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PII:	S0040-4039(18)31316-9		
DOI:	https://doi.org/10.1016/j.tetlet.2018.10.075		
Reference:	TETL 50385		
To appear in:	Tetrahedron Letters		
Received Date:	30 August 2018		
Revised Date:	26 October 2018		
Accepted Date:	31 October 2018		



Please cite this article as: Kuimov, V.A., Gusarova, Nina.K., Malysheva, S.F., Trofimov, B.A., Transition metalfree regioselective access to 9,10-dihydroanthracenes *via* the reaction of anthracenes with elemental phosphorus in the KOH/DMSO system, *Tetrahedron Letters* (2018), doi: https://doi.org/10.1016/j.tetlet.2018.10.075

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Transition metal-free regioselective access to 9,10-dihydroanthracenes via the reaction of anthracenes with elemental phosphorus in the KOH/DMSO system

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ARTICLE INFO

Received in revised form

Article history: Received

Available online

Accepted

ABSTRACT

Anthracene and its 9- or 9,10-substituted (Me, Ph, Cl, Br) derivatives react with red phosphorus (P_n) in the KOH/DMSO superbase system at 85-120 °C to afford 9,10-dihydroanthracenes in good to excellent yields, thus providing simple and clean access to these extensively used dihydroaromatics.

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Keywords: anthracenes 9,10-dihydroanthracenes reduction red phosphorus superbase

In the last decade, 9,10-dihydroanthracenes and their analogues have been the focus of a diverse number of research areas. Representative examples include their application in the design of fluorescent chemosensors,¹ luminophores² and other optoelectronic materials.³ They are also claimed as additives to electrolytes for rechargeable batteries⁴ and capacitors.⁵ 9,10-Dihydroanthracenes are known as photoinitiators for organocatalytic processes.⁶ Dihydroanthracenes and their analogues are also precursors of cardiovascular and cerebrovascular drugs.⁷

Dihydroanthracenes are typically synthesized by reduction of the parent aromatics.⁸ The transition-metal catalyzed reduction of anthracenes by hydrogen under high pressure (up to 200 atm) leads to a complex mixture of diverse hydroisomers.^{8e-i} Among the selective syntheses of 9,10-dihydroanthracenes are the reactions of anthracenes with hydrogen (100 atm, 80 °C) in the presence of complex Lewis acids such as B(C₆F₅)₃/dibenzo[24]crown-8 (35-59% yield).⁹9,10-Dihydroanthracenes were prepared from anthracenes using Et₃SiH in the superacidic complex BF₃•CF₃CH₂OH.¹⁰ For the regioselective reduction of anthracenes to 9,10dihydroanthracenes, catalytic systems such as nano-Co/Li, nano-Mn/Li, nano-Pd, SmI₂, and NiCl₂/NaBH₄ have been employed.¹¹ Therefore, the search for simpler methods for 9,10dihydroanthracene synthesis from less expensive and more readily available starting materials remains topical.

Herein, we describe an approach based on our previous work regarding the phosphorylation of 9-bromoanthracene with red phosphorus (1:3.3) in the KOH/DMSO superbase system (19 mmol of KOH•0.5H₂O per 5 mL of DMSO), wherein, along with anthracen-9-ylphosphinic acid, anthracene and 9,10-dihydroanthracene were formed (Scheme 1).¹²



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Scheme 1. Phosphorylation of 9-bromoanthracene with red phosphorus (P_n) in the KOH/DMSO superbase system.¹²

This reaction outcome indicated that the $P_n/KOH/DMSO$ system might represent an efficient reagent for the reduction of 9-haloanthracenes to 9,10-dihydroanthracene, if optimized by suppressing the formation of anthracen-9-ylphosphinic acid and anthracene.

