NJC

Synthesis of aryl esters using carboxylic acids, triarylphosphites, and N-iodosuccinimide

Journal:	*New Journal of Chemistry*
Manuscript ID	NJ-ART-09-2024-004215.R2
Article Type:	Paper
Date Submitted by the Author:	07-Dec-2024
Complete List of Authors:	Acharya, Sandhya; The University of Texas at San Antonio, Department of Chemistry Jha, Dhiraj; The University of Texas at San Antonio, Department of Chemistry Torres, Marc; The University of Texas at San Antonio, Department of Chemistry Chapa, Samantha; The University of Texas at San Antonio, Department of Chemistry Ravi, Anshuman; The University of Texas at San Antonio, Department of Chemistry Mathew, Rishi; The University of Texas at San Antonio, Department of Chemistry Zhao, John; The University of Texas at San Antonio, Department of Chemistry

ARTICLE

Synthesis of aryl esters using carboxylic acids, triarylphosphites, and *N*-iodosuccinimide

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

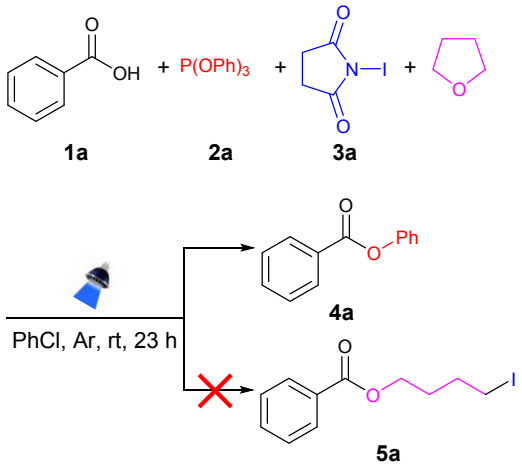
Sandhya Acharya,[a†] Dhiraj K. Jha,[a†] Marc Torres,[a] Samantha Chapa,[a] Anshuman Ravi,[a] Rishi Mathew[a] and John C. -G. Zhao[a]*

The direct synthesis of aryl esters from carboxylic acids has been achieved by using triarylphosphites and *N*-iodosuccinimide in chlorobenzene under neutral reaction conditions. This straight-forward green esterification method provides the desired aryl esters in good to high yields (42 to 99% yield) and a wide range of aromatic and aliphatic carboxylic acids can serve as substrates in this esterification reaction. For more acidic acids, the addition of DBU enhances the reaction yields. A radical mechanism, supported by the results of a radical trapping experiment and ^{31}P NMR studies, was proposed to explain the reaction outcome.

Introduction

Esters are vital synthetic intermediates and industrial materials, playing significant roles in the production of medicines, fragrances, and lubricants.[1] Moreover, ester moiety is also ubiquitous in natural products.[2] While alkyl esters can be easily synthesized directly from carboxylic acids and alcohols using the Fischer esterification protocol,[3] the direct synthesis of aryl esters from carboxylic acids and phenols is much more challenging. This difficulty arises from the fact that phenols are significantly less nucleophilic than alcohols.[4,5] As a result, Steglich esterification[1f,6] and Mitsunobu reaction[7] have been developed for the synthesis of aryl esters. Other reported methods for synthesizing aryl esters involve the use of acylating reagents,[4] special activating reagents,[4,8] or metal catalysis[9] to achieve the desired results. During our recent study on the visible-light-assisted ring-opening reaction of THF with benzoic acid (**1a**), mediated by *N*-iodosuccinimide (NIS, **3a**) and triphenylphosphine,[10] we observed an interesting outcome. Specifically, when triphenylphosphine was replaced by triphenylphosphite (**2a**), no desired ring-opening product **5a** was obtained. Instead, we isolated phenyl benzoate (**4a**) in a low yield from this reaction (Scheme 1).

Further control reactions confirmed that the formation of **4a** resulted from the reaction between **1a**, **2a**, and **3a** (data not shown). Moreover, light was not required for this reaction. It should be noted that phosphites have seldom been employed in the synthesis of aryl esters. To our knowledge, only Schwyzer and colleagues briefly reported the synthesis of aryl esters from carboxylic acids and triarylphosphites using pyridine as a solvent.[8i] Our current reaction offers a direct synthesis of aryl esters from readily available starting materials under neutral and metal-free conditions.



