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

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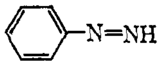
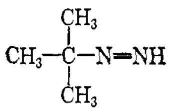
t-Butyldiimide

Sir:

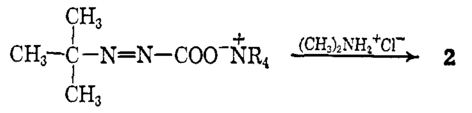
Monosubstituted alkyl- and aryldiimides have been postulated as intermediates in many reactions.[1] We have generated phenyldiimide (1) by decarboxylation[1] and found that 1 was stable enough for further study.[2] We now report the detection of the monoalkyldiimide, *t*-butyldiimide (2).


1


2

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

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 ~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.



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

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.

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]

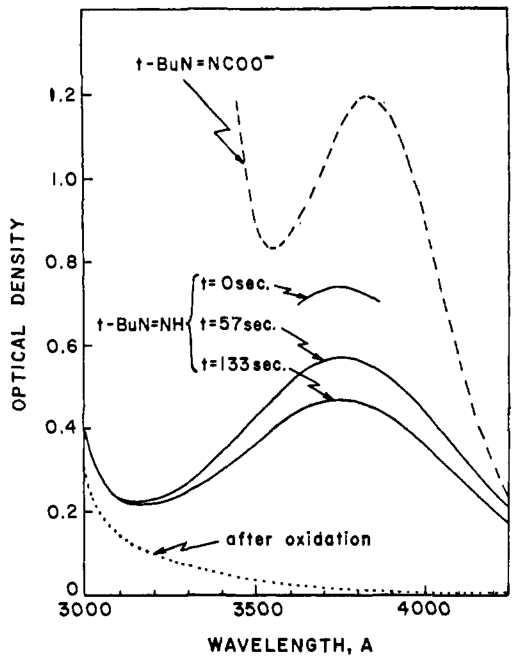


Figure 1. Absorption spectrum of *t*-butylazoformate (3) ($n \rightarrow \pi^*$ transition) (- - - -), of *t*-butyldiimide (2) at $t = 0$ (estimated from rate), $t = 57$, and $t = 133$ sec (———), and of a solution of *t*-butyldiimide exposed to air at $t = 217$ sec with recording begun within 39 sec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

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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.

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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 compounds and 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).