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.

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

(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).

dation of camphor hydrazone implicated diazocamphane as an intermediate in the oxidation process, and established that the tricyclene produced as the major product in a variety of solvents did not incorporate deuterium when ethanol-d_1 was used as the solvent. The latter workers consequently suggested that protonation of diazocamphane by hydroxylic solvents does not occur.[4]

We now report the results of a joint study of this problem.

Table I summarizes the experimental findings for both reactions.

TABLE I

Solvent	Temp., °C.	Base	Percentage tricyclene[a] Hydrazone[b]	Percentage tricyclene[a] Sulphonhydrazone
C_2H_5OH	79	−	75[c]	
C_2H_5OH	79	+	65	
C_2H_5OH	138	+		86
CF_3CH_2OH	76	−	13[d]	
$(—CH_2OH)_2$	80	−	74	
$(—CH_2OH)_2$	82	+	55	
$(—CH_2OH)_2$	138	−	57	17
$(—CH_2OH)_2$	138	+		25
$HO(CH_2)_3OH$	80	−	75	
$HO(CH_2)_3OH$	132	+		46
$CH_3O(CH_2)_2OH$	80	−	62	
$C_2H_5O(CH_2)_2OH$	132	+		92
$(CH_3OCH_2—)_2$	81	−	98	

[a] The volatile products are tricyclene and camphene. [b] The oxidation of camphor hydrazone has been found to be more sensitive to variations in the mercuric oxide than previously suspected. Using a uniform sample of mercuric oxide and freshly distilled camphor hydrazone, an error of ±3% was observed for experiments made over a 3–4 week period. [c] The discrepancy between this value and the >97% tricyclene reported earlier[3] is probably due to the use of different samples of mercuric oxide. A third sample recently investigated gave 98% tricyclene under similar conditions. [d] Tricyclene is recovered unchanged after 1-hr. reflux in CF_3CH_2OH.

The striking change in the predominant product from the oxidation reaction, when β,β,β-trifluoroethanol is used as a solvent in place of ethanol is most reasonably interpreted in terms of the previously mentioned solvent protonation mechanism. The rather mediocre protonating ability of ethanol has been further demonstrated by the large proportion of tricyclene obtained from base-catalyzed decomposition of camphor sulphonhydrazone in ethanol at 138°.

The previously reported[3] insensitivity of the mercuric oxide oxidation reaction to variations in the solvent is now thought to be due to at least two factors. First, none of the solvents investigated earlier were strongly protonating (in terms of the Bamford-Stevens reaction). Second, the heterogeneous mercuric oxide phase could easily catalyze the decomposition of diazocamphane to tricyclene. Evidence supporting this proposal may be found in the smaller change in the tricyclene–camphane product ratio observed for the mercuric oxide oxidation reaction in ethylene glycol *vs.* ethanol (1.5×) as compared with the sulphonhydrazone decomposition reaction in the same two solvents (18×). This comparison is not strictly valid, since the temperatures at which these reactions are carried out are quite different. A higher temperature would, however, be expected to increase the rate of tricyclene formation.[2]

The rather slight effect that added base appears to have on product composition is expected if the protonation step is interpreted as proceeding mainly by general acid catalysis—*i.e.*, by ROH and not ROH_2^+).

The experimental procedures used in this work have been described in previous papers.[1a,3]

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1,4-Reduction of 1-Duroylcyclohexenes

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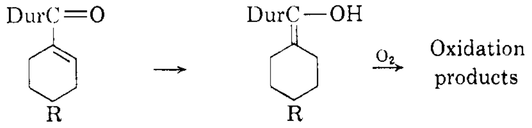
In the synthesis of cyclohexyl duryl ketone by reduction of the corresponding α,β-unsaturated ketone I with lithium aluminum hydride, cyclohexanone, and duroic acid were obtained as by-products.



I (R = H) II (R = H)
Ia (R = CH_3) IIa (R = CH_3)

Since these compounds are the expected oxidative cleavage products[2] of the enol II of cyclohexyl duryl ketone, it seemed likely that 1,4-reduction had occurred.[3] Treatment of cyclohexyl duryl ketone with lithium aluminum hydride, on the other hand, converted it nearly quantitatively into the corresponding carbinol.

Oxidative cleavage has been observed also with 1-duroyl-4-methylcyclohexene (Ia). Reduction without addition of oxygen gave only the corresponding saturated ketone; when oxygen was passed into the reaction mixture just before and just after hydrolysis, however, 4-methylcyclo-

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(3) W. Reusch, M. Di Carlo, and L. Traynor, *J. Org. Chem.*, **26**, 1711 (1961).

(4) Unfortunately the glycol solvents used in the sulphonhydrazone decomposition studies were not employed in the latter investigation.

(1) Chas. Pfizer and Co. Fellow, 1960–1961.

(2) E. P. Kohler, *Am. Chem. J.*, **36**, 177 (1906).

(3) R. E. Lutz and D. F. Hinkley, *J. Am. Chem. Soc.*, **72**, 4091 (1950).