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HYPERVALENT IODINE OXIDATION OF ACID HYDRAZIDES: A NEW SYNTHESIS OF N,N'-DIACYLHYDRAZINES

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Abstract: Hypervalent iodine oxidation of p-substituted benzohydrazides (1a-h), phenylacetohydrazide (1i) and heterocyclic acid hydrazides (1j-l) using one equivalent of iodobenzene diacetate in dry dichloromethane or acetonitrile leads to dimerization thereby providing a new and facile method for the synthesis of N,N-diacylhydrazines 2.

Hypervalent iodine compounds such as iodobenzene diacetate (IBD) and [hydroxy(tosyloxy)iodo]benzene (HTIB) have attracted a great deal of interest because of their increasing utility in organic synthesis.¹ There is recent interest in the hypervalent iodine oxidation of hydrazones,² hydrazides³ and related compounds.⁴ As a part of our ongoing program on the applications of iodine(III) reagents^{3c,5} we now report a new and facile method for the dimerization of various acid hydrazides.

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Treatment of the 4-substituted benzohydrazides (1a-h) and phenylacetohydrazide (1i) with one equivalent of IBD in dry dichloromethane or acetonitrile at room temperature afforded the corresponding *N*,*N*-diacylhydrazines (2a-i)(Scheme1). Reaction is exothermic and proceeds with the vigorous evolution of nitrogen gas.

The oxidative dimerization of acid hydrazides was successfully extended to N,Ndiacylhydrazines **2j-1** which contain heteroaryl moieties such as pyridyl and 2benzothiazolyl (Scheme 1).





Then we investigated the scope of this method to achieve cross coupling starting from two different hydrazides. Thus, when a mixture of benzoic hydrazide (1a) and *p*-methoxybenzoic acid hydrazide (1e) was treated with two equivalents of IBD in dry dichloromethane, it afforded the desired cross product *N*-benzoyl-*N*'-*p*-anisoylhydrazine (3e) as a major product along with symmetrical products 2a and

2e in minor amounts. Other hydrazides which underwent smooth cross-coupling with 1a include 1b-d (Scheme 2) (Table).



Scheme 2

A plausible mechanism for the dimerization of acid hydrazides (1 to 2) involves an electrophilic attack of IBD on the lone pair of terminal nitrogen of hydrazide 1 to give intermediate 4 which then undergoes reductive loss of iodobenzene along with expulsion of a molecule of acetic acid to generate the acyldiimide 5. Subsequent oxidation of 5 with second molecule of IBD, followed by the nucleophilic attack of the hydrazide 1 itself at the carbonyl of resultant 6 results in the formation of product 2 (Scheme 3).

It is noteworthy that when similar reaction is performed in the presence of nucleophiles such as alcohol or water, formation of esters or acids occurs.^{3c}

The intermediacy of acyldiimide 5 in the oxidative dimerization of hydrazides has previously been suggested by others. ⁶⁻⁸ The diacylhydrazines are also obtained from the oxidation of hydrazides with lead tetraacetate⁹ or selenium oxidants⁶ or halogens¹⁰.

Producta	Yield (%)	mp ℃	Lit. mp ^{Ref.}
2a	66	237-38	238-40 ^{12a}
2ь	74	290-91	292 ^{12b}
2c	65	221-22	219-21 ¹⁰
2d	71	254-55	253-54 ^{12c}
2e	50	227-29	228-28.5 ^{12b}
2f	54	287-89	289 ^{12d}
2g	51	296-97	298 ^{12d}
2h	38	300-01	301 ¹² e
2i	70	235-36	236-37 ^{12f}
2ј	65	223-24	225 ^{12b}
2k	66	252-53	253-55 ¹² g
21	62	262-63	Ь
3b ^c	55	224-25	224-25 ^{12h}
3c ^{<i>c</i>}	53	178-79	179 ¹²ⁱ
3d ^{<i>c</i>}	58	217-18	217-18 ¹²ⁱ
3e ^c	52	185-86	186-87 ^{12j}

TABLE: N,N'-Diacylhydrazines

a. Spectral properties (¹H NMR, IR) of all products agreed with required/reported data.

b. Calc. for C16H10N4O2S2: C 54.23, H 2.82, N 15.82; Found C 54.01, H 2.90, N 15.63.

c. Symmetrical diacylhydrazines formed in these cases (detected by tlc) were not isolable because of low concentration.

Finally, the new oxidative conversion of 1 to 2 provides an easy access to symmetrical and unsymmetrical diacylhydrazines which are useful precursors of industrially important heterocyclic compounds such as oxadiazoles and thiadiazoles. Yields are generally moderate to good with the exception of 1f



Scheme 3

which afforded product 2f in only 38% yield presumably due to the presence of oxidizable phenolic group¹¹. Of course, we were not able to isolate any other product from the oxidation of 1f.

EXPERIMENTAL

Preparation of N,N'-Diacylhydrazines (2a-i) (A General Procedure).

To a suspension of an acid hydrazide 1 (5 mmol) in dry dichloromethane or acetonitrile (15 mL) at room temperature was added IBD (5 mmol, 1.61 g) in four portions and the resulting mixture was stirred for 10 min. An exothermic reaction took place with the strong evolution of nitrogen gas. The reaction mixture first becoming homogenous turned again to suspension on cooling. Filtration followed by washing with dichloromethane and hexanes gave the title product as crystalline solid (from ethanol). Characterization data of the pure products is summarized in Table.

Preparation of Unsymmetrical N,N'-Diacylhydrazines (2j-l). A mixture of benzohydrazide (5 mmol) and *p*-subtituted benzohydrazide (5 mmol) in dry

acetonitrile (40-50 mL) was heated on steam bath and to the resulting solution (after cooling to room temperature) was added IBD (10 mmol, 3.22 g). After the nitrogen evolution ceased the reaction mixture was heated under reflux for 5 minutes and then cooled to room temperature. The crude product separated out of solution, was filtered and purified by recrystallization from ethanol.

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