Scheme 1 Attempted ring-opening of THF with benzoic acid using triphenylphosphite and NIS.

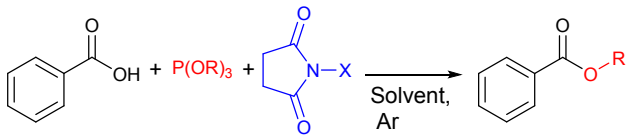
Results and discussion

We have chosen to optimize the reaction conditions further to enhance the yield of **4a**. The results of these optimizations are collected in Table 1. When 1.0 equiv. of **2a** and 1.0 equiv. of **3a** was used with **1a** in chlorobenzene (2.0 M), the desired phenyl benzoate (**4a**) was obtained in 69% yield after reacting at rt under argon for 20 hours (Table 1, entry 1). The yield of product **4a** was dramatically increased (to 90%) when the loading of **2a** was increased to 1.5 equiv. (entry 2). Nonetheless, further increasing the loading of **2a** to 2.0 equiv. failed to improve the product yield (entry 3). Similarly, using the optimal loading of **2a** (1.5 equiv.), variations in the amount of **3a**—whether increased or decreased—led to decreased yields of product **4a** (entries 4 and 5). Moreover, conducting the reaction under air also led to

[a] *Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0623; orcid.org/0000-0001-7174-5956; Email: cong.zhao@utsa.edu.*

† Both authors contribute equally.
Supplementary Information available: Detailed experimental procedures; compound characterization data and copy of NMR spectra. See DOI: 10.1039/x0xx00000x

Table 1 Optimization of the reaction conditions[a]



1a **2** **3** **4**

2a, **4a**: R = Ph; **3a**: X = I; **3b**: X = Br; **3c**: X = Cl

Entry	**2** (equiv.)	**3** (equiv.)	Solvent	T (°C)	Time (h)	Yield of **4** (%)[b]
1	**2a** (1.0)	**3a** (1.0)	PhCl	rt	20	**4a** (69)
2	**2a** (1.5)	**3a** (1.0)	PhCl	rt	20	**4a** (90)
3	**2a** (2.0)	**3a** (1.0)	PhCl	rt	20	**4a** (66)
4	**2a** (1.5)	**3a** (1.5)	PhCl	rt	20	**4a** (12)
5	**2a** (1.5)	**3a** (0.5)	PhCl	rt	20	**4a** (37)
6[c]	**2a** (1.5)	**3a** (1.0)	PhCl	rt	20	**4a** (64)
7[d]	**2a** (1.5)	**3a** (1.0)	PhCl	rt	20	**4a** (78)
8[e]	**2a** (1.5)	**3a** (1.0)	PhCl	rt	20	**4a** (44)
9	**2a** (1.5)	**3a** (1.0)	$PhCF_3$	rt	20	**4a** (88)
10	**2a** (1.5)	**2a** (1.0)	Toluene	rt	20	**4a** (40)
11	**2a** (1.5)	**3a** (1.0)	CH_2Cl_2	rt	20	**4a** (54)
12	**2a** (1.5)	**3a** (1.0)	Acetone	rt	20	**4a** (24)
13	**2a** (1.5)	**3a** (1.0)	DMF	rt	20	**4a** (17)
14	**2a** (1.5)	**3a** (1.0)	THF	rt	20	**4a** (38)
15	**2a** (1.5)	**3a** (1.0)	1,4-Dioxane	rt	20	**4a** (63)
16	**2a** (1.5)	**3a** (1.0)	MeOH	rt	20	**4a** (24)
17	**2a** (1.5)	**3a** (1.0)	PhCl	40	6	**4a** (92)
18	**2a** (1.5)	**3a** (1.0)	PhCl	60	6	**4a** (99)
19	**2a** (1.5)	**3b** (1.0)	PhCl	60	6	**4a** (65)
20	**2a** (1.5)	**3c** (1.0)	PhCl	60	6	**4a** (0)

[a]Reaction conditions: benzoic acid (**1a**, 1.0 mmol), phosphite (**2**, 1.5 mmol), and *N*-halosuccinimide (**3**, 1.0 mmol), under argon in chlorobenzene (0.50 mL). [b]Yield of the isolated product after column chromatography. [c]The reaction was conducted under air. [d]The reaction was conducted in 0.10 mL of chlorobenzene. [e]The reaction was conducted in 2.0 mL of chlorobenzene.

