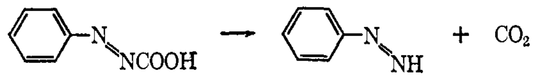
Properties of Phenyldiimide

Sir:

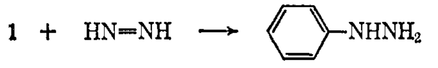
Phenyldiimide (**1**) has been detected as the product of decarboxylation of phenylazoformic acid (**2**) in neutral aqueous solution.[1] We communicate here the preparation of **1** in acetonitrile and a study of the unusual chemical properties of **1**, the most notable of which is the reaction of **1** with itself.[2]



2 **1**

The conversion of **2** to **1** is very rapid.[1] The primary problem in the preparation of **1** is in finding convenient methods for supplying a proton to the anion of **2** under oxygen-free conditions. We have successfully used three combinations: (a) the potassium salt of **2**, lithium chloride, and a weakly acidic ion-exchange resin; (b) the potassium salt of **2** and dimethylamine hydrochloride; and (c) the tetra-*n*-butylammonium salt of **2** and dimethylamine hydrochloride. The last combination permits the preparation of solutions of **1** in concentrations of at least 0.1 *M*.

The presence of **1** is confirmed by ultraviolet and visible spectra (λ_{max} 2600 A (ϵ 7400), 4175 (74)),[1] stoichiometric conversion to phenylhydrazine (**3**) with diimide generated from $K^{+-}OOCN{=}NCOO^{-}K^{+}$ and $(C_2H_5)_3NH^{+}Cl^{-}$, and volatility consistent with its molecular weight (codistillation with acetonitrile, $p_{298} \sim 10^{-3}$ mm).



3

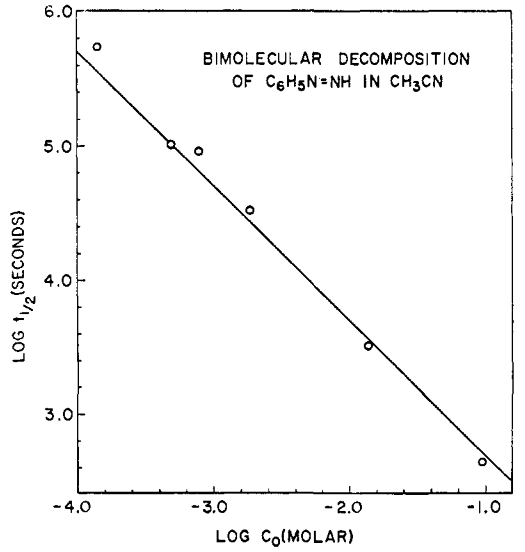


Figure 1. A plot of log $t_{1/2}$ (half-life) against log C_0 (initial concentration) of phenyldiimide in acetonitrile. The straight line is drawn so that the slope is equal to -1. k_2 = antilog ($-$log C_0 $-$ log $t_{1/2}$) = 0.020 l. mole^{-1} sec^{-1}.

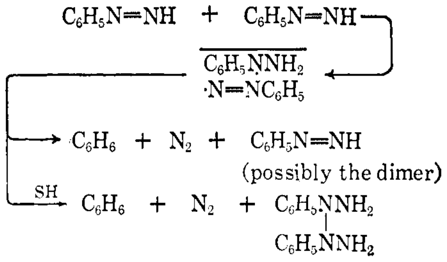
Very dilute solutions of **1** in acetonitrile are fairly stable, with a half-life of about 500,000 sec at $C_0 = 10^{-4}$ *M* at 25°. Attempts to prepare more concentrated solutions indicate that **1** reacts with itself in a bimolecular reaction. The rate constant for this reaction is almost unchanged over a concentration range of 650, as illustrated by a plot of log $t_{1/2}$ *vs.* log C_0 (see Figure 1), giving strong support to the interpretation of the reaction of **1** with itself as a bimolecular reaction.

