ORGANOMETALLICS

Investigation into the Organobismuth Dismutation and Its Use for Rational Synthesis of Heteroleptic Triarylbismuthanes, Ar¹₂Ar²Bi

Thomas Louis-Goff, Arnold L. Rheingold, and Jakub Hyvl*

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ABSTRACT: Organobismuthanes undergo dismutation, a substituent scrambling process, complicating the synthesis of unsymmetrically trisubstituted bismuthanes of the general formula $Ar^{1}_{2}Ar^{2}Bi$. Although the dismutation is a mechanistically diverse phenomenon, at ambient or lower temperatures, dismutation is triggered mainly by an electrophilic bismuth source. Therefore, the selection of the electrophile, $Ar^{1}_{2}BiX$ (X = tosylate or iodide if Ar^{1} = mesityl) or $Ar^{1}BiX_{2}$ (X = tosylate), and its use in low concentration during the reaction is key to suppressing the dismutation, leading to new, streamlined protocols utilizing direct arylations of $Ar^{1}_{2}BiX$ (X = OTs or I) or $Ar^{1}Bi(OTs)_{2}$ with organozincs affording heteroleptic triarylbismuthanes $Ar^{1}_{2}Ar^{2}Bi$.



T he growing interest in organobismuth chemistry is driven by applications in synthetic chemistry,¹⁻⁴ catalysis,⁵⁻⁷ medicinal chemistry,⁸ and material science⁹ without the toxicity and environmental risks¹⁰ typically associated with its

toxicity and environmental risks⁻¹ typically associated with its heavy-atom congeners. Despite its potential, organobismuth chemistry is far less developed in comparison with other maingroup organometallic chemistry due to two obstacles. First, the C–Bi bond is weak (bond dissociation energy (BDE) = 46 kcal/mol¹¹), making it prone to homolytic cleavage. Second, dismutation, a substituent scrambling process first reported by Challenger¹² and further studied by Gilman, revealed that tri(*p*-tolyl)bismuthane exchanged substituents with *n*-butyllithium (eq 1).¹³ This complicates a selective synthesis of unsymmetrical organobismuthanes of general formula $Ar_2^1Ar^2Bi$ $(Ar^1 \neq Ar^2).^{14}$

$$(p-\text{Tol})_3\text{Bi} + 3n-\text{BuLi} \rightarrow 3p-\text{TolLi} + (n-\text{Bu})_3\text{Bi}$$
 (1)

In 1967, Wittig observed the same exchange process for all triaryl pnictogens, except nitrogen, and proposed a mechanism involving an ate-complex.¹⁵ This ate-complex was suggested to be an intermediate responsible for the formation of side product, PhBi(n-Bu)₂, in addition to the main product, Ph₂Bi(n-Bu), generated from reaction of Ph₂BiCl and n-BuLi (eq 2).¹⁶

$$Ph_{2}Bi - R \xleftarrow{+R - Li}_{ate-complex} [Ph_{2}BiR_{2}]^{-}Li^{+} \xleftarrow{-Ph - Li}_{ate-complex} Ph - BiR_{2}$$
(2)

Furthermore, Barton observed that the unsymmetrical triarylbismuthanes $Ar_2^1Ar^2Bi$, where $Ar^1 \neq Ar^2$, are also prone to dismutation (eq 3).¹⁷ On the basis of this report, unsymmetrical triarylbismuthanes were viewed as an unstable and elusive species.

$$Ar_{2}^{1}Ar^{2}Bi \rightleftharpoons Ar^{1}Ar_{2}^{2}Bi \rightleftharpoons Ar_{3}^{1}Bi^{+}Ar_{3}^{2}Bi$$
(3)

Besides the ate-complex-promoted mechanism of dismutation, other mechanistic modes have been proposed. For the monoaryldialkylbismuthanes, a light-induced dismutation was observed,¹⁸ suggestive of a radical mechanism, and in the presence of bismuth trihalides an electrophilic mode likely operates.¹⁷ Moreover, other factors are also involved; for example, steric congestion around the bismuth center can suppress the dismutation process completely.¹⁹ This investigation focuses on comparison of the ate-complex-promoted and the electrophilic modes of dismutation, how to suppress them, and then uses the information to optimize Bi-C bond formation leading to an efficient and streamlined synthesis of electronically diverse unsymmetrical organobismuthanes $Ar_2^1Ar^2Bi$ (1). These compounds (1) can now be prepared through a simple two-step procedure that is no longer limited by reagent scope²⁰ or multistep processes.²¹