a lower product yield (64% vs. 90%, entry 6 vs. entry 2). The reactant concentration was also found to impact the product yield: with both higher (10.0 M) or lower (0.5 M) concentrations of **1a** resulted in decreased yields of **4a** (entries 7 and 8). Next, various organic solvents were screened for this reaction. It was observed that, except for trifluorotoluene, which yielded slightly lower amounts of **4a** (88%, entry 9) compared to chlorobenzene, all other chlorinated or non-chlorinated solvents resulted in poor product yields (entries 10-16). Finally, the reaction temperature was investigated, revealing that the reaction proceeded much faster at 40 °C and 60 °C (entries 17 and 18). The highest yield of **4a** (99%, entry 18) was achieved at 60 °C after just 6 hours of reaction time. Nonetheless, the use of *N*-bromosuccinimide (**3b**) instead of **3a** under the optimized conditions led to a lower product yield (65%, entry 19). Moreover, using *N*-chlorosuccinimide (**3c**) instead of **3a** gave no formation of **4a** at all (entry 20). Thus, the conditions described in entry 18 were identified as the optimal ones for this esterification reaction.

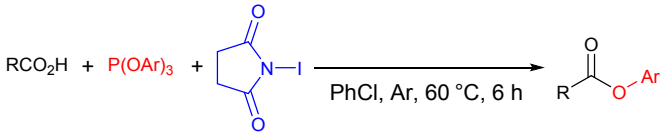
Once the reaction conditions were optimized, the scope of this reaction was established. As shown in Table 2, besides benzoic acid, benzoic acids with an electron-donating group or a mildly electron-withdrawing group in the para-position of the benzene ring also yield the desired phenyl esters in good to high yields (**4b** to **4h**). However, benzoic acids with a strong electron-withdrawing group, such as the cyano and nitro groups, in the *para*-position of the benzene ring failed to react under the optimized reaction conditions. After some fine tunings, the desired phenyl ester products (**4i** and **4j**) could be obtained in low to moderate yields by conducting the reaction in the presence of 2.0 equiv. of DBU at rt for 16 h. High yield of the corresponding phenyl esters could also be obtained from 3-methoxybenzoic acid (**4k**) and 2-naphthoic acid (**4l**). However, the more acidic nicotinic acid also requires DBU to yield the corresponding phenyl ester **4m** (in 63% yield). In contrast, no desired product could be obtained from coumalic acid or *N*-Boc-proline, even in the presence of DBU. Nevertheless, *N*-CBZ-proline produced the expected phenyl ester **4p** in 61% yield in the presence of DBU, suggesting that coumalic acid or *N*-Boc-proline do not work well because they are not compatible with the reaction conditions. In addition to aromatic acids, aliphatic carboxylic acids are also good substrates for this reaction. As the results in Table 2 show, the corresponding phenyl esters of aliphatic carboxylic acids with a primary, a secondary, or even a tertiary substituent were obtained in high yields (**4q**-**4u**). Moreover, the phenyl esters of 3-bromopropionic acid (**4v**), cinnamic acid (**4w**), and α-tocopheryl succinate (**4x**) were also obtained in moderate to high yields, showing this esterification reaction has a good functional group tolerance. In addition to triphenylphosphite, other triarylphosphites can also be applied in this reaction to produce the corresponding aryl esters. For examples, 4-methylphenyl, 4-*tert*-butylphenyl, and 4-methoxyphenyl benzoates (**4y**, **4z**, and **4aa**) were obtained in good to excellent yields. Lower yields of 4-iodophenyl, 4-nitrophenyl, and 2,5-dimethylphenyl benzoates (**4ab**, **4ac**, and **4ad**) were also obtained. These could be attributed to either the electronic effects (**4ab** and **4ac**) or the steric effects of the substituents (**4ad**). However, the yield of **4ac** could be improved to 76% by conducting the reaction in the presence of DBU. Moreover, a high yield of [1,1'-biphenyl]-4-yl benzoate (**4ae**) was obtained from the reaction of benzoic acid and tri([1,1'-biphenyl]-4-yl)phosphite. Finally, to demonstrate the synthetic utility of the current method, a gram-scale reaction was conducted with the model acid **2a**, and a high yield of 94% was obtained (For details, please see the Supporting Information).

