× 1 ml of diethyl ether), and 1 ml of saturated aqueous NaCl was added to the remaining aqueous portion, which was then extracted again (2 × 1 ml of diethyl ether). The combined organic portions were washed (2 × 1 ml of saturated aqueous $NaHCO_3$, 1 × 1 ml of saturated aqueous NaCl), dried ($MgSO_4$), and filtered; GC showed only unreacted **2** and **1** to be present.

Registry No.—**1**, 60718-74-3; **2**, 3675-00-1; **4**, 5299-11-6; **5**, 60718-75-4; **6**, 60718-76-5; **7**, 60718-77-6; **9**, 60718-78-7; **10**, 36999-94-7; **11**, 38227-49-5; **12**, 60718-79-8; *N*-bromosuccinimide, 128-08-5; H_3PO_4, 7664-38-2; acetic acid, 64-19-7.

References and Notes

(1) Department of Chemistry, University of Missouri, Columbia, Mo. 65201.
(2) E. E. van Tamelen and J. P. McCormick, *J. Am. Chem. Soc.*, **91**, 1847 (1969).
(3) E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Am. Chem. Soc.*, **90**, 5616 (1968).
(4) (a) E. E. van Tamelen and T. J. Curphey, *Tetrahedron Lett.*, 121 (1962); (b) E. E. van Tamelen and K. B. Sharpless, *ibid.*, 2655 (1967).
(5) J. P. McCormick and D. L. Barton, manuscript in preparation.
(6) R. D. Gandour, *Tetrahedron Lett.*, 295 (1974).
(7) The involvement of the more basic (nucleophilic) oxygen of the acetoxy group, as pictured, requires the formation of medium-sized rings; this is consistent with observations made by Gandour (see ref 6). Smaller rings would be required if the other oxygen atom of the acetoxy group is involved; such a possibility cannot be excluded.
(8) (a) S. P. McManus, *J. Chem. Soc. D*, 235 (1969); (b) T. Sasaki, S. Eguchi, and M. Sugimoto, *Bull. Chem. Soc. Jpn.*, **44**, 1382 (1971); (c) R. M. Moriarty and H. Gopal, *Tetrahedron Lett.*, 347 (1972).
(9) E. J. Hessler, Ph.D. Thesis, Stanford University, Stanford, Calif., 1964.
(10) Prepared according to the described[3] procedure and purified by chromatography on silica gel (2% ethyl acetate/hexane); GC analysis (170 °C, 4 °C/min increase, retention time, 15.1 min) indicated greater than 98% isomeric purity.
(11) A mixture (ca. 85:15) of *E,E* and *Z,E* isomers, by GC.

On the Transformation of Benzoin to Tetraphenylfuran in the Presence of *p*-Toluenesulfonic Acid in Boiling Xylene

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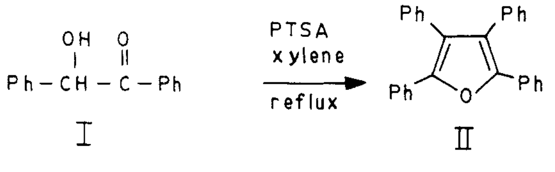
Benzoin (I) is known to undergo an interesting transformation to tetraphenylfuran (II) when refluxed with *p*-toluenesulfonic acid (PTSA) in dry xylene with azeotropic removal of water. This observation, originally made by Berger and Summerbell,[2] is still the best method for making II:[3,4]



Owing to the simplicity of the reaction and its possible potentiality of opening up of a novel route for the synthesis of furans, the present study was undertaken. In our hands benzoin (I), when refluxed under identical conditions, besides giving II, yielded five more compounds, namely, tetraphenyl-1,4-dioxadiene (III),[2] *cis*-dibenzoylstilbene (IV),[5] tetraphenyllactone (V),[6] benzil (VI),[7] and deoxybenzoin (VII),[8] all of which were identified by comparison with authentic compounds.