First, a systematic study of the effect of the type of nucleophile and electrophile on the formation of the unsymmetrical bismuthane 1 ($Ar_2^1Ar^2Bi$) and the related dismutated products ($Ar_2^2Ar^1Bi$, Ar_3^1Bi , and Ar_3^2Bi) was investigated. Our reaction of choice utilized diphenylbismuth halide or tosylate, Ph₂BiX, as the electrophilic source and an organometallic nucleophile prepared from 4-bromobenzalde-hyde dimethyl acetal affording easily separable diphenyl-

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(dimethoxymethylphenyl)bismuthane (1a) from the main dismutated side product, triphenylbismuthane (Ph_3Bi). The ratio of products served as a measure of the dismutation process (Scheme 1). Another advantage of this system is the

Scheme 1. A Model Reaction^a



M = MgBr, Li, $CuC_6H_4CH(OCH_3)_2$, CuCN, ZnCl X = Cl, I, OTs

 a A model reaction for testing various nucleophiles and electrophiles in Bi–C bond-forming reactions.

relatively similar electronic properties of these two aryl groups $(Ar^1 = Ph \text{ and } Ar^2 = C_6H_4CH(OCH_3)_2)$, limiting the electronic influence on Bi–C bond formation process.

Dismutation was evaluated by varying the nucleophilic sources (Table 1, entries 1-6) from hard nucleophiles,

Table 1. Isolated Yields^a

entry	reagent	Ph_2BiX	1a	$BiPh_3$
1	ArMgBr	Ph ₂ BiCl	30%	30%
2	ArLi	Ph ₂ BiCl	40%	9%
3	[Ar ₂ Cu]MgX	Ph ₂ BiCl	64%	4%
4	[Ar ₂ Cu]Li	Ph ₂ BiCl	59%	7%
5	[ArCuCN]MgX	Ph ₂ BiCl	19%	23%
6	ArZnX	Ph ₂ BiCl	74%	12%
7	ArMgBr	Ph ₂ BiI	25%	15%
8	ArLi	Ph ₂ BiI	4%	13%
9	[Ar ₂ Cu]MgX	Ph ₂ BiI	32%	14%
10	[Ar ₂ Cu]Li	Ph ₂ BiI	64%	17%
11	ArZnX	Ph ₂ BiI	74%	7%
12	ArMgBr	Ph ₂ BiOTs	92%	<1%
13	ArLi	Ph ₂ BiOTs	21%	15%
14	[Ar ₂ Cu]MgX	Ph ₂ BiOTs	95%	1%
15	[Ar ₂ Cu]Li	Ph ₂ BiOTs	40%	4%
16	ArZnX	Ph ₂ BiOTs	94%	0%

^{*a*}Isolated yields of triarylbismuthane 1a and Ph₃Bi from the model reaction in Scheme 1. Typical reaction conditions: THF, -10 °C, 1 h 40 min. For more details please see the Supporting Information.

operating often through a single electron transfer mechanism to soft nucleophiles operating by an ionic mechanism.²² All the nucleophiles were compared to a single electrophile, diphenylbismuth chloride, Ph_2BiCl . Grignard reagents (entry 1) showed a rather poor yield of the product **1a** (30%) accompanied by a relatively high amount of the Ph_3Bi (30%). Organolithiums (entry 2) only slightly increased the yield of **1a** to 40% while significantly decreasing the amount of Ph_3Bi to 9%. Organocuprates (entries 3–5), prepared from a Grignard reagent (entry 3) or an organolithium (entry 4), showed improved yields of **1a** 64% and 59% and decreased the formation of the triphenylbismuthane to 4% and 7%, respectively. Surprisingly, the cyanocuprate formed from the Grignard reagent (entry 5) showed a poor yield of 1a (19%), and increased the amount of triphenylbismuthane (23%). The highest yield was achieved with an organozinc (entry 6), affording 1a in 74% yield with a somewhat elevated amount of the Ph_3Bi (12%). In entries 7–16, we varied the electrophile. In comparison with diphenylbismuth chloride, diphenylbismuth iodide (entries 7-11) showed a somewhat similar trend, with the best result achieved by the organozinc nucleophile (entry 11) reaching the same yield of 1a (74%) as with Ph₂BiCl, reducing formation of triphenylbismuth to 7%. The best-performing electrophile turned out to be diphenylbismuth tosylate, Ph₂BiOTs (2a), which afforded poor and moderate vields with organolithium (entry 13) and lithium diorganocuprates (entry 15), respectively, but excellent yields (exceeding 90%) with Grignard (entry 12, 92%), magnesium diorganocuprate (entry 14, 95%), and organozinc (entry 16, 94%) reagents. For further experiments, we selected organozinc reagents, which demonstrated virtually no dismutation and, moreover, displayed better functional group tolerance in comparison with Grignard reagents, consuming less starting material in comparison with diorganocuprate reagents that utilize only one out of two aryl groups. These initial results suggest that the selection of the electrophile is more significant for a selective synthesis of heteroleptic triarylbismuthanes than the selection of the nucleophile.