On the other hand, instead of triarylphosphites**,** using trialkylphosphites, such as triethylphosphite, tribenzylphosphite, and triisopropylphosphite, and mixed phosphites, such as diethylphenylphosphite and diethyl(4-methylphenyl)phosphite, together with benzoic acid under the optimized conditions did not yield the corresponding alkyl or aryl benzoates at all (data not shown). In the case of trialkylphosphite, there was no reaction. In the case of the mixed phosphites, only low yields of benzoic anhydride were obtained, suggesting that the reaction went through a polar mechanism instead.

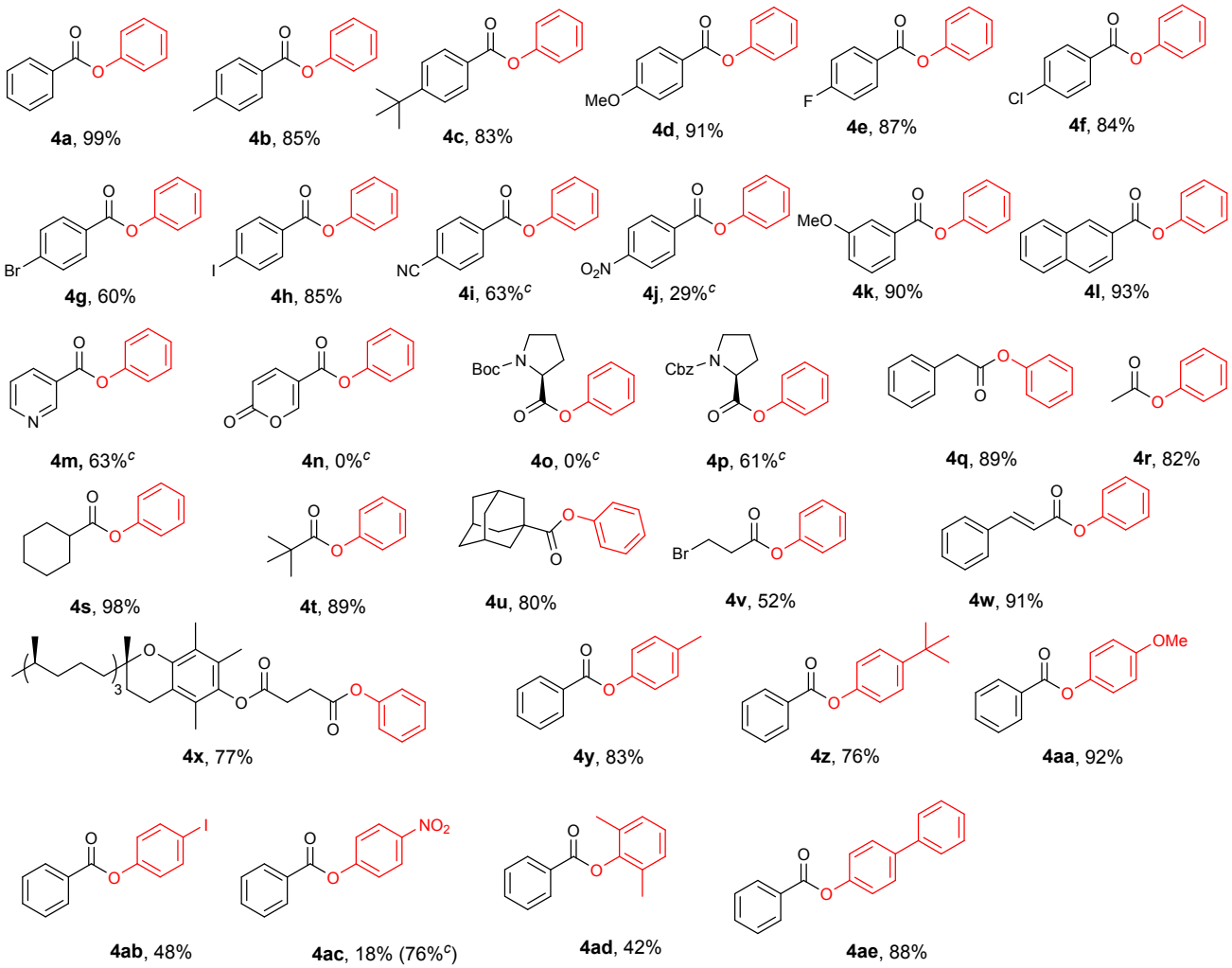
We noticed that the reaction gave a lower yield under air (Table 1, entry 6) than under argon (Table 1, entry 2), suggesting a possible radical mechanism for this reaction, which is

