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Hypervalent iodine in synthesis. Part 54:[†] One-step conversion of aryl aldehydes to aroyl azides using a combined reagent of (diacetoxyiodo)benzene with sodium azide

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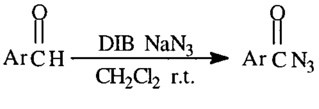
Abstract

Aroyl azides are readily prepared from the corresponding aryl aldehydes with the aid of (diacetoxyiodo)benzene (DIB) and sodium azide in high yields. © 2000 Elsevier Science Ltd. All rights reserved.

The versatile synthetic utility of hypervalent iodine reagents is of current interest. When the combined reagent of iodosylbenzene or [bis(acyloxy)iodo]benzene with trimethylsilyl azide or sodium azide is employed, an azido function is introduced to the substrate through a radical mechanism. Typical examples include the azidonation of olefins to α-azidoketones[1] and vincinal diazides,[1,2] β-dicarbonyl compounds to α-azido-β-dicarbonyl compounds,[3] 2-(trimethylsilyoxy)-furan to 5-azido-2(5H)-furanone,[4] silyl enol ethers to β-azido silyl enol ethers,[5] and *p*-alkylanisoles to arylalkyl azides.[6] These encouraging results, coupled with the susceptibility to homolytic rupture of aldehydic C–H bonds,[7] prompted us to examine the possibility of achieving direct oxidative azidonation of aldehydes to acyl azides using this methodology.

Our method is limited to the synthesis of thermally stable and isolable aroyl azides (Scheme 1), which are of substantial utility as precursors of isocyanates leading to other amine derivatives.[8]

Simple stirring of a mixture of an aryl aldehyde, DIB and NaN_3 in CH_2Cl_2 under a N_2 atmosphere at room temperature gave, after work-up and isolation, the desired aroyl azide free of


$$\mathrm{ArC(=O)H} \xrightarrow[\mathrm{CH_2Cl_2\ r.t.}]{\mathrm{DIB\ NaN_3}} \mathrm{ArC(=O)N_3}$$

Scheme 1.

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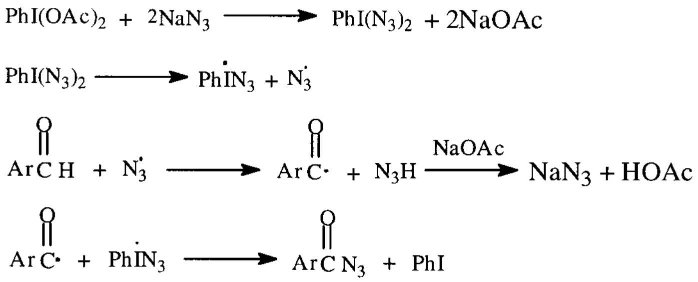
Curtius rearrangement product. The products were characterized by ^{1}H NMR, IR and m.p. which were consistent with literature data.[9,10]

The effect of substituents was observed by comparing the results with a strongly electron donating aryl group (entry 2, Table 1) and an electron withdrawing one (entry 8). The reaction is applicable to a variety of aryl substituents.

Table 1
Synthesis of aroyl azides ($ArCON_3$)[11]

entry	Ar	time(h)	m.p.(Lit[10] °C)	yield(%)
1	Ph	2	25-27(27)	87
2	*p*-MeO-Ph	2	68-71(70-71)	92
3	*p*-Me-Ph	2.5	32-34(35)	82
4	*p*-t-Bu-Ph	2.5	61-63(63-65)	78
5	*p*-Cl-Ph	3	42-43(43)	75
6	*p*-Br-Ph	3	46(47)	77
7	*m*-Br-Ph	3	oil	72
8	*p*-NO_2-Ph	6	64-66(65)	43

As depicted in Scheme 2, the mechanism of this conversion may involve [bis(azido)iodo]-benzene, which is formed by ligand exchange followed by homolytic decomposition to generate an azido radical.[6] The starting aldehyde is azidonated via a usual H-abstraction and coupling process.



Scheme 2.

Even though numerous procedures for the preparation of aroyl azides are available,[12–26] the majority involve the conversion of carboxylic acids to acid chlorides or anhydrides, which are then reacted with azide reagents.[12–18] In view of this, investigations in this field have been mainly concerned with the starting carbonyl compounds.[21–26] Herein, we provide a facile and efficient synthetic route to aroyl azides starting from aryl aldehydes. Having advantage over recent methods such as ease of manipulation, mild conditions and accessible starting materials, our approach serves as a practical alternative for the synthesis of aroyl azides.