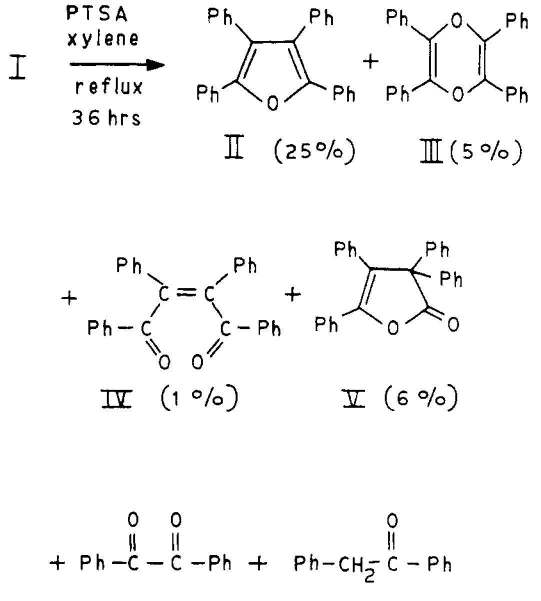


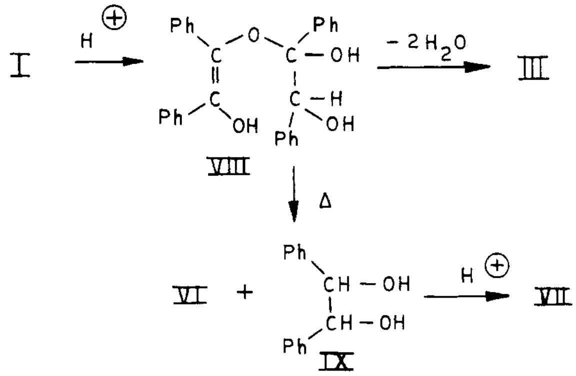
Table I. Yields of the Products Obtained in Different Reactions of I (%)

Reaction	II	III	IV	V	VI	VII
1	25.0	5.0	1.0	6.0	45.0	4.0
2	26.0	8.0	2.5	9.0	45.0	5.0
3	30.0	5.0	5.0	9.0	46.0	3.0
4	13.0	3.0	3.0	30.0	23.0	3.0

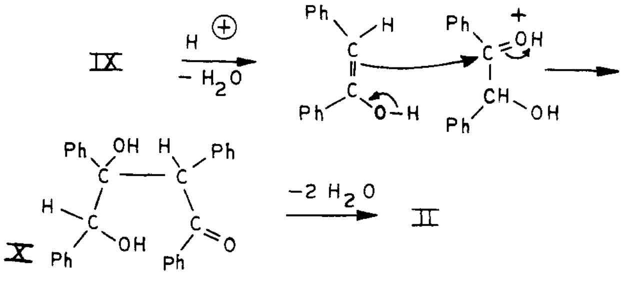
Slightly enhanced yields of all the products were obtained when an equimolar mixture of benzoin and benzoin acetate[9] was refluxed in dry xylene under identical conditions. With deoxybenzoin (VII) added to the reaction mixture yields of the furan (II), *cis*-dibenzoylstilbene (IV), and the lactone (V) increased appreciably.

Similarly when *cis*-dibenzoylstilbene (IV) was added to the reaction mixture the lactone (V) was obtained in higher yields. On the basis of all these observations (Table I) and other related evidences we have rationalized the transformation of benzoin (I) to the observed products in the following manner.

In the presence of acid benzoin (I) undergoes a self-condensation reaction giving rise to the intermediate VIII which then can form III, VI, and VII as follows.

