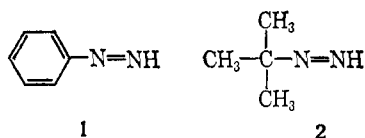Pih-kuei C. Huang,[8] Edward M. Kosower[7]
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Received March 22, 1967

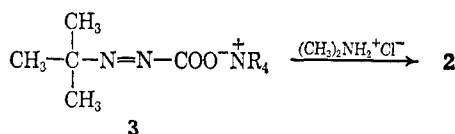## t-Butyldiimide

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).

$$\text{C}_6\text{H}_5\text{---N=NH} \qquad \text{CH}_3\text{---}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{---N=NH}$$

1   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.

$$\text{CH}_3\text{---}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{---N=N---COO}^-\overset{+}{\text{N}}\text{R}_4 \xrightarrow{\text{(CH}_3)_2\text{NH}_2{}^+\text{Cl}^-} \mathbf{2}$$

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 $\rightarrow$ π^* 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 gener-

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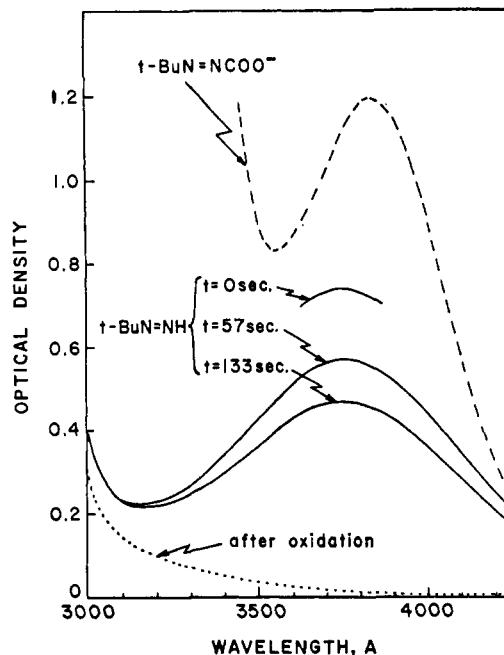
Figure 1. Absorption spectrum of t-butylazoformate (3) (n $\rightarrow$ π^* transition) (- - - -), of t-butyldiimide (2) at $t = 0$ (estimated from rate), $t = 57$, and $t = 133$ sec (————), and of a solution of t-butyldiimide exposed to air at $t = 217$ sec with recording begun within 39 sec ($\cdots\cdots$).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

ated and examined. It is even reasonable to speculate that diimide itself, HN=NH, might be observed in a suitable flow apparatus.[4,5]

(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.

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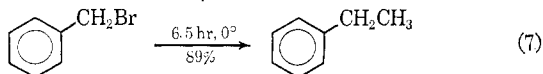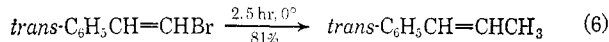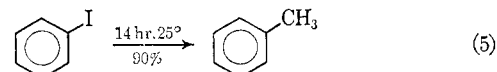Stony Brook, New York 11790
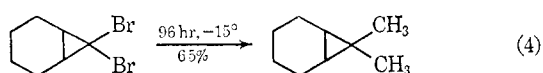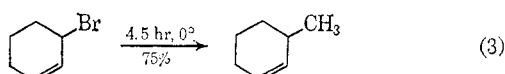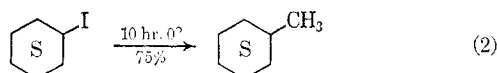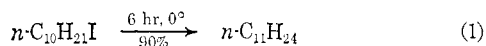Received March 22, 1967

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.

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

Communications to the Editor

Gilman and co-workers[2] have previously prepared two methylcopper derivatives, one an insoluble, probably polymeric reagent, $(CH_3Cu)_n$, from equimolar amounts of methyllithium (or methyl Grignard reagent) and cuprous halide in ether, and the other an ether-soluble complex from 2 mole equiv of methyllithium to 1 of cuprous halide, perhaps representable as Li^+-$(CH_3)_2Cu^-$, in which the anion is isoelectronic with dimethylzinc.[3] Our studies indicate that the latter complex, referred to herein as lithium dimethylcopper, is an excellent reagent for the selective replacement of iodine or bromine in a wide variety of substrates by methyl. In general, ethereal solutions of the reagent were prepared from the reaction of ethereal methyllithium (from lithium and methyl bromide) with cuprous iodide (molar ratio 2:1) at 0° under nitrogen, and most of the methylations were performed at 0° [4] with 5 moles of the copper reagent (concentration ca. 0.5 M) per mole of halide. In all cases products were analyzed by vapor phase chromatography, isolated, and characterized by comparison with authentic samples.[5] Equations 1–7 typify the transformations which have been observed with the lithium dimethylcopper reagent in ether solution.

$$n\text{-}C_{10}H_{21}I \xrightarrow[90\%]{6 \text{ hr, } 0°} n\text{-}C_{11}H_{24} \quad (1)$$

(2)

(3)

(4)

(5)

$$trans\text{-}C_6H_5CH=CHBr \xrightarrow[81\%]{2.5 \text{ hr, } 0°} trans\text{-}C_6H_5CH=CHCH_3 \quad (6)$$

(7)

Appreciable amounts of by-products were observed in some instances, specifically exo-7-methylnorcarane[6] (25%) in reaction 4 and trans,trans-1,4-diphenylbutadiene (12%) in the case of reaction 6.