Next, a comparison of nucleophilic and electrophilic modes of dismutation by the addition of either a sub-stoichiometric amount of PhMgBr, PhZnX (X = Br or Cl), MgCl₂, ZnCl₂, Ph₂BiCl, Ph₂BiI, or Ph₂BiOTs to diphenyl(4-methoxyphenyl)bismuthane **1b** was explored (Scheme 2). We chose bismuthane **1b**, since an electron-rich group is a better leaving

Scheme 2. Dismutation of Bismuthane 1b Triggered by Addition of Nucleophilic and Electrophilic Reagents



^aRecovered material. ^bMolar ratio.

Scheme 3. Preparation of Triarylbismuthanes 1 utilizing Diarylbismuth Precursors 2 and Arylbismuth Ditosylates 3



group than an electron-poor one,²³ making 1b an ideal substrate for studying dismutation of triarylbismuthanes. To our surprise, the Grignard reagent (entry 1), organozinc (entry 2), MgCl₂ (entry 3), and ZnCl₂ (entry 4) had no effect within the time period, and 1b was recovered in essentially quantitative yields. However, the bismuth-based electrophiles, Ph₂BiCl (entry 5), Ph₂BiI (entry 6), and Ph₂BiOTs (entry 7) decreased the amount of recovered 1b to 30%, 43%, and 33% and afforded a mixture of three additional dismutated products A, B, and C in a molar ratios of 11.3:9.2:5.7:1, 17.5:15.1:5.6:1, and 18.6:15.1:3.7:1 of 1b/A/B/C after 1 h at room temperature in tetrahydrofuran (THF), respectively. Subsequent experiments with Ph2BiI demonstrated that the time frame for equilibration is variable, sometimes taking up to 6 h. This induction period may indicate that a secondary reagent or process derived from the reaction or decay of Ph₂BiI might be responsible for the dismutation. Nevertheless, these results indicate that the ate-complex-intermediate mechanism is accessible when the nucleophile is in excess but only at higher temperatures (reflux in diethyl ether) and elongated reaction times (20 h).¹

In general, the dismutation is far more likely when triggered by the electrophilic Ph_2BiX , and it occurs at ambient temperatures and shorter reaction times (1–6 h). Therefore, keeping the concentration of the electrophile to a minimum, achieved by slow addition of the electrophile into a solution of nucleophile, rather than the previously reported reversed order of the reagents, is a logical step in obtaining high yields of heteroleptic triarylbismuthanes.¹⁶ To support this statement, we ran two experiments differing in the order of the reagent addition. In the first experiment, 1 equiv of nucleophile *p*-CH₃OC₆H₄ZnX was added in four portions into 1 equiv of electrophile Ph₂BiI over 2 h at room temperature affording the isolated yield of **1b** in 31% with the ratio of **1b/A/B** being 2.8:2.1:1. In the second experiment, four portions of the electrophile were added into the nucleophile under the same conditions providing an isolated yield of **1b** in 55% with the ratio of **1b/A/B** being 13.9:0.85:1 (see Supporting Information for more details). This result supports our conclusion and is in agreement with our previous results (Scheme 2).