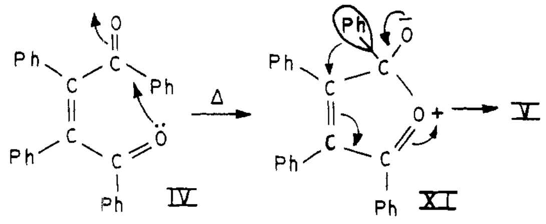


The formation of tetraphenylfuran (II) in this reaction has to involve the condensation of two species forming a carbon–carbon bond and it is quite likely that deoxybenzoin (VII) formed in this reaction condenses with benzoin in the presence of acid to give the intermediate X which could ultimately yield



tetraphenylfuran (II) as given above. This also explains why in the presence of added deoxybenzoin (VII) the furan (II) is formed in higher yield.

The lactone (V) is arising from *cis*-dibenzoylstilbene (IV) through a well-known valence isomerization giving rise to the intermediate XI followed by phenyl migration.[2]



It is not clear how *cis*-dibenzoylstilbene (IV) is formed in this reaction. However, II and III do not yield any detectable amount of IV under the reaction conditions.

Experimental Section[10]

Reflux of Benzoin (I) with *p*-Toluenesulfonic Acid in Dry Xylene (Reaction 1). Benzoin (4.24 g, 20 mmol) and *p*-toluenesulfonic acid (0.1 g) were refluxed in dry xylene (100 ml) with azeotropic removal of water for 36 h. Solvents were removed and the residue was chromatographed over silicic acid. Elution with hexane–benzene (5:1), benzene, and finally with benzene–ethyl acetate (10:1) gave 0.93 g of II (25%), mp 172–174 °C (lit.[2] mp 173.5–175 °C); 0.19 g of III (5%), mp 215–217 °C (lit.[2] mp 214–215 °C); 0.04 g of IV (1%), mp 213–214 °C (lit.[5] mp 212.6–213 °C); 0.23 g of V (6%), mp 137–138 °C (lit.[2] mp 137.1–137.6 °C); 1.89 g of VI (45%), mp 96 °C (lit.[7] mp 94–95 °C); and 0.16 g of VII (4%), mp 56 °C (lit.[8] mp 54–55 °C).

Benzoin (2.12 g, 10 mmol) and benzoin acetate (2.54 g, 10 mmol) (reaction 2), benzoin (4.24 g, 20 mmol) and deoxybenzoin (1.96 g, 10 mmol) (reaction 3), and benzoin (4.24 g, 20 mmol) and *cis*-dibenzoylstilbene (3.88 g, 10 mmol) (reaction 4) were refluxed separately in dry xylene in the presence of *p*-toluenesulfonic acid for 36 h. After the removal of solvents and usual workup products (II–VII) were obtained whose melting points are identical with those of the products obtained in reaction 1 and the yields are given in Table I.

Registry No.—I, 119-53-9; II, 1056-77-5; III, 6963-24-2; IV, 6313-26-4; V, 6963-25-3; VI, 134-81-6; VII, 451-40-1; *p*-toluenesulfonic acid, 104-15-4; benzoin acetate, 574-06-1.

References and Notes

(1) Department of Biological Sciences, BITS, Pilani 333031, India.
(2) D. R. Berger and R. K. Summerbell, *J. Org. Chem.,* **24,** 1881 (1959).
(3) D. H. R. Barton, I. A. Blair, P. D. Magnus, and R. K. Norris, *J. Chem. Soc., Perkin Trans. 1,* 1037 (1973).
(4) S. K. Kar, Ph.D. Thesis, IIT Kanpur, India, 1973.
(5) N. M. Bikales and E. I. Becker, *J. Org. Chem.,* **21,** 1405 (1956).
(6) N. Zinin, *Chem. Ber.,* **5,** 1104 (1872).
(7) H. T. Clarke and E. E. Dreger, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 87.
(8) C. F. H. Allen and W. E. Barker, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 156.
(9) B. B. Corson and N. A. Saliani, ref 8, p 69.
(10) All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model-137 instrument. The mixture melting points of all the compounds with their authentic compounds did not show any depression. All the compounds gave superimposable IR spectra with those of the respective authentic compounds.