References

1. (a) Zbiral, E.; Nestler, G. *Tetrahedron* **1970**, *26*, 2945; (b) Arimoto, M.; Yamaguchi, H.; Fujita, E.; Ochiai, M.; Nagao, Y. *Tetrahedron Lett*. **1987**, *28*, 6289.
2. Moriarty, R. M.; Khosrowshahi, J. S. *Tetrahedron Lett*. **1986**, *27*, 2809; Idem. *Synth. Commun*. **1987**, *17*, 89.
3. Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603.
4. Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Tuncay, A. *Tetrahedron Lett*. **1989**, *30*, 3019.
5. Magnus, P.; Lactor, J. *J. Am. Chem. Soc*. **1992**, *114*, 767.
6. Kita, Y.; Tohma, H.; Takada, T.; Mitoh, S.; Fjuita, S.; Gyoten, M. *Synlett* **1994**, 427.
7. Chryssostomos, C.; David, C.; Mistuo, K.; Ilhyong, R. *Chem. Rev*. **1999**, *99*, 1991, and references cited therein.
8. (a) Smith, P. A. S. *Organic Reactions*; Adams, R., Ed.; John Wiley & Sons, 1946; Vol. 3, 337. (b) L'Abbé, G. *Chem. Rev*. **1968**, *69*, 345. (c) Lwowski, W. *The Chemistry of the Azido Group*; Patai, S.; Ed.; Wiley-Interscience: New York, 1971; 503. (d) Scriven, E. F. V.; Turnbull, K. *Chem. Rev*. **1988**, *88*, 297.
9. Lieber, E.; Oftedahl, E. *J. Org. Chem*. **1959**, *24*, 1014.
10. Yukawa, Y.; Tsuno, Y. *J. Am. Chem. Soc*. **1957**, *79*, 5530.
11. In a typical procedure, benzaldehyde (1 mmol) was treated under a N_2 atmosphere with (diacetoxyiodo)benzene (1.5 mmol) and sodium azide (2.5 mmol) in CH_2Cl_2 at room temperature. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was washed with H_2O, dried with $MgSO_4$, concentrated in vacuo, and chromatographed on silica gel plate (petroleum ether:EtOAc = 8:1) to give benzoyl azide (128mg) as pale yellow solid (m.p. 25–27°C). ^{1}H NMR (60 MHz, CCl_4) δ: 7.15–8.25 (m, 5H), IR (KBr): 2180, 2140, 1700, 1602, 1455, 1240, 1180, 990, 700 cm^{-1}.
12. Wagner, R. B.; Zook, H. D. *Synthetic Organic Chemistry*; John Wiley & Sons: New York, 1953; 575.
13. Horning, D. E.; Muchowski, J. M. *Can. J. Chem*. **1967**, *45*, 1247.
14. Washburne, S. S.; Peterson, W. R. *Synth. Commun*. **1972**, *2*, 227.
15. Kricheldorf, H. R. *Synthesis* **1972**, 695.
16. Kricheldorf, H. R.; Leppert, E. *Synthesis* **1976**, 329.
17. Starks, Ch. M.; Liotaa, Ch. *Phase Transfer Catalysis*; Academic Press: New York, 1978; 156.
18. Prakash, G. K. S.; Iyer, P. S.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem*. **1983**, *48*, 3358.
19. Kaiser, C.; Weinstock, *J. Org. Syn*. **1971**, *51*, 48.
20. Van Reigendam, J. W.; Baardmam, F. *Synthesis* **1973**, 413.
21. Cremlyn, R. J. W. *Aust. J. Chem*. **1973**, *26*, 1591.
22. Lago, J. M.; Arrieta, A.; Palomo, C. *Synth. Commun*. **1983**, *13*, 289.
23. Kim, K.; Kim, Y. H. *Arch. Pharmacal. Res*. **1993**, *16*, 94.
24. Rawal, V. H.; Zhong, H. M. *Tetrahedron Lett*. **1994**, *35*, 4947.
25. Froeyen, P. *Phosphorus, Sulfur, Silicon Relat. Elem*. **1994**, *89*, 57.
26. Elmorsy, Saad S. *Tetrahedron Lett*. **1995**, *36*, 1341. Also see Ref. 8.