ARTICLE

Table 2 Substrate scope of the aryl esterification reaction[a,b]



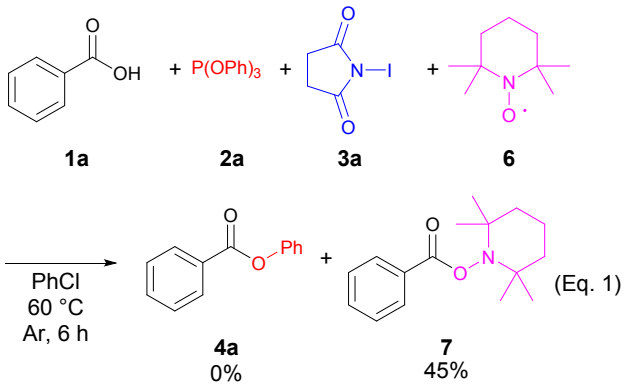
1 **2** **3a** **4**



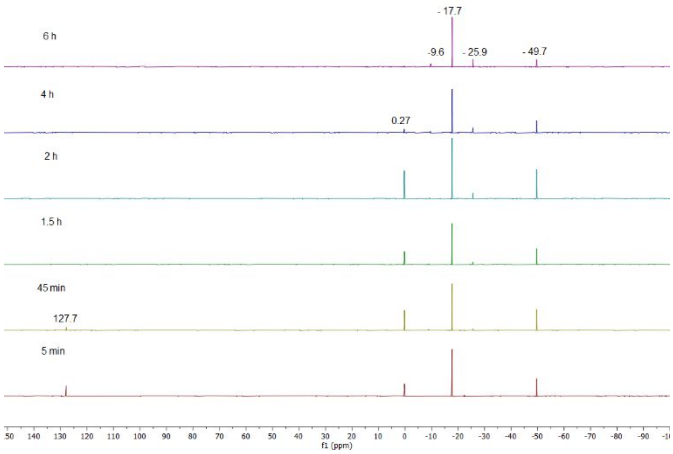
[a]Reaction conditions: carboxylic acid **1** (1.0 mmol), triarylphosphite **2** (1.5 mmol), and NIS (**3a**, 1.0 mmol) under argon in chlorobenzene (0.5 mL) at 60 °C for 6 h. [b]Yield of the isolated product after column chromatography. [c]The reaction was conducted in the presence of DBU (2.0 mmol) at room temperature for 16 h.

completely different from the polar reaction reported by Schwyzer.[8i] To further elucidate the reaction mechanism, a radical inhibition experiment was conducted using TEMPO (**6**) as the radical inhibitor. As the results in Eq. 1 show, in the presence of **6** (2.0 equiv.), no formation of the desired **4a** was observed under the optimized conditions. Instead, product **7**

was obtained in 45% yield. This trapping result supports the involvement of benzoyl radical in this reaction.



To gain further insight into the reaction mechanism, the progress of the model reaction was monitored by ^{31}P NMR (Scheme 2). It is not surprising to find that the peak for triphenylphosphite (δ 127.7 PPM)[11] quickly diminished and disappeared completely after 1.5 hours of reaction. Three new peaks appeared in the ^{31}P NMR spectrum: at δ 0.27 PPM, -17.7 PPM, and -49.7 PPM, respectively, from the beginning of the reaction. The intensity of the peak at 0.27 PPM initially increased and then decreased as the reaction progressed, disappearing completely by the end of the reaction. The peak at -49.7 PPM followed a similar trend but persisted until the end of the reaction. In contrast, the peak at -17.7 PPM remained relatively constant throughout the reaction. Additionally, two minor peaks emerged gradually during the reaction: the peak at δ -25.9 PPM began appearing after 1.5 hours, and the peak at δ -9.6 PPM started to appear after 4 hours. Both peaks became more pronounced as the reaction continued.



Scheme 2 ^{31}PNMR Study of the esterification reaction.