Autocatalysis in the Nitrosation of Dihexylamine

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The kinetics of nitrosation of secondary amines, including catalytic effects, have recently received much attention[1,2] because of the carcinogenic activity of *N*-nitrosamines and their occurrence in the environment. Here we report a novel type of autocatalysis in the nitrosation of dihexylamine.

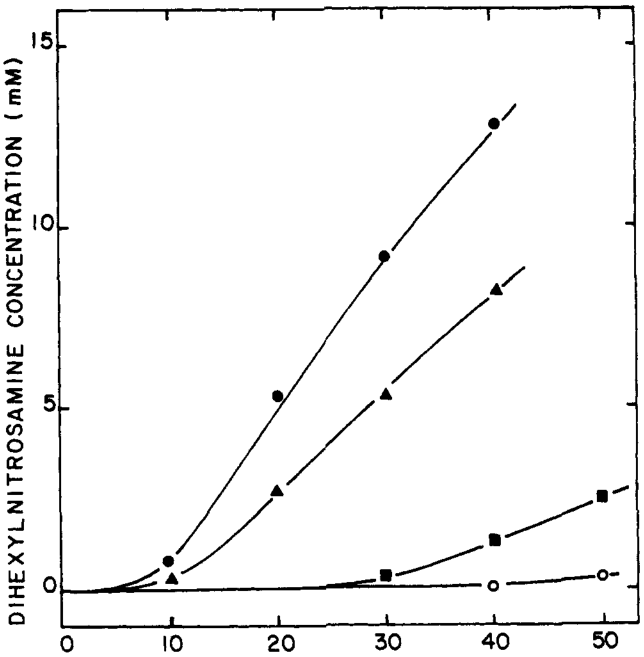

Figure 1. Time course of dihexylnitrosamine formation. Conditions: 20 mM dihexylamine; 30 mM (○), 40 mM (■), 50 mM (▲), and 60 mM (●) nitrite; pH 3.5; 25 °C.

Figure 1 illustrates the time course of dihexylamine nitrosation at four different nitrite concentrations. The initial rates (not shown clearly in Figure 1 because of the expanded ordinate scale) were as expected for the nitrosation of a secondary dialkylamine with a pK_a of 11.01[3] and yielded a second-order rate constant of 0.0004 $M^{-2}\ s^{-1}$ at pH 3.5.[1] At a particular, well-defined product concentration, however, the rate of the reaction increased abruptly by about 100-fold. At each nitrite concentration, the reaction rate began to increase at a dihexylnitrosamine concentration of 2×10^{-5} M. The reaction rates were proportional to the square of the nitrite concentration in both the initial and catalytic regions of the reaction.

Reaction mixtures, which were initially clear, colorless solutions, became cloudy at the point when the rate began to increase. The point of clouding, determined spectrophotometrically at 500 nm, coincided with a dihexylnitrosamine concentration of 2×10^{-5} M. Surface tension measurements at various times throughout the course of the reaction revealed no abrupt changes of surface tension.

In experiments with dipentyl- and dibutylamine, no autocatalytic effect was observed even when the nitrosation reaction was allowed to proceed almost to completion. Also no cloud point was observed in these reactions. When dihexylamine was mixed with an equimolar concentration of either dipentylamine or dibutylamine, and the resulting solution nitrosated, both amines showed increased rates of nitrosation (Figure 2). The magnitudes of the rate enhancements corresponded to the increasing alkyl chain length of the amine.

In a previous study,[4] we have shown that nitrosation of dihexylamine is strongly catalyzed in the presence of cationic and nonionic surfactants that form micelles in aqueous solution. A similar phenomenon may explain the autocatalytic effect described here for the nitrosation of dihexylamine and the catalytic effect on dipentyl- and dibutylamine nitrosation in the presence of dihexylamine. As the concentration of dihexylnitrosamine exceeds its solubility in aqueous solution, spontaneous emulsification occurs. Hydrophobic interactions lead the amine to concentrate in the dihexylnitrosamine mi-