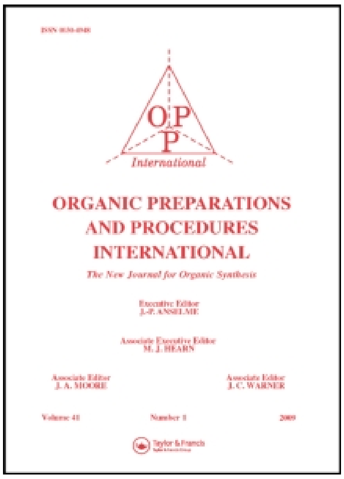


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED STEREOSELECTIVE REDUCTION FOR THE PREPARATION OF *endo*-7-PHENYLNORCARANE

Paul R. Morris[a]; James D. Woodyard[a]
[a] Department of Chemistry and Killgore Research Center, West Texas State University, Canyon, Texas

To cite this Article Morris, Paul R. and Woodyard, James D.(1973) 'AN IMPROVED STEREOSELECTIVE REDUCTION FOR THE PREPARATION OF *endo*-7-PHENYLNORCARANE', Organic Preparations and Procedures International, 5: 6, 275 — 279

To link to this Article: DOI: 10.1080/00304947309356856

URL: http://dx.doi.org/10.1080/00304947309356856

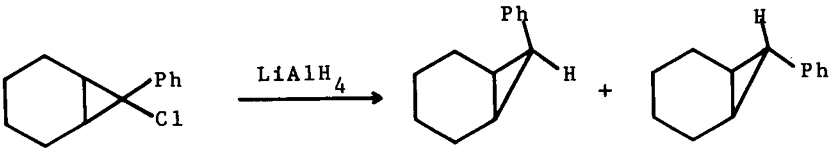
ORGANIC PREPARATIONS AND PROCEDURES INT. 5(6), 273-277 (1973)

AN IMPROVED STEREOSELECTIVE REDUCTION FOR THE PREPARATION OF endo-7-PHENYLNORCARANE

Paul R. Morris and James D. Woodyard*

Department of Chemistry and Killgore Research Center
West Texas State University, Canyon, Texas 79016

The first reductions of the epimeric 7-chloro-7-phenylnorcaranes (I) furnished a mixture of endo- and exo-7-phenylnorcarane (IIa and IIb) and an unidentified olefin.[1] The inherent difficulties involved in purification of this mixture led Jensen and Patterson[2] to employ a modified procedure of Kuivila.[3] This provided a much superior procedure for reduction of the 7-chloro-7-phenylnorcaranes in that it furnished essentially only one of the 7-phenylnorcaranes and an olefin. The reduction of I with three equivalents of lithium aluminum hydride and 0.1 equivalent of triphenyltin chloride in refluxing glyme, gave 80% IIa, 1% IIb and 19% of olefin;[2] the olefin was removed with ozone according to the procedure of Hodgkins, Woodyard and Stephenson[1] resulting in a 50-60% overall yield of endo-7-phenylnorcarane based on the mixed chloro compounds.



97% 3%

I IIa IIb

We found that the reported procedure gave incomplete reduction of the chloro compounds and noted that varying reaction conditions did not effect the percentage of olefin while the ratio of endo- to exo-7-phenylnorcarane varied. This suggested that the olefinic material found in the reaction mixture was formed by reduction of a chlorinated olefin produced during the preparation of 7-chloro-7-phenylnorcarane. Analysis of the reaction mixture of the preparation of I by vpc[4] prior to distillation, demonstrated the presence of three components the second of which, presumably an olefin, could be removed by ozonization. The reduction of a sample of ozonized undistilled I furnished a 50% yield of 7-phenylnorcarane (96% IIa and 4% IIb) and no olefin, demonstrating that the olefin was not produced during the reduction of I, in fact, we also observed that the triphenyltin chloride adds nothing to the reaction either in terms of the stereoselectivity or rate of the reaction.

TABLE I. REDUCTION OF 7-CHLORO-7-PHENYLNORCARANE

Reaction	Reaction Conditions					Vpc Analysis of