The peak at -17.7 PPM was identified as triphenyl phosphate (compound **12** in Scheme 3) based on the ^{31}P chemical shift of an authentic sample isolated from the reaction mixture. The peak at -49.7 PPM most likely corresponds to diphenyl phosphoriodidate (compound **10** in Scheme 3), which has a reported ^{31}P chemical shift of -47.0 PPM.[12] The minor peak at -9.6 PPM was attributed to diphenyl phosphate (compound **11** in Scheme 3), which was verified by the fact that an authentic sample of **11** added to the reaction mixture enhanced the intensity of this peak. [13] Moreover, compound **11** could also be isolated from the reaction mixture. While we are not certain about the species corresponding to the peak at -25.9 PPM, we believe it is not the intermediate responsible for the formation of the ester product, as it appears in the later stage of the reaction and persists until the end. In contrast, the species with a ^{31}P chemical shift of 0.27 PPM is most likely responsible for the formation of the ester product. To find out whether this peak belongs to the iodosuccinimidotriphenoxyphosphorane **8** or the benzoyloxyiodotriphenoxyphosphorane intermediate **9** (Scheme 3), we conducted the esterification reaction using iodine instead of NIS and monitored the reaction the progress with ^{31}P NMR (For details, please see the Supporting Information). It turned out that the presumed intermediate **9** has a very similar ^{31}P NMR chemical shift as **8**, thus, the peak at 0.27 PPM can be either intermediate **8** or **9**. Our experiments also show that both of these intermediates do lead to the formation of the expected product.

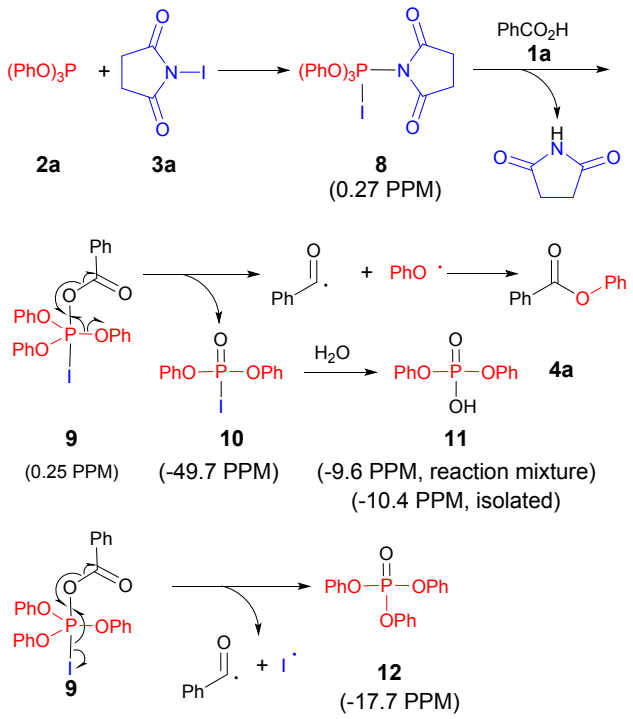
Based on the results of the trapping experiment and the ^{31}P NMR study, the following mechanism is proposed to explain this esterification reaction. As shown in Scheme 3, triphenylphosphite (**2a**) reacts with NIS (**3a**) to yield the iodosuccinimidotriphenoxyphosphorane intermediate (**8**). The reaction of intermediate **8** with benzoic acid (**1a**) produces intermediate **9**.[14] The homolytic cleavage of intermediate **9** generates a benzoyl radical, a phenoxy radical, and diphenyl phosphoriodidate (**10**). The recombination of the benzoyl radical and the phenoxy radical yields the expected product **4a**. The hydrolysis of diphenyl phosphoriodidate (**10**) (slow under the reaction conditions, but fast during column chromatography) generates diphenyl phosphate (**11**). Alternatively, intermediate **9** can cleave into benzoyl and iodo radicals, yielding the observed side product triphenyl phosphate (**12**, Scheme 3, bottom equation).

The proposed mechanism can explain why more acidic acids are less reactive in this reaction: the second step involves a nucleophilic addition of the acid to phosphorane intermediate **8**. More acidic acids are less nucleophilic and the reaction gets slower; However, their nucleophilicity can be increased by deprotonation with a base such as DBU. Additionally, the proposed mechanism can explain why the formation of **4ad** is more difficult than that of **4a**: the 4-nitrophenoxy radical is less stable than the phenoxy radical, causing the homolytic cleavage much more difficult.