To demonstrate the generality and applicability of our new findings, a set of diverse unsymmetrical triarylbismuthines, $Ar_2^1Ar^2Bi$, 1a-1h, was targeted through a two-step process (Scheme 3, Methods A and B). Overall, bismuthanes 1 were formed in good to high yields (83–99%) regardless of the electronic properties of their substituents. In the first step, previously reported diphenylbismuth tosylate (2a) (Method A) was prepared from a simple combination of triphenylbismuthane with a slight excess of *p*-toluenesulfonic acid (*p*-TsOH·H₂O) in diethyl ether.²⁴ We attempted to synthesize

other diarylbismuth tosylates from the corresponding triarylbismuthanes, such as $Bi(p-CH_3OC_6H_4)_3$, $Bi(p-NCC_6H_4)_3$ and trimesitylbismuthane, but were unable to isolate them in sufficient purity, often obtaining inseparable mixtures of the desired products Ar2BiOTs, starting materials Ar3Bi, and arylbismuth ditosylates ArBi(OTs)₂. Although these impure species could be used in the following step, the yield was diminished, and the corresponding product needed to be isolated from a complicated reaction mixture (see Supporting Information for more details). As stated previously, increased steric congestion retards the dismutation process; therefore, dimesitylbismuth iodide,¹⁹ Mes₂BiI (2b), prepared by treatment of trimesitylbismuthane with BiCl₃ followed by halide exchange with sodium iodide (Method B), afforded comparable results to the monotosylate 2a with minimal formation of the dismutated byproducts (vide infra). In the second step, diarylbismuth tosylate or iodide 2 was added to 1.2 equiv of organozinc reagent, Ar^2ZnX , at -10 °C, and the resulting reaction mixtures were stirred for 100 min, affording the target set of products 1 in favorable yields without formation of the dismutated byproducts.

We also explored an alternative approach utilizing monoarylbismuth ditosylates 3, prepared from the corresponding homoleptic triarylbismuthane and 2 equiv of p-TsOH·H₂O under reflux in high yields (Scheme 3, Method C). In the following step, compound 3 was treated with the organozinc reagent yielding the corresponding heteroleptic triarylbismuthanes **1i**-**1i**. However, in comparison with the previous protocols, the yields obtained for **1i**-**1i** were fairly low (52–91%) relative to the first two synthetic protocols accessed through diarylbismuth tosylates **2**. To unambiguously confirm the structure of our heteroleptic triarylbismuthanes **1**, we obtained an X-ray of **1k**. The bond lengths and angles closely match the parent triphenylbismuthane (see Supporting Information for more details).²⁵

In conclusion, we investigated the critical factors responsible for the dismutation of heteroleptic triarylbismuthanes that had previously obscured their syntheses. Our discovery is that selection of the electrophile is crucial, improving efficiency by minimizing dismutation, which otherwise diminishes the yield and purity of the product. When the bismuth electrophiles were compared, the best results were obtained with diphenylbismuth tosylate (2a), which afforded the highest yields of product 1 with virtually no formation of byproducts. The superior performance of 2a over diphenylbismuth halides may result from the chelate-like coordination of the tosylate ligand to the organobismuth counterpart, or its inability to form a bridged species, thus increasing its stability to dismutation. Alternatively, it may reduce solubility, effectively shortening the time the reactive species exists in solution. The soft or hard nature of the nucleophile does not seem to have much of an effect, since the Grignard and organozinc reagents give comparable yields and amounts of dismutated byproducts. Steric congestion around the bismuth center significantly reduces dismutation, which can be demonstrated by better performance in yield and selectivity of dimesitylbismuth iodide (2b) versus Ph₂BiI. A second crucial observation according to our study (Scheme 2) is maintaining a minimal concentration of the bismuth electrophile during the course of the reaction. This was accomplished by adding the electrophile to a solution of the nucleophile. These findings permit an efficient two-step synthetic protocol utilizing either diarylbismuth or monoaryl precursors and afford an electronically diverse set of heteroleptic triarylbismuthanes 1, $Ar_2^1Ar^2Bi$, without the formation of dismutated contaminants.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00777.

Complete experimental details with NMR spectra (PDF)

Accession Codes

CCDC 1984672 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Jakub Hyvl – Department of Chemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822, United States; • orcid.org/ 0000-0002-5509-5567; Email: hyvl@hawaii.edu

Authors

Thomas Louis-Goff – Department of Chemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822, United States Arnold L. Rheingold – Department of Chemistry, University of California, San Diego, La Jolla, California 92093, United States;
[●] orcid.org/0000-0003-4472-8127

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.9b00777

Notes

The authors declare the following competing financial interest(s): A provisional patent application was filed by University of Hawai'i, which is not yet published.

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