Indeed, after a series of experiments we found that haloanthracenes could be transformed regioselectively into 9,10dihydroanthracene in good to excellent yields. For this it was necessary to increase the equivalent ratio of haloanthracene:P (from 1:3.3 up to 1:~6-9) and to conduct the process at a much higher temperature (100 °C instead of 60 °C) in a 10 times more dilute solution. Selected examples of the reduction of 9haloanthracenes **1a**,**b** and 9,10-dibromoanthracene **1c**, featuring the effect of the haloanthracene structure and the reaction conditions on the yield of dihydroanthracene **2a** are reported in Table 1. 2

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Table 1. Reduction of 9-haloanthracenes 1a,b and 9,10dibromoanthracene 1c with P_n in the KOH/DMSO system.^a



 $X^{1} = H, X^{2} = CI$ (1a); $X^{1} = H, X^{2} = Br$ (1b); $X^{1} = X^{2} = Br$ (1c)



^aReagents and conditions: 1 (2.0 mmol), P_n (5.4-19.0 mg-atom), KOH•0.5H₂O (29.0 mmol), DMSO (48 mL), 100 °C, 3 h, Ar. ^b Anthracene (72%) was formed.

As seen from Table 1, bromoanthracenes **1b**,**c** (90-95%) were more easily reduced to dihydroanthracene **2a** compared to chloroanthracene **1a** (79%) (Entries 1-3). The ratio of **1**:P had a crucial influence on the reduction. When this ratio was decreased in accordance with the previous work,¹² the yield of dihydroanthracene **2a** dropped from 79% to 11% (Table 2, *cf*. entries 1 and 4) and anthracene was isolated in 72% yield. From this result as well as from Scheme 1, it can be assumed that anthracenes could also be regioselectively reduced by elemental phosphorus to the corresponding 9,10-dihydro derivatives under similar conditions.

Unlike the reduction of haloanthracenes (Table 1), the reduction of anthracenes **3a-c** was effective with 15 mg-atom of P_n (Table 2). The exception was 9-methylanthracene **3b** (Entry 4) which required 30 mg-atom of P_n , as well as a higher temperature (120 °C instead of 100 °C). The yield of 9,10-dihydroanthracenes **2a-c** was also remarkably responsive to the reaction temperature, *e.g.* it dropped from 100% to 85% when the reaction temperature decreased by 15 °C (Table 2, *cf.* entries 1 and 2). The superbase system KOH/DMSO was more effective for this reaction than NaOH/DMSO (Table 2, *cf.* entries 1 and 3). The reaction tolerated mono- and 9,10-disubstituted anthracene derivatives with both alkyl (Me) and aromatic (Ph) groups (Table 2).

Table 2. Regioselective reduction of anthracenes **3a-c** to 9,10dihydroanthracenes **2a-c** with P_n in the KOH/DMSO system.^a



Entry	Anthracene 3	Temp.	Product 2	Yield 2
		(°C)		(%)





Under the above conditions, 9,10-diphenylanthracene 2c formed a mixture of *cis-trans* isomers in an ~1:6 ratio (¹H NMR, ESI). Such isomerism was also observed upon the reduction of anthracene 2c with HI/AcOH and SmI₂/H₂O systems.^{11f,13}

In the both reduction processes (Table 1, 2), DMSO plays an important role not as only a solvent but as a component of the superbase KOH/DMSO system.¹⁴ Other polar non-hydroxylic solvents typically produce inferior superbase media.¹ Presumably, the reduction mechanism involves single-electron transfer (SET) steps, such as in the 1-bromonaphthalene case, which was supported by ESR data and by reaction inhibition with the free radical scavengers hydroquinone and TEMPO.¹⁵ Herein we extend the previous scheme by including the hydrogen radical transfer from the phosphinite species as being more likely than that from DMSO (Scheme 2). As expected, ¹⁶ cleavage of the P-P bond in the P_n macromolecule by the activated ⁻OH anion leads to oligomeric phosphide- (A) and phosphinite (B) species. The former transfers its electron to the haloanthracene moiety (as shown on 9-chloroanthracene). The radical-anion (C), thus formed, releases the Cl^{-} anion, and the anthracene radical (**D**) abstracts a hydrogen radical from oligophosphinite B to give anthracene. The phosphorus-centered radicals E and F recombine to afford the oxidized phosphorus macromolecule, $P_n(O)$ (Scheme 2). Furthermore, anthracenes undergo SET sequences, *i.e.* accepting an electron from oligophosphide anion A to give radical-anions G which after protonation by water are converted to radicals H. Then the latter abstracts a hydrogen radical from oligophosphinite B to give 9,10-dihydro derivatives 2 (Scheme 2).