Conclusions

In summary, we developed a direct synthesis of aryl esters from carboxylic acids using triarylphosphites and *N*-iodosuccinimide in chlorobenzene under mild reaction conditions. The desired aryl esters were obtained in good to high yields, with yields reaching up to 99%. The addition of 2.0 equivalent of DBU is

necessary to achieve good yields when using more acidic acids or triarylphosphites with strong electron-withdrawing groups.



Scheme 3 Proposed mechanism of the esterification reaction (^{31}P chemical shifts are included in parentheses).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data underlying this study are available in the published article and its Supporting Information.

Acknowledgements

The authors thank the UTSA Mass Spectrometry & Proteomics Core Facility and Dr. Wendell Griffith for help with the HRMS analysis and National Science Foundation (CHE 2117691) for the TOF instrument.

References

1 (a) M. Sedighi and M. A. Lipton, A Convenient, General Synthesis of 1,1-Dimethylallyl Esters as Protecting Groups for Carboxylic Acids, *Org. Lett.,* 2005, **7**, 1473-1475. (b) M. Zabadal, A. P. Pelliccioli, P. Klán and J. Wirz, 2,5-Dimethylphenacyl Esters: A Photoremovable Protecting Group for Carboxylic Acids, *J. Phys. Chem. A,* 2001, **105**, 10329-10333. (c) S. Rayne and K. Forest, Carboxylic acid ester hydrolysis rate constants for food and beverage aroma compounds, *Flavour Fragr. J.,* 2016**,** ***31***, 385-394. (d) I. Bassanini, K. Hult and S. Riva, Dicarboxylic esters: Useful tools for the biocatalyzed synthesis of hybrid compounds and polymers, *Beilstein J. Org. Chem.,* 2015, **11**, 1583-1595. (e) J.-W. Lee and C. T. Trinh, Towards renewable flavors, fragrances, and beyond, *Curr. Opin. Biotechnol.,* 2020, **61**, 168-180.. (f) A. Jordan, K. D. Whymark, J. Sydenham and H. F. Sneddon, A solvent-reagent selection guide for Steglich-type esterification of carboxylic acids, *Green Chem.,* 2021, **23**, 6405-6413.

2 M. Tsakos, E. S. Schaffert, L. L. Clement, N. L. Villadsen and T. B. Poulsen, Ester coupling reactions – an enduring challenge in the chemical synthesis of bioactive natural products, *Nat. Prod. Rep.* 2015, **32**, 605-632.

3 E. Fischer and A. Speier, Darstellung der Ester, *Ber. Dtsch. Chem. Ges,* 1895, **28**, 3252-3258.

4 For a summary, see: Z. Zhang, Z. Zhao, M. Liu, H. Liu, Q. Li, J. Xiang, T. Wu and B. Han, Acylation of phenols to phenolic esters with organic salts, *Green Chem.,* 2022, **24**, 9763-9771.

5 W. W. Lawrence, Boric acid-catalyzed esterification of phenols, *Tetrahedron Lett.,* 1971, **12**, 3453-3454.

6 B. Neises and W. Steglich, Simple Method for the Esterification of Carboxylic Acids, *Angew. Chem. Int. Ed. Eng.,* 1978, **17**, 522-524.

7 (a) V. P. Fitzjarrald and R. Pongdee, A convenient procedure for the esterification of benzoic acids with phenols: a new application for the Mitsunobu reaction, *Tetrahedron Lett.,* 2007, **48**, 3553-3557. (b) N. Iranpoor, H. Firouzabadi, D. Khalili and S. Motevalli, Easily Prepared Azopyridines As Potent and Recyclable Reagents for Facile Esterification Reactions. An Efficient Modified Mitsunobu Reaction, *J. Org. Chem.,* 2008, **73**, 4882-4887.

