SHORT PAPER

J. Chem. Research (S), 2003, 700–701

Preparation of acyl azides from aromatic carboxylic acids using triphosgene in ionic liquids†

Weiliang Bao* and Qiang Wang

Zhejiang University, Xixi Campus, Department of Chemistry, Hangzhou, Zhejiang 310028, P. R. China

Acyl azides are obtained in high yields from aromatic carboxylic acids and sodium azide at room temperature in ionic liquids using triphosgene as a synthetic auxiliary under mild reaction conditions and with a short reaction time.

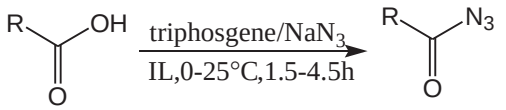
Keywords: acyl azides, carboxylic acids, triphosgene

One of the prime concerns of industry and academia is the search for replacements to environmentally damaging solvents which are used on a large scale. With a widely accessible temperature range, lack of vapor pressure and flammability, and moisture stability at room temperature, the application of ionic liquids has attracted attention over the last few years.[1,2] These liquids, particularly those based on 1, 3-dialkylimidazolium cations, have been found to be excellent solvents for a number of purposes.[3–7]

Acyl azides are valuable synthetic intermediates. They are useful for the preparation of isocyanates, urethanes, ureas, amines and other compounds. Acyl azides are usually prepared from acyl halides or anhydrides with sodium azide,[8-11] tetraalkylammonium or guanidinium azide[12] or tributylstannyl azide[13] and trimethylsilyl azide.[14-16] The combinations of chromic anhydride-trimethylsilyl azide[17] and triazidochlorosilane-active manganese dioxide[18] have been reported for the preparation of acyl azides from aldehydes. Subhas Bose *et al*. described a one-step conversion of aldehydes into the correspounding acyl azides by using Dess–Martin periodinane and sodium azide.[19] Recently, there have been some further reports on the preparation of acyl azides directly from carboxylic acids. These include the use of acid activators such as diphenylphosphoryl azide (DDPA),[20] 3,4,5-trifluorobenzeneboronic acid,[21] $SOCl_2$-DMF,[22] NCS-PPh_3 [23] and BTC.[24] However, most of these methods have some drawbacks. The transformation of the carboxylic acid into the corresponding acyl halide must be completed before sodium azide is added, and in most cases the reactions required a large volume of solvent and a long reaction time.

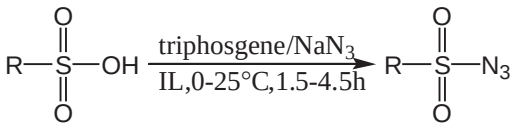
At room temperature, ionic liquids are entirely constituted of ions, and they are more powerful solvents to dissolve ionic substrates than conventional organic ones, and hence more suitable to carry the reactions employing ionic substrates.[25] In the recent years, triphosgene [bis(trichloromethyl) carbonate] has emerged as a versatile synthetic auxiliary for the synthesis of some important classes of organic compounds.[26] This white crystalline compound has proved to be safer and more useful in comparison with its gaseous congener, phosgene.

We now report the preparation of acyl azides from the carboxylic acids and sodium azide at room temperature in ionic liquids using triphosgene as a reagent under very mild reaction conditions. We chose $[emim]^+[BF_4]^-$ (1-ethyl-3-methylimidazolium tetrafluoroborate) as the reaction media and obtained high yield of acyl azides from carboxylic acids around 0–25°C (Scheme 1, Scheme 2). Compared with 24h long reaction time in acetone,[24] the rate of the reaction was faster, and most of the reactions were completed in less than 3h. The products were readily separated from the ionic liquids and the yields of aroyl azides were satisfactory. However, the



R=aryl, alkyl IL=$[emim]^+[BF_4]^-$

Scheme 1



R=*p*-CHC_6H_5 IL=$[emim]^+[BF_4]^-$

Scheme 2

yields of alkanoyl azides were not very high, possibly because they are thermally unstable [27](see Table 1).

Another merit of this reaction lies in the recycling of the solvent. We found that the ionic liquids almost could be quantitatively recovered by a simple procedure. After the product was extracted with ether, acetone was added to the lower layer, and the inorganic salts were filtered off. The filtrate was the recovered ionic liquid which can be reused. [25]

In summary, we have developed a new procedure for the preparation of the acyl azides directly from carboxylic acids with the aid of triphosgene. The ionic liquid, $[emim]^+BF_4^-$, is an excellent media for the above synthesis. Further studies of possible applications of the moisture stable room temperature ionic liquids in the synthesis of acyl derivatives are being actively pursued.

Exerimental

Reactions were carried out in a 25ml flask equipped with a magnetic stirrer with no special precaution in the fume cupboard. All the compounds were characterised by NMR, MS and physical constants and gave satisfactory results in comparison with authentic samples. Melting points are in good agreement with literature (Table 1).

General procedure: To a stirred solution of cinnamic acid (0.4g, 2.7mmol) in $[emim]^+BF_4^-$ (3 ml) was added triethylamine (0.5g, 4.9mmol) at 0°C. The reaction mixture was stirred at this temperature for 5 min and triphosgene (0.4g, 1.3mmol) was added at 0°C over 15 min. After adding sodium azide (0.35g, 5.4mmol), the reaction mixture was slowly allowed to warm up to room temperature and stirred for 2 h. The reaction mixture was extracted with ether (3×10ml). The ether layer was separated. The lower ionic liquid phase can be reused. The product was further purified by column chromatography (10:1, petroleum ether/ethyl acetate), yield: 87%.

