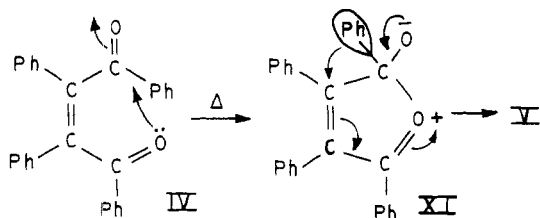


tetraphenylfuran (II) as given above. This also explains why in the presence of added deoxybenzoin (VII) the furan (II) is formed in higher yield.

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.<sup>2</sup>



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<sup>10</sup>

**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.<sup>2</sup> mp 173.5–175 °C); 0.19 g of III (5%), mp 215–217 °C (lit.<sup>2</sup> mp 214–215 °C); 0.04 g of IV (1%), mp 213–214 °C (lit.<sup>5</sup> mp 212.6–213 °C); 0.23 g of V (6%), mp 137–138 °C (lit.<sup>2</sup> mp 137.1–137.6 °C); 1.89 g of VI (45%), mp 96 °C (lit.<sup>7</sup> mp 94–95 °C); and 0.16 g of VII (4%) (mp 56 °C (lit.<sup>8</sup> 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.

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- 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<sup>1,2</sup> 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.

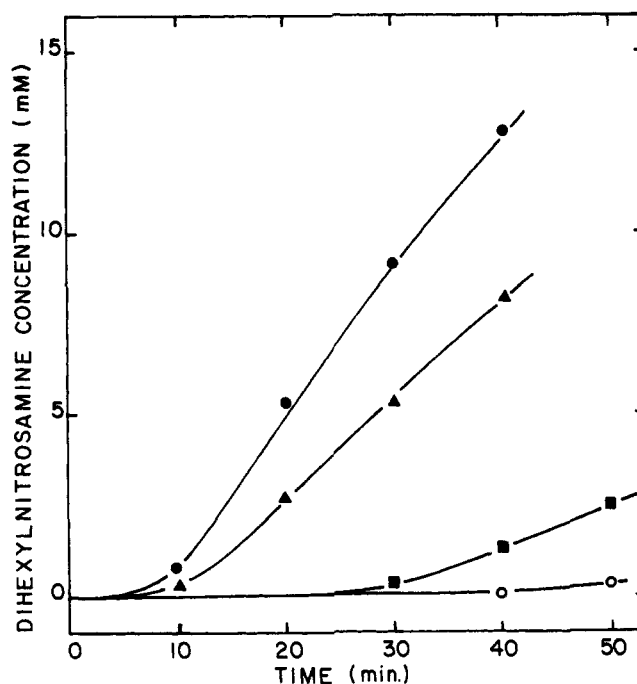


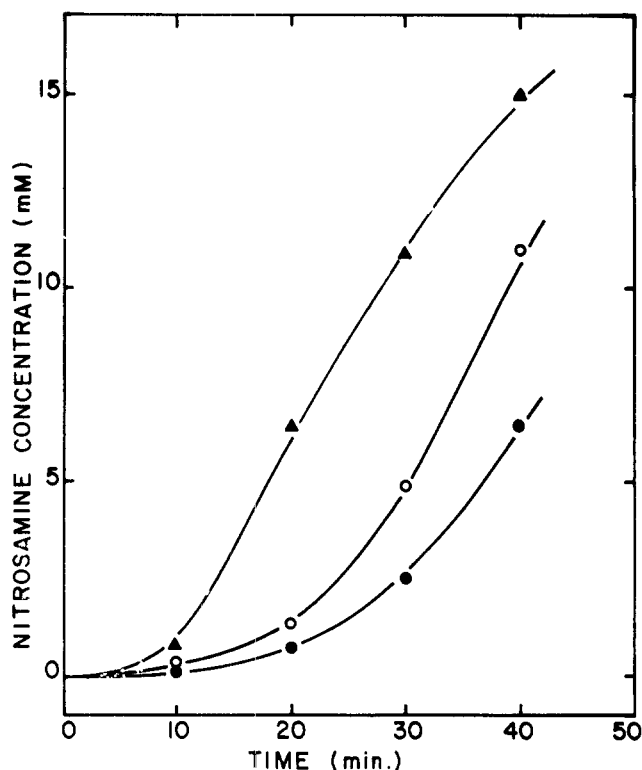
Figure 1. Time course of dihexylamine nitrosation. Conditions: 20 mM dihexylamine; 30 mM (○), 40 mM (■), 50 mM (▲), and 60 mM (●) nitrite; pH 3.5; 25 °C.

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<sup>3</sup> and yielded a second-order rate constant of  $0.0004 \text{ M}^{-2} \text{ s}^{-1}$  at pH 3.5.<sup>1</sup> 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  $2 \times 10^{-5} \text{ M}$ . 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  $2 \times 10^{-5} \text{ M}$ . 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,<sup>4</sup> 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-



**Figure 2.** Time course of formation of dipentylnitrosamine (○) and dibutylnitrosamine (●) in the presence of dihexylnitrosamine (▲). Conditions: 20 mM dihexylamine plus 20 mM dipentylamine or 20 mM dibutylamine; 50 mM nitrite; pH 3.5; 25 °C.

crodroplets. Catalysis then occurs in a manner analogous to that observed in the presence of added surfactant.

#### Experimental Section

Dibutylnitrosamine, dibutylamine, dipentylamine, and dihexylamine were purchased from Eastman Organic Chemicals, Rochester,

N.Y. Dihexylnitrosamine was a generous gift from Dr. Harold Röper of the University of Hamburg. Dipentylnitrosamine was synthesized from the parent amine by the method of Druckrey et al.<sup>5</sup> All amines were purified by distillation prior to use; the purity of the nitrosamines was established by gas chromatography.

Kinetic runs were performed in triplicate for each time period in stoppered centrifuge tubes. Reaction mixtures (5-ml volumes) contained 20 mM amine and 20 mM sodium nitrite in citrate-phosphate buffer, pH 3.5 at 25 °C. The buffer was prepared by mixing 0.1 M citric acid with 0.2 M Na<sub>2</sub>HPO<sub>4</sub>.

Reactions were initiated by adding 3 ml of amine solution; at various times the nitrosation reaction was stopped by adding an excess of solid ammonium sulfamate. After incubation for about 5 min to ensure destruction of nitrite, the contents of the tubes were extracted with an equal volume of methylene chloride and the nitrosamine concentration was determined by a combined gas chromatography-thermal energy analysis system, described by Fine and Roubehler.<sup>6</sup> Chromatography was performed on a 0.125 in. × 10 ft column packed with 5% Carbowax 20M on Chromosorb W. Column temperatures ranged from 155 to 210 °C depending on the nitrosamine investigated. In separate experiments, extraction of all nitrosamines from the aqueous phase into methylene chloride was found to be 98–100% efficient. Surface tension measurements were made with a Fisher surface tensiometer (Fisher Scientific, Pittsburgh, Pa.).

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**Registry No.**—Dihexylnitrosamine, 6949-28-6; dihexylamine, 143-16-8; dipentylnitrosamine, 13256-06-9; dibutylnitrosamine, 924-16-3; dipentylamine, 2050-92-2; dibutylamine, 111-92-2.

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