8 (a) J. S. Ruso, N. Rajendiran and R. S. Kumaran, Metal-free synthesis of aryl esters by coupling aryl carboxylic acids and aryl boronic acids, *Tetrahedron Lett.,* 2014, **55**, 2345-2347. (b) K. S. Keshavamurthy, Y. D. Vankar and D. N. Dhar, Preparation of Acid Anhydrides, Amides, and Esters Using Chlorosulfonyl Isocyanate as a Dehydrating Agent, *Synthesis,* 1982, 506-508. (c) M. Ueda and H. Oikawa, 1,2-Benzisoxazol-3-yl diphenyl phosphate: a new, reactive activating agent for the synthesis of amides, esters, and peptides via condensation, *J. Org. Chem.,* 1985, **50**, 760-763. (d) M. Ueda and H. Mori, Diphenyl (2,3-Dihydro-2-thioxo-3-benzoxazolyl)phosphonate: A New, Reactive Condensing Agent for the Synthesis of Amides, Esters, Peptides, and β-Lactams via Condensation, *Bull. Chem. Soc. Jpn.,* 2006, **65**, 1636-1641. (e) H. Eshghi, M. Rafei and M. H. Karimi, P_2O_5/SiO_2 as an Efficient Reagent for Esterification of Phenols in Dry Media, *Synth. Commun.,* 2001, **31**, 771-774. (f) J.-E. Won, H.-K. Kim, J.-J. Kim, H.-S. Yim, M.-J. Kim, S.-B. Kang, H.-A. Chung, S.-G. Lee, Y.-J. Yoon, Effective esterification of carboxylic acids using (6-oxo-6H-pyridazin-1-yl)phosphoric acid diethyl ester as novel coupling agents, *Tetrahedron,* 2007, **63**, 12720-12730. (g) T. B. Petersen, R. Khan and B. Olofsson, Metal-Free Synthesis of Aryl Esters from Carboxylic Acids and Diaryliodonium Salts, *Org. Lett.,* 2011, **13**, 3462-3465. (h) W. Phakhodee, C. Duangkamol and M. Pattarawarapan, Ph_3P-I_2 mediated aryl esterification with a mechanistic insight. *Tetrahedron Lett.,* 2016, **57**, 2087-2089. (i) B. Iselin, W. Rittel, P. Sieber and R. Schwyzer, Neue Methoden zur Herstellung von Carbonsäure-arylestern. Über aktivierte Ester VIII, *Helv. Chim. Acta,* 1957, **40**, 373-387.

9 (a) F. Luo, C. Pan, P. Qian and J. Cheng, Copper-Catalyzed Sequential Alkyl/Aryl or Vinyl Esterification of Dicarboxylic Acid Anhydrides with Alkoxysilanes, *J. Org. Chem.,* 2010, **75**, 5379-5381. (b) F. Luo, C. Pan, P. Qian and J. Cheng, Copper(II)-Catalyzed Esterification of Arenecarboxylic Acids with Aryl- and Vinyl-Substituted Trimethoxysilanes, *Synthesis,* 2010, 2005-2010. (c) D.-L. Zhu, H.-X. Li, Z.-M. Xu, H.-Y. Li, D. J. Young and J.-P. Lang, Visible light driven, nickel-catalyzed aryl esterification using a triplet photosensitiser thioxanthen-9-one, *Org. Chem. Front*., 2019, **6**, 2353-2359.

10 D. K. Jha, S. Acharya, N. Sakkani, S. Chapa, A. Guerra and J. C. G. Zhao, Visible Light-Assisted Ring-Opening of Cyclic Ethers with Carboxylic Acids Mediated by Triphenylphosphine and N-Halosuccinimides, *Org. Lett.,* 2024, **26**, 172-177.
11 Triphenylphosphite has a reported ^{31}P chemical shift of 128.2 PPM, see: C. K. Tseng, Reinvestigation of dihalotriphenoxyphosphoranes, *J. Org. Chem.,* 1979, **44**, 2793-2795.
12 K. M. Armstrong and P. Kilian, Catalytic Synthesis of Triaryl Phosphates from White Phosphorus, *Eur. J. Inorg. Chem.,* 2011, 2138-2147.
13 Diphenyl phosphate has reported ^{31}P chemical shift of -9.83 PPM, see: I. E. Nifant'eva, A. N. Tavtorkina, S. A. Korchaginaa, I. F. Gavrilenko, N. N. Glebova, N. N. Kostitsyna, V. A. Yakovlev, G. N. Bondarenko and M. P. Filatova, Neodymium tris-diarylphosphates: Systematic study of the structure–reactivity relationship in butadiene and isoprene polymerisation, *Appl. Catal. A: Gen.,* 2014, **478**, 219-227. Our isolated sample of diphenyl phosphate has a ^{31}P chemical shift of -10.4 PPM.
14 For a related reaction, see Ref. 8h.

Data availability statement:

The data underlying this study are available in the published article and its Supporting Information.