The bimolecular rate constant for the disappearance of phenyldiimide-*d* (**1**-*d*) is considerably lower than that for **1** ($k_H/k_D \sim 6$), showing that hydrogen transfer is important in the rate-determining step. The lack of solvent effect on the rate constant renders an electron-transfer step unlikely. The activation energy for the bimolecular reaction in acetonitrile is only ~9 kcal/mole, corresponding to an entropy of activation of ~$-$23 eu.

The major product of the bimolecular reaction of **1** with itself is benzene in about 80% yield from 0.1 *M* solutions, accompanied by an approximately equivalent quantity of nitrogen. The yield of benzene does not appear to vary appreciably with concentration of **1**, suggesting that long radical chains cannot be significant steps in the mechanism of the reaction.

The details of the mechanism of the bimolecular reaction of **1** will be discussed in a full paper. A plausible scheme involves the formation of radical *reaction partners*[3] within a solvent cage and may be formulated as shown in Scheme I.

Scheme I



Other reactions of phenyldiimide which we have examined in less detail are with oxygen (extremely rapid, k_2 probably above 10^3 l. mole^{-1} sec^{-1}) and 1,4-benzoquinone ($k_2 \sim 10$ l. mole^{-1} sec^{-1}). As expected, **1** yields benzene on reaction with base. Like other azo compounds, **1** is nonnucleophilic and fails to react with methyl chloroformate or benzenesulfonyl chloride, either in the presence or in the absence of triethylamine.

Interesting aspects of the behavior of **1** as an intermediate in a number of reactions may be found in the work of Cohen[4] and Hoffmann.[5]

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(1) E. M. Kosower and P. C. Huang, *J. Am. Chem. Soc.*, **87**, 4645 (1965).

(2) A preliminary account of some of this work was presented at the 150th National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(3) See Section 2.10 of E. M. Kosower, "Introduction to Physical-Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., in press.

(4) (a) S. G. Cohen and J. Nicholson, *J. Am. Chem. Soc.*, **86**, 3892 (1964); (b) S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965); (c) J. Nicholson and S. G. Cohen, *J. Am. Chem. Soc.*, **88**, 2247 (1966).

(5) R. W. Hoffmann, *et al.*, *Chem. Ber.*, **97**, 2763, 2772 (1964); **98**, 222 (1965); **100**, 1465, 1474 (1967).

(6) Predoctoral Fellow of the National Institutes of Health, 1964–1966.

(7) The authors are grateful for support from the Army Research Office (Durham), the National Institutes of Health, and the National Science Foundation.

Acknowledgment. The authors wish to thank Professor R. Hoffman, Cornell University, for a useful discussion.

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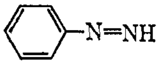
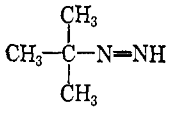
t-Butyldiimide

Sir:

Monosubstituted alkyl- and aryldiimides have been postulated as intermediates in many reactions.[1] We have generated phenyldiimide (**1**) by decarboxylation[1] and found that **1** was stable enough for further study.[2] We now report the detection of the monoalkyldiimide, *t*-butyldiimide (**2**).



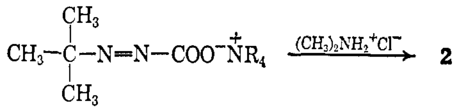
1



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-N{=}NH$$

2

A degassed solution of tetra-*n*-butyl- (or tetramethyl-) ammonium *t*-butylazoformate (**3**) was prepared in acetonitrile[3] and mixed with a solution of a slight excess of dimethylamine hydrochloride in the same solvent. The concentration of the reactants in the final solution was about 0.004 *M*. Immediately after mixing the solution was poured into a 10-cm cell and recording of the spectra was begun (within 60–70 sec). The anion **3** has a maximum at 3835 A (ϵ 28). The reaction solution displayed a new maximum at about 3750 A (ϵ 17 extrapolated to $t = 0$) which disappeared in a manner consistent with the occurrence of a bimolecular reaction with a k_2 of $\sim$0.9 l. mole^{-1} sec^{-1} at 25°. The rate constant for the disappearance of *t*-butyldiimide is approximately 65 times greater than the constant for the reaction of phenyldiimide under the same conditions.