Representative data: *Product* **11**: m.p: 82°C[24], ^{1}H NMR ($CDCl_3$/TMS): δ_H 6.46 (d, J = 16.0 Hz, 1H), 7.43–7.45(m, 3H), 7.56–7.58(m, 2H), 7.78(d, J = 16.0Hz, 1H). ^{13}C NMR δ 119.50, 128.97, 129.44, 131.51, 134.25, 147.12, 172.47. IR 1629, 1681, 2142, 3042cm^{-1}.

* To receive any correspondence. E-mail: wbao@hzcnc.hz.zj.cn

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Azides products and the yields

Entry	Substrate	Products	Time/h	Yield[a,b]/%	M.p./b.p./°C[c]
1	PhCOOH	$PhCON_3$	1.5	90	27 (27[28])
2	*p*-$CH_3PhCOOH$	*p*-CH_3PhCON_3	2	95	34–35 (35[28])
3	*p*-$CH_3OPhCOOH$	*p*-$CH_3OPhCON_3$	2	92	70 (70–71[28])
4	*p*-ClPhCOOH	*p*-$ClPhCON_3$	2	85	42 (43[28])
5	*p*-FPhCOOH	*p*-$FPhCON_3$	2.5	80	71/1.0mm (72[28])
6	*p*-$O_2NPhCOOH$	*p*-$O_2NPhCON_3$	3	78	66 (65[28])
7	3,5-$(O_2N)_2PhCOOH$	3,5-$(O_2N)_2PhCON_3$	3	70	104 (104–105[29])
8	*m*-$O_2NPhCOOH$	*m*-$O_2NPhCON_3$	2.5	76	67–68 (68[30])
9	*p*-CH_3PhSO_2OH	*p*-$CH_3PhSO_2N_3$	1.5	89	21–22 (22[31])
10	$PhCH_2COOH$	$PhCH_2CON_3$	2	85	87 (86–88[24])
11	PhCHCHCOOH	$PhCHCHCON_3$	2.5	87	82–83 (82–84[24])
12	$CH_3(CH_2)_5COOH$	$CH_3(CH_2)_5CON_3$	4.5	40	Oil(Oil[24])

[a]Isolated yield after chromatographic purification; [b]all the product characterised by b.p. m.p., elemental analyses, IR and NMR spectroscope; [c] number in parenthesis refers to literature.

Received 5 June 2003; accepted 25 June 2003
Paper 03/1957

References

1 T. Welton, *Chem. Rev*., 1999, **99**, 2071.
2 P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed*., 2000, **39**, 3772.
3 J.G. Hunddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser and R.D. Rogers, *Chem. Commun*., 1998, 1765.
4 T. Fischer, A. Sethi, T. Welton and J. Woolf, *Tetrahedron Lett.*, 1999, 793.
5 V.M. Kobryanskii and S.A. Arnautov, *Chem. Commun*., 1992, 727.
6 C.M. Gordon and A. McCluskey, *Chem. Commun*., 1999, 1431.
7 A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac and K.R. Seddon, *Org. Lett*., 1999, **1**, 997.
8 W. Lowoski, *Chemistry of the Azide Group*, S. Patai, Ed., New York, 1969, 503.
9 P.A.S. Smith, *Organic Reaction*, R. Adams, Ed., John Wiley and Sons, 1975, **3**, 337.
10 D.E. Horning and J.M. Muchowski, *Can. J. Chem.*, 1967, **45**, 1247.
11 R.B. Wagner and H.D. Zook, *Synthetic Organic Chemistry*, John Wiley, Ed., New York, 1953, 575.
12 C.M. Starks and C. Liotta, *Phase Transfer Catalysis*, Academic Press, New York, 1978, 156.
13 H.R. Kricheldorf and E. Leppert, *Synthesis*, 1976, 329.
14 S.S. Washburne and W.R. Peterson Jr, *Synth. Commun.*, 1972, **2**,227.
15 J.H. Macmillan and S.S. Washburne, *J. Org. Chem.*, 1973, 38, 2982.
16 H.R. Kricheldrof, *Synthesis*, 1972,695.
17 J.G. Lee and K.H. Kwak, *Tetrahedron Lett*., 1992, **33**, 3165.
18 S.S. Elmorsy, *Tetrahedron Lett*., 1995, **36**, 1341.
19 D. Subhas Bose and A.V. Narsimha Reddy, *Tetrahedron Lett*., 2003, **44**, 3543.
20 H. Shao, M. Colucci, S. Tong, H. Zhang and A.L. Castelhano, *Tetrahedron Lett*., 1998, **39**, 7235.
21 R.H. Tale and K.M. Patil, *Tetrahedron Lett.*, 2002**, 43**, 9715.
22 A. Arrieta, J.M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, 1984, **25**, 3365.
23 P. Froeyen, *Phosphorous, Sulfur Silicon Relat. Elem*., 1994, **89**, 57.
24 V.K. Gumaste, B.M. Bhawal and A.R.A.S. Deshmukh, *Tetrahedron Lett.*, 2002, **43** 1345.
25 Y.X. Li, W.L. Bao and Z.M. Wang, *Chin. Chem. Lett.*, 2003, **14**, 239.
26 L. Cotarca, P. Delogu, A. Nardelli and V. Sunjic, *Synthesis*, 1996, 553.
27 G.K. Surya Prakash, P.S. Iyer, M. Arvanaghi and G.A. Olah, *J. Org. Chem*., 1983, **48**, 3358.
28 Y. Yukana and Y. Tsuno, *J. Am. Chem. Soc.*, 1957, **79**, 5530.
29 J.M. Lago, A. Arrieta and C. Palomo, *Synth. Commun*., 1983, **13**, 289.
30 R. Mestres and C. Palomo, *Synthesis*, 1981, 218
31 J. Buckingham, *Dictionary of Organic compounds*, Mack Printing Company, United States of America, Easton, Pennsylvania, 5 Ed., 1982, **4**, 3750.