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Scheme 2. Plausible mechanism for the reduction of anthracenes

In summary, a transition-metal free, regioselective transformation of anthracenes into the corresponding 9,10dihydro derivatives using elemental phosphorus in the superbase KOH/DMSO system was developed. The reduction is clean and proceeds under mild conditions (85-120 °C, 3 h) to afford the target products in 79-100% yield.

Acknowledgments

The main results were obtained using the equipment of Baikal analytical center of collective using SB RAS.

A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

References

- (a) Tu Z, Mach R, Yu L, Kotzbauer P. Patent U. S. 20130315825, 2013; (b) Yang L, Li X, Yang J, Qu Y, Hua J. Acs Appl Mater Inter. 2013;5:1317-1326; (c) Yang L, Li X, Qu Y, Qu W, Zhang X, Hang Y, Ågren H, Hua J. Sens Actuators, B. 2014;203:833-847; (d) Li J, Fleetham T. Patent WO 2016,029,137, 2016.
- (a) Park JH, Kim SI. Patent KR 2013,118,084, 2013; (b) Miyazaki T. Patent JP 2014037353, 2014; (c) Parham AH, Pflumm C, Jatsch A, Eberle T, Kroeber JV. Patent WO 2014008967, 2014.
- 3. Choi DS, Cho YH. Patent KR 2015033272, 2015.
- (a) Watanabe S, Iwamoto K, Ueda A, Nunome J, Koshina H. Patent JP 4,411,691, 2010; (b) Horikawa Y. Patent JP 2010015718, 2010; (c) Jung MH, Lee HH, Kim JS. Patent KR 2016005638, 2016.
- 5. Kanno H, Ohtsuki M. Patent JP 2008084946, 2008.
- (a) Theriot JC, Lim C-H, Yang H, Ryan MD, Musgrave CB, Miyake GM. Science. 2016;352:1082-1086; (b) Miyake G, Theriot JC, Ryan MD, Pearson RM, French TA, Yang H, Lockwood A, Musgrave C, Lim C-H. Patent WO 2017070560, 2017; (c) Ramsey BL, Pearson RM, Beck LR, Miyake GM. Macromolecules. 2017;50:2668-2674; (d) Koyama D, Dale HJA, Orr-Ewing AJ. J Am Chem Soc. 2018;140:1285-1293;
- (a) Rajagopalan R, Lin T-S, Karwa AS, Poreddy AR, Asmelash B, Dorshow RB. Acs Med Chem Lett. 2012;3:284-288; (b) Lin T-S, Rajagopalan R, Shen Y, Park S, Poreddy AR, Asmelash B, Karwa AS, Taylor J-SA. J Phys Chem A. 2013;117:5454-5462; (c) Wang Q, Tang W, Feng X, Xu X, Yin M, Shan Y, Chen Y, Wang M, Guan F, Zhao Y, Zhang J. Patent CN 103641688, 2014.
- (a) Ma YM, Zhou X, Wei XY, Zong ZM. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2010;32:1201-1206;

(b) Pan H-B, Wai CM. New J Chem. 2011;35:1649-1660; (c) Hubert
C, Bile EG, Denicourt-Nowicki A, Roucoux A. Green Chem.
2011;13:1766-1771; (d) Borowski AF, Vendier L, Sabo-Etienne S,
Rozycka-Sokolowska E, Gaudyn AV. Dalton T. 2012;41:1411714125; (e) Liu C, Rong Z, Sun Z, Wang Y, Du W, Wang Y, Lu L. Rsc
Adv. 2013;3:23984-23988; (f) Breso-Femenia E, Chaudret B, Castillon
S. Catalysis Science & Technology. 2015;5:2741-2751; (g) Huyen PT,
Krivec M, Kočevar M, Bucur IC, Rizescu C, Parvulescu VI.
Chemcatchem. 2016;8:1146-1156; (h) Chciuk TV, Li AM, VazquezLopez A, Anderson WR, Flowers RA. Org Lett. 2017;19:290-293; (i)
Sahle-Demessie E, Devulapelli VG, Hassan AA. Catalysts. 2012;2:85.