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-N{=}N-COO^-\overset{+}{N}R_4 \xrightarrow{(CH_3)_2NH_2^+Cl^-} \mathbf{2}$$

3

The identification of **2** as the unstable intermediate is supported by: (1) the mode of formation; (2) the shift in the position of the long-wavelength $n \rightarrow \pi^*$ transition (85 A) from that found in the anion **3** (the corresponding shift for **1** is 185 A); (3) the extremely rapid reaction of **2** with oxygen, with k_2 of perhaps 10^4 l. mole^{-1} sec^{-1} (see Figure 1); and (4) the bimolecular disappearance of **2**. Both the rapid reaction with oxygen and the bimolecular reaction with itself are characteristic of **1** and may well be general properties of diimides with at least one hydrogen bonded to nitrogen.

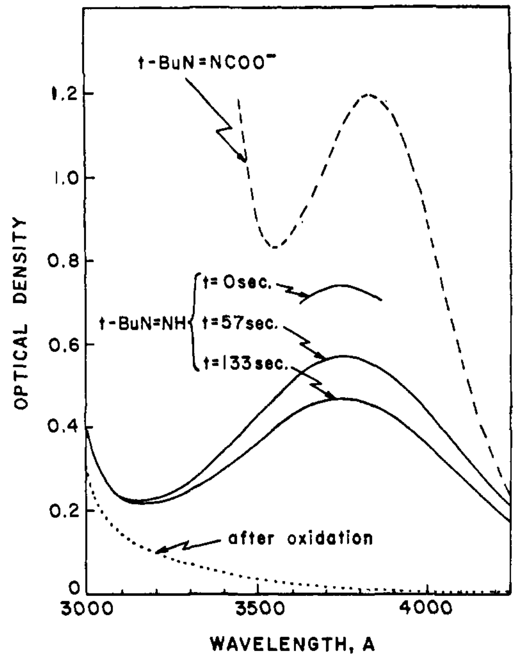


Figure 1. Absorption spectrum of *t*-butylazoformate (**3**) ($n \rightarrow \pi^*$ transition) (- - - -), of *t*-butyldiimide (**2**) at $t = 0$ (estimated from rate), $t = 57$, and $t = 133$ sec (———), and of a solution of *t*-butyldiimide exposed to air at $t = 217$ sec with recording begun within 39 sec (· · · · ·). Acetonitrile was used as the solvent; C_0 (**2**, **3**) = 4.27×10^{-3} *M*.

The stability of *t*-butyldiimide is sufficient for further investigations, and the implication is strong that many other monosubstituted diimides can be generated and examined. It is even reasonable to speculate that diimide itself, HN=NH, might be observed in a suitable flow apparatus.[4,5]

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[1] E. M. Kosower and P. C. Huang, *J. Am. Chem. Soc.*, **87**, 4645 (1965).

[2] P. C. Huang and E. M. Kosower, *ibid.*, **89**, 3910 (1967).

[3] The salt was prepared from the corresponding methyl ester. The ethyl ester has been reported by M. C. Chaco and N. Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

[4] See, for example, the selectivity reported by E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965).

[5] Compare with the results of Kj. Rosengren and G. C. Pimentel, *J. Chem. Phys.*, **43**, 507 (1965), and previous papers.

[6] Predoctoral Fellow of the National Institutes of Health, 1964–1966.

[7] The authors are grateful for support from the Army Research Office (Durham), the National Institutes of Health, and the National Science Foundation.

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Selective Formation of Carbon–Carbon Bonds between Unlike Groups Using Organocopper Reagents

Sir:

An efficient and useful method for the attachment of an allylic group to an alkyl, vinyl, or aryl unit by means of allylnickel reagents has recently been described.[1] The further extension of this investigation toward even more general selective cross-coupling reactions and to other organo-transition metal compounds has yielded results which are of considerable synthetic interest. This communication deals with the reaction between organocopper compoundsand organic halides as a promising new general synthetic method and, more particularly, with the process of methylation which has received most of our attention thus far.

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[1] E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967).