Reaction 6 occurs stereospecifically and, in addition, cis-1-bromo-2-phenylethylene is stereospecifically converted to cis-1-phenylpropene. In contrast, however, cis-1-bromo-4-t-butylcyclohexane[7] reacts with lithium dimethylcopper nonstereospecifically to give a mixture of

(2) H. Gilman, R. G. Jones, and L. A. Woods, J. Org. Chem., 17, 1630 (1952); also see H. Gilman and J. M. Straley, Rec. Trav. Chim., 55, 821 (1936).

(3) See H. O. House, W. L. Respess, and G. M. Whitesides, J. Org. Chem., 31, 3128 (1966).

(4) All reactions involving organocopper reagents were carried out with the usual precautions for rigorous exclusion of air and moisture. The insoluble methylcopper is inferior to lithium dimethylcopper as a nucleophilic methylating reagent, since the reactions of the former are inordinately slow.

(5) Using infrared, nuclear magnetic resonance, and in some cases mass spectroscopy in addition to vapor chromatographic data.

(6) G. Wittig and M. Jautelat, Ann., 702, 24 (1967); M. Jautelat, Ph.D. Thesis, Heidelberg, 1966; H. E. Simmons, E. P. Blanchard, and R. D. Smith, J. Am. Chem. Soc., 86, 1347 (1964). For the previously described several-step synthesis of 7,7-dimethylnorcarane see E. D. Andrews and W. E. Harvey, J. Chem. Soc., 4636 (1964).

(7) E. L. Eliel and R. G. Haber, J. Org. Chem., 24, 143 (1959).

45% trans-1-methyl-4-t-butylcyclohexane and 10% cis-1-methyl-4-t-butylcyclohexane, in addition to some t-butylcyclohexane and 4-t-butylcyclohexene. Further study is required before the stereochemical and mechanistic details of these methylation reactions can be understood. However, the broad scope and utility of the method are apparent.[8,9] It should be noted that methyllithium itself is a totally unsatisfactory reagent for the majority of the transformations 1–7. For example, the reaction of methyllithium with 7,7-dibromonorcarane affords little if any 7,7-dimethylnorcarane,[10,11] and the reaction of methyllithium with the 1-bromo-2-phenylethylenes produces mainly phenylacetylene.

A number of previous studies are clearly relevant to the presently reported results. These include observations on the intermediacy of arylcopper compounds in the Ullmann synthesis of biphenyls,[12–14] the coupling of cuprous acetylides with aryl iodides,[15] and the well-known substitution reactions of cuprous cyanide and cuprous mercaptides with aromatic halides.[16]

Investigations are continuing on the extension, refinement, and application of the cross-coupling method reported here.

(8) For the application of organocopper reagents in conjugate addition to α,β-unsaturated ketones which originates from the work of Kharasch, see ref 3 and literature cited therein.

(9) For recent studies on the formation of symmetrical coupling products by thermal decomposition of vinylcopper compounds (and vinylsilver compound), see (a) G. M. Whitesides and C. P. Casey, J. Am. Chem. Soc., 88, 4541 (1966); (b) T. Kauffmann and W. Sahm, Angew. Chem. Intern. Ed. Engl., 6, 85 (1967); (c) G. Köbrich, H. Fröhlich, and W. Drischel, J. Organometal. Chem. (Amsterdam), 6, 194 (1966).

(10) (a) W. R. Moore and H. R. Ward, J. Org. Chem., 25, 2073 (1960); (b) ibid., 27, 4179 (1962); (c) W. R. Moore, H. R. Ward, and R. F. Merritt, J. Am. Chem. Soc., 83, 2019 (1961).

(11) E. T. Marquis and P. D. Gardner, Tetrahedron Letters, 2793 (1966).

(12) R. G. R. Bacon and H. A. O. Hill, Quart. Rev. (London), 19, 95 (1965).

(13) A. H. Lewin and T. Cohen, Tetrahedron Letters, 4531 (1965).

(14) M. Nilsson, ibid., 679 (1966).

(15) C. E. Castro, E. J. Gaughan, and D. C. Owsley, J. Org. Chem., 31, 4071 (1966), and earlier papers cited therein.

(16) See, for example, R. Adams, W. Reifschneider, and A. Ferretti, Org. Syn., 42, 22 (1962).

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Construction of Ring Systems Containing the gem-Dimethylcyclopropane Unit Using Diphenylsulfonium Isopropylide

Sir:

The generation of the highly reactive sulfur ylide diphenylsulfonium isopropylide (I) and the interaction of this reagent with nonconjugated aldehydes and ketones to form oxiranes have recently been described.[1–3]

(1) E. J. Corey, M. Jautelat, and W. Oppolzer, Tetrahedron Letters, 2325 (1967).

(2) Diphenylsulfonium isopropylide can be generated by two different procedures:[1] (a) from diphenylethylsulfonium fluoroborate in dimethoxyethane by the sequence ylide formation (dichloromethyllithium, produced in situ from lithium diisopropylamide and methylene chloride, as base at −70°), methylation (methyl iodide), and ylide formation (dichloromethyllithium at −70°); (b) from diphenylisopropylsulfonium fluoroborate in tetrahydrofuran at −70° using t-butyllithium as base.