$ region (cyclic anhydride).

Reaction of 6,7,14,15,17,19,22,24-Octahydro-5,8,13,16-hexacenetetrone (I) with Bromine.—A mixture of the octahydronaphthalene[4] (3.3 g., 0.008 mole] in 75 ml. of 1,2,4-trichlorobenzene was heated under reflux (210–215°) and to it was added bromine (6 g., 0.037 mole) dropwise over a period of 1 hr. Hydrogen bromide evolved, and a brown precipitate formed in the reaction mixture. Heating was continued 2 hr. longer, and then the mixture was allowed to cool to room temperature. The yellow-brown product that separated weighed 3 g. It was insoluble in dimethylformamide, tetramethylene sulfone, acetone, and ethyl acetate. It was purified by trituration with hot trichlorobenzene.

Anal. Calcd. for $C_{26}H_{12}O_4$: C, 80.5; H, 3.06. Found: C, 79.98; H, 3.26.

Identity of this product as 5,8,13,16-hexacenetetrone (II) was confirmed by its infrared spectrum: 3080 (w) (aromatic CH), 1680 (s) (carbonyl), 1590 (s) (aromatic C=C), 1395 (s), 1320 (s), 1275 (vs), 1205 (m), 1165 (m), 1145 (m), 1125 (m), 953 (s), 715 cm.$^{-1}$ (s). For comparison, the infrared spectrum of I has bands at: 3060 (w), 2880 (m), 2840 (m), 1690 (s), 1590 (s), 1445 (m), 1365 (m), 1340 (m), 1280(s), 1245 (s), 1205 (m), 1070 (m), 993 (m), 944 (m), 806 (m), 780 (m), 739 (s), 712 (m), 690 cm.$^{-1}$ (m).

Addition of Phenylmagnesium Bromide to 2-Phenyl-4-benzoylfuran[1]

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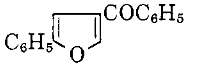
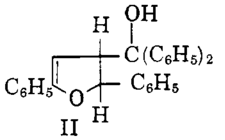
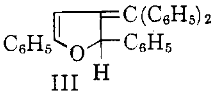
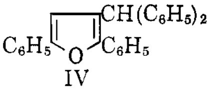
2-Phenyl-4-benzoylfuran (I) has been shown to be extremely susceptible to ring cleavage by alkaline reagents.[3] Treatment with dilute sodium hydroxide or with potassium carbonate led to ring opening. Ammonia or aniline converted the furan into the corresponding pyrrole. This behavior is predictable for a compound that is vinylogous with an ester of benzoic acid. Grignard reagents, therefore, might also be expected to cause opening of the ring. Experiments with phenylmagnesium bromide, however, led to unexpected results. The product was neither the open-chain compound nor the carbinol resulting from 1,2-addition to the carbonyl group; it corresponded, instead, to the compound to be expected from 1,4-addition followed by 1,2-addition. What appeared to be the primary product was the carbinol, II.


I


II


III

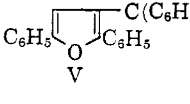

IV

The over-all change is similar to that observed when duryl phenyl ketone is condensed with benzyl- and *p*-chlorobenzylmagnesium chloride.[4] The alcohol was easily dehydrated to the olefin, III; in fact, in most experiments the alcohol was dehydrated during the work-up, and the olefin was isolated directly.

Isomerization of the olefin by transfer of the exocyclic double bond to the ring, although expected to occur readily, proved to be fairly difficult to effect. It was necessary to heat the olefin at reflux in ethanol with a small amount of hydrochloric acid to bring about this conversion. The product, 2,5-diphenyl-3-benzohydrylfuran (IV), was subsequently synthesized by an independent route. Cyclization of 1,4-diphenyl-1,4-butanedione with polyphosphoric acid gave 2,5-diphenylfuran in good yield; alkylation of this furan by means of benzohydrol and polyphosphoric acid yielded a compound that was identical in all respects to the furan obtained by isomerization of the olefin, III.

An attempt was made to form a benzoyl derivative by adding benzoyl chloride to the reaction mixture produced by condensation of phenylmagnesium bromide with ketone I; only furan IV was obtained. In a similar way the reaction mixture was treated with carbon dioxide, but no acid could be isolated; olefin III was formed in the usual yield. Attempts to prepare a mono-adduct by limiting the amount of Grignard reagent failed. The usual diaddition products were formed when at least 2.5 moles of the reagent were employed for each mole of ketone; when less than this amount of Grignard reagent was used, starting material was recovered.

3- Benzoyl - 2,5 - diphenylfuran reacted with


V

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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U.S. Army (Contract No. DA-11-022-ORD-874).

[2] California Research Corporation Fellow, 1958–1959.

[3] R. C. Fuson, C. L. Fleming, and R. Johnson, *J. Am. Chem. Soc.*, **60**, 1994 (1938).

[4] R. C. Fuson, J. P. Freeman, and J. J. Looker, *J. Org. Chem.*, **26**, 4217 (1961).

phenylmagnesium bromide, taken in excess, to give only the 1,2-addition product, V.

Experimental

Reaction of 2-Phenyl-4-benzoylfuran with Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide in ether, prepared from 1.0 g. (0.042 g.-atom) of magnesium turnings and 6.9 g. (0.044 mole) of bromobenzene, was added, with stirring, 4.0 g. (0.016 mole) of 2-phenyl-4-benzoylfuran over a period of 1 hr. The mixture was stirred at reflux for an additional hour and then cooled with an ice bath while 35 ml. of a saturated solution of ammonium chloride was added slowly. After this mixture had been stirred for 20 min., the organic layer was removed, washed with water, and dried over anhydrous sodium sulfate; the solvent was then removed under vacuum. The yellow, oily residue was dissolved in a mixture of ether and petroleum ether and allowed to stand in a refrigerator for several days. The diphenyl-(2,5-diphenyl-2,3-dihydro-3-furyl)carbinol (II) crystallized in yellow plates, which became colorless when washed with ether, yield 3.9 g. (60%). An analytical sample, recrystallized twice from ether–petroleum ether, melted at 135–136°. Dehydration occurred at the melting point; the sample became yellow in color, and bubble formation was observed.