- (a) Hounjet LJ, Bannwarth C, Garon CN, Caputo CB, Grimme S, Stephan DW. Angew Chem Int Ed. 2013;52:7492-7495; (b) Gärtner D, Welther A, Rad BR, Wolf R, von Wangelin A. Angew Chem Int Ed. 2014;53:3722-3726.
- (a) Prakash GKS, Mathew T, Marinez ER, Esteves PM, Rasul G, Olah GA. J Org Chem. 2006;71:3952-3958; (b) Larson GL, Fry JL Organic Reactions; Wiley, NY, 2008; Vol. 71. pp 1-737.
- (a) Khurana JM, Kumar S, Nand B. Can J Chem. 2008;86:1052-1054;
 (b) Nandi P, Dye JL, Jackson JE. J Org Chem. 2009;74:5790-5792; (c) Costanzo MJ, Patel MN, Petersen KA, Vogt PF. Tetrahedron Lett. 2009;50:5463-5466; (d) Nador F, Moglie Y, Vitale C, Yus M, Alonso F, Radivoy G. Tetrahedron. 2010;66:4318-4325; (e) Michal S, Malcolm S, J. PD. Angew Chem Int Ed. 2013;52:7237-7241; (f) Szostak M, Spain M, Procter DJ. J Org Chem. 2014;79:2522-2537; (g) Chciuk TV, Boland BP, Flowers RA. Tetrahedron Lett. 2015;56:3212-3215; (h) Chciuk TV, Flowers RA. J Am Chem Soc. 2015;137:11526-11531; (i) Yu Z, Jie Z, Yun-Tao X, Xiao-Tao S, Lei W. Adv Synth Catal. 2016;358:3039-3045; (j) Zhang Y, Mao M, Ji Y-G, Zhu J, Wu L. Tetrahedron Lett. 2016;57:329-332;
- V. A. Kuimov, E. A. Matveeva, A. A. Telezhkin, S. F. Malysheva, N. K. Gusarova, B. A. Trofimov, *Russ J Org Chem.* 2016;52:1059–1061.
- Athans, A. J.; Briggs, J. B.; Jia, W. L.; Miller, G. P. J. Mat. Chem. 2007;17:2636-2641.
- 14. (a) Trofimov BA Curr Org Chem. 2002;6:1121-1162; (b) Trofimov

BA Superbase catalysts and reagents: the concept, application, perspectives. *In Modern Problems of Organic Chemistry*, N 14; Eds.: Potekhin A.A., Kostikov R.R., Baird M.S., St.Peterburg University press:BBM, 2004, p.131-175; (c) Trofimov BA, Mikhaleva AI, EY Schmidt, LN Sobenina, Chemistry of Pyrroles, Ch.1, CRC Press, Florida, 2014, pp.1-12.

- (a) Kuimov, V. A.; Malysheva, S. F.; Gusarova, N. K.; Vakul'skaya, T. I.; Khutsishvili, S. S.; Trofimov, B. A. Heteroatom Chem. 2011;22:198-203; (b) Kuimov, V. A.; Matveeva, E. A.; Khutsishvili, S. S.; Vakul'skaya, T. I.; Sinegovskaya, L. M.; Malysheva, S. F.; Gusarova, N. K.; Trofimov, B. A. Tetrahedron 2017;73:4723-4729.
- Trofimov BA, Gusarova NK. Mendeleev Commun. 2009;19:295-302;
 (b) N. K. Gusarova, S. N. Arbuzova , Trofimov BA. Pure Appl Chem. 2012;84:439-459.

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Highlights

- Reduction of anthracenes with red phosphorus •
- Metal-free synthesis of dihydroanthracenes •
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