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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

HYPERVALENT IODINE IN SYNTHESIS. 65: A NEW ROUTE TO SYNTHESIZE N-ACYLBENZOTRIAZOLES VIA PALLADIUM CATALYZED CARBONYLATION OF BENZOTRIAZOLE AND HYPERVALENT IODONIUM SALTS IN THE PRESENCE OF CARBON MONOXIDE

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To cite this article: Li Wang & Zhen-Chu Chen (2001) HYPERVALENT IODINE IN SYNTHESIS. 65: A NEW ROUTE TO SYNTHESIZE N-ACYLBENZOTRIAZOLES VIA PALLADIUM CATALYZED CARBONYLATION OF BENZOTRIAZOLE AND HYPERVALENT IODONIUM SALTS IN THE PRESENCE OF CARBON MONOXIDE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:11, 1633-1637, DOI: <u>10.1081/SCC-100103981</u>

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ABSTRACT

N-acylbenzotriazoles are obtained directly in fair yields by palladium-catalyzed carbonylation of diaryliodonium salts with benzotriazoles in the presence of carbon monoxide.

As a synthetic auxiliary, benzotriazole offers many advantages. It is an inexpensive, stable compound, and can be easily removed at the end of the synthetic sequence, benzotriazole residue can be introduced into a molecule, and activate groups to which they are attached. So, the versatile applications of benzotriazole in organic chemistry has been explored and many papers

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have been published including some reviews.¹ N-acylbenzotriazoles are powerful acylation agents and have many applications in organic chemistry, such as in the anionic polymerization of lactants to obtain polymers² in the acetvlation of proteins,³ with trialkylaluminums to give ketones⁴ and in the acetone-sensitized photolysis to form a cyclopentadiene derivative.⁵ Several methods for N-acylbenzotriazoles are available. synthetic Most previous preparations of acylbenzotriazoles have utilized acid chlorides by reaction with 1-(trimethylsilyl)-benzotriazole,⁶ with 1-(tributylstannyl)benzotriazole⁷ or with 1-(hydroxymethyl)benzotriazole.⁸ However, the disadvantages of using acid chlorides are obvious. They are highly reactive and often result in undesired complications; many acid chlorides are unstable, difficult to prepare, and liquids with unpleasant odors. Recently, Katritzky et al., reported the directly reaction of carboxylic acids with N-acylbenzotriazoles.8 1-(methanesulfonyl)benzotriazole to form the However, to prepare the 1-(methanesulfonyl)benzotriazole requires several steps. In our attempts to find a method to avoid using acids chlorides for reaction at mild conditions, we focused our attention to palladium-catalyzed carbonylation of diaryliodonium salts with easily available benzotriazole. Recently, as a highly active electrophilic reagents, diaryliodonium salts have been used extensively in our lab.¹⁰ We now report palladium-catalyzed carbonylation of diaryliodonium and benzotriazole under one atmosphere pressure of carbon monoxide at room temperature which is shown in Scheme 1. The results are summarized in Scheme 1 and Table 1.

$$Ar_{2}I^{*}BF_{4}^{-} + \underbrace{Pd(OAc)_{2,} CO(1atm)}_{H} \underbrace{K_{2}CO_{3}, DMF, 50^{\circ}C}_{O}$$

Scheme 1.

To optimize the reaction conditions, a series of experiments have been carried out. Among the palladium catalysts $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$ tested, $Pd(OAc)_2$ is the best choices. The reaction was found to be general. Several diaryliodonium salts containing various substituents, such as methoxy, methyl and chloro groups were successfully reacted. The PhI(OH)OTs (entry 2) and $(PhCH = CH)I^+PhBF_4^-$ (entry 6) also reacted smoothly.

In conclusion, a new synthetic route to N-acylbenzotriazoles has been developed by the palladium-catalyzed carbonylation of diaryliodonium salts with the benzotriazole under one atmosphere pressure of carbon monoxide.

Entry	$Ar_2I^+BF_4^-$	Catalysts	Base	Product	Yield (%) ^b
1	$Ph_2I^+BF_4^-$	Pd(OAc) ₂	K ₂ CO ₃	1PhCOBt-1	66
2	PhI(OH)OTs	Pd(OAc) ₂	K ₂ CO ₃	1PhCOBt-1	60
3	$(p-CH_3C_6H_4)_2I^+BF_4^-$	$Pd(OAc)_2$	K_2CO_3	p-CH ₃ C ₆ H ₄ COBt-1	71
4	$(p-CH_3OC_6H_4)_2I^+BF_4^-$	$Pd(OAc)_2$	K_2CO_3	p-CH ₃ OC ₆ H ₄ COBt-1	75
5	$(p-ClC_{6}H_{4})_{2}I^{+}BF_{4}^{-}$	$Pd(OAc)_2$	K_2CO_3	p-ClC ₆ H ₄ COBt-1	60
6	$E-(PhCH = CH)I^+$	$Pd(OAc)_2$	K_2CO_3	E-(PhCH = CH)	62
	$PhBF_4^-$			COBt-1	

Table 1. N-Substituted Phenacyl Benzotriazoles^a

^a Reagent and conditions: 1 mmol iodonium salt, 2.5 mmol K_2CO_3 , 5 mol% Pd(OAc)₂ and 1 mmol benzotriazole, in 5 ml DMF at 80C under one atmosphere of carbon monoxide; ^b isolated yields.