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 85.81; H, 6.14.

The infrared spectrum of the alcohol contained a sharp band at 3600 cm.$^{-1}$ (hydroxyl group). When the alcohol was heated on a hot plate at its melting point for 30 min., it underwent dehydration to give the olefin, III, in 75% yield. It crystallized from a mixture of ether and ethanol as yellow prisms melting at 148–149°.

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.28; H, 5.91.

The infrared spectrum had no absorption bands assignable to a carbonyl or an alcohol function.

Isomerization of 2,5-Diphenyl-3-diphenylmethylene-2,3-dihydrofuran (III).—A mixture of 0.1 g. of the olefin, 25 ml. of 95% ethanol, and 5 ml. of concentrated hydrochloric acid was heated at reflux for 12 hr. during which time the yellow color disappeared completely. Water was then added dropwise until a faint, permanent turbidity was produced. When the mixture was cooled in a refrigerator, 0.08 g. of a white, fluffy solid separated. One recrystallization from ethanol–benzene gave 2,5-diphenyl-3-benzohydrylfuran, m.p. 178–179°.

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.09; H, 5.81.

The infrared spectrum showed no absorption in the carbonyl or hydroxyl regions.

2,5-Diphenyl-3-benzohydrylfuran.—2,5-Diphenylfuran was prepared according to the procedure of Nowlin.[5] To 10 g. of 1,4-diphenyl-1,4-butanedione was added 40 g. of polyphosphoric acid, and the mixture was heated at 135° for 1.5 hr. with efficient stirring. The mixture was cooled to 70°, and 10 g. of polyphosphoric acid was added; stirring was continued while 3.8 g. of benzohydrol was introduced in small portions over a 30-min. period. The reaction mixture was heated at 50° for 1 hr. after addition was complete. The dark brown mixture was then poured on cracked ice; recrystallization of the product from ethanol–benzene gave colorless needles melting at 178–179°, yield 3.0 g. A mixture melting point with the furan IV showed no depression; the infrared spectra of the two compounds were identical.

Reaction of 3-Benzoyl-2,5-diphenylfuran with Phenylmagnesium Bromide.—To a Grignard reagent prepared from 1.2 g. (0.05 g.-atom) of magnesium and 7.8 g. (0.05 mole) of bromobenzene was added, over a period of 45 min., 3.5 g. (0.012 mole) of 3-benzoyl-2,5-diphenylfuran in 50 ml. of ether. The reaction mixture was then heated and stirred under reflux for 5 hr. At the end of this period it was treated with 50 ml. of a saturated solution of ammonium chloride. The yellow organic layer was washed with water and dried with anhydrous sodium sulfate. Removal of the solvent left a pale yellow solid. Recrystallization from ether to give 3.3 g. (76%) of carbinol V, m.p. 175–178°. An analytical sample, recrystallized three times from ether, melted at 181–181.5°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51. Found: C, 86.16; H, 5.55.

The infrared spectrum of the carbinol had a sharp band at 3550 cm.$^{-1}$. When the carbinol V was reduced with zinc dust in glacial acetic acid at 65°, furan IV was obtained in 73% yield; this material was identical in all respects to an authentic sample of the furan.

Reaction of 2-Phenyl-4-benzoylfuran with Phenylmagnesium Bromide. Addition of Benzoyl Chloride to the Reaction Mixture.—The reaction of the furan with the Grignard reagent was carried out as described above; the Grignard reagent was prepared from 0.84 g. (0.035 g.-atom) of magnesium and 5.8 g. (0.037 mole) of bromobenzene. The furan (2.5 g., 0.01 mole) was added dropwise over a 1-hr. period, and the mixture was heated at gentle reflux for 9 hr., freshly distilled benzoyl chloride (4.9 g., 0.035 mole) was then added slowly, and stirring was continued for 1 hr. Hydrolysis was effected by stirring the reaction mixture with 20 ml. of a saturated solution of ammonium chloride containing a small amount of concentrated hydrochloric acid. The organic layer was washed with water until neutral and dried over sodium sulfate. Removal of the solvent left a black oil, which was chromatographed on alumina. The major product, eluted with cyclohexane, was furan IV; yield 1.8 g.

Several attempts were made to isolate a carbonation product; in each of these cases olefin III was obtained in approximately the usual yield.

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[5] G. Nowlin, *J. Am. Chem. Soc.*, **72**, 5754 (1950).

Solvent Effects in the Decomposition of Diazocamphane

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Recent investigations[1] of the base-catalyzed decomposition of sulphonhydrazones (the Bamford-Stevens reaction) have led the Oxford and Ohio State workers to propose that the protonating ability of the solvent employed was of major importance in determining the mode of decomposition of the presumed diazo intermediate. Whiting and Powell supported this view by showing that diazocamphane prepared in an independent unambiguous manner decomposed in 2-ethoxyethanol solutions to give mixtures rich in camphene, whereas etherela solutions were known[2] to decompose to tricyclene.

A subsequent study[3] of the mercuric oxide oxi-

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[1] (a) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959). (b) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959). (c) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **82**, 634 (1960).

[2] V. Heubaum and W. A. Noyes, *ibid.*, **52**, 5070 (1930).