EXPERIMENTAL

¹H-NMR spectra were recorded on a PMX-60 spectrometer, using CDCl₃ as the solvent with TMS as an internal standard. IR spectra were determined on a PE-683 Spectrophotometer. Melting Points are uncorrected.

General Procedure for Synthesis of N-Substituted Phenylacylbenzotriazoles

The benzotriazole (1 mmol) was added to a stirred solution of diaryliodonium tetrafluoroborate (1 mmol), Pd(OAc)₂ (11 mg, 5 mol%), $K_2CO_3(345 \text{ mg}, 2.5 \text{ mmol})$ and anhydrous DMF (10 mL) under one atmosphere of carbon monoxide at 50°C. The mixture was stirred at 50°C for 10 hours, evaporated in vacuo and then quenched in a saturated NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (2 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated in vacuo. The crude product was separated by preparative thin layer chromatography on silica gel with 1:5 ethyl acetate-hexane as eluent to afford the product, N-substituted phenylacylbenzotriazoles.

1-Benzoylbenzotriazole (Entry.1, 2) m.p. 111–113°C (lit.¹¹ 112–114°C) ¹H NMR 7.45–7.70 (m, 5H) 8.05–8.35 (m, 4H); IR.(KBr) 1702, 1643, 1289 cm⁻¹. 1-4'-methylbenzoylbenzotriazole (Entry.3) m.p. $115-116^{\circ}$ C (lit.¹¹ 114-116°C) ¹H-NMR 2.32 (s, 3H) 7.28-7.60 (m, 4H) 7.95-8.26 (m, 4H) I.R.(KBr) cm⁻¹ 1702, 1643, 1289 cm⁻¹.

1-4'-methyoxybenzoylbenzotriazole (Entry.4) m.p. 110–111°C (lit.¹¹ 108–110°C) ¹H-NMR 3.79 (s, 3H), 7.40–8.40(m, 8H), IR.(KBr) 1714, 1620, 1260 cm⁻¹.

1-4'-chlorobenzoylbenzotriazole (Entry.5) m.p. 119–120°C (lit.¹¹ 118–120°C) ¹H-NMR 7.45–7.70 (m, 4H), 8.10–8.42 (m, 4H); IR.(KBr) 1695, 1680, 1270 cm⁻¹.

1-Cinnamoylbenzotriazole (Entry.6) m.p. 158–160°C (lit.¹² 158–159°C) ¹H-NMR 7.23–7.80 (m, 9H), 8.12–8.45 (m, 2H); IR.(KBr) 1685, 1605, 1279 cm⁻¹.

ACKNOWLEDGMENT

We appreciate the financial support of the National Science Foundation of China (Project 29472036).

REFERENCES

- (a) Katritzky, A.R.; Rachwal, S.; Hitchings, G.J. Tetrahedron 1991, 47, 2683.
 (b) Katritzky, A.R. Bull. Soc. Chim. Belg. 1992, 101, 409.
 (c) Katritzky, A.R.; Lan, X. Chem. Soc. Rev. 1994, 363.
 (d) Katritzky, A.R.; Lan, X.; Fan, W.-Q. Synthesis 1994, 445.
 (e) Katritzky, A.R.; Lan X.; Yang, J.-Z.; Denisko, O.V. Chem. Rev. 1998, 98, 409.
- Reimschuessel, H. K.; Boardman, F. US Pat. 3,350,364 1967. Chem. Abstr. 1968, 68, 3357m.
- 3. Reboud-Ravaux, M.; Ghelis, C. Eur. J. Biochem. 1976, 65, 25.
- Tolstikov, G.A.; Valito, F. Kh.; Kuchin, A.V. Dokl. Akad. Nauk SSSR 1982, 265, 1406. Chem. Abstr. 1983, 98, 52710z.
- Tsujimoto, K.; Ohashi, M.; Yonezawa, T. Bull. Chem. Soc. Jpn. 1972, 45, 515.
- Gasparani, J.P.; Gassend, R.; Maire, J.C.; Elguero, J. J. Organomet. Chem. 1980, 188, 141.
- Gassend, R.; Marie, J.C.; Pommier, J.C. J. Organomet. Chem. 1977, 137, 185.
- 8. Gaylord, N.G. J. Am. Chem. Soc. 1954, 76, 285.

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- 9. Katritzky, A.R.; Shobana, N.; Pernak, J.; Afridi, A.S.; Fan, W.-Q. Tetrahedron **1992**, *48*, 7817.
- (a) Min, Xia; Chen, Z.-C. J. Chem. Res. (s) **1999**, *5*, 328. (b) Min, Xia; Chen, Z.-C. J. Chem. Res. (s) **1999**, *6*, 400. (c) Min, Xia; Chen, Z.-C. Synth. Commun. **1999**, *29*, 2457. (d) Min, Xia; Chen, Z.-C. Synth. Commun. **2000**, *30*, 63.
- 11. Yaoxian, Li; Fuan, Lin; Huamin, Huang. JiLin Daxue Ziran Kexue Xuebao **1991**, 103 (Ch).
- 12. Kreutzberger, A.; Dietz, E. Tetrahedron Lett. 1970, 14.

Received in Japan June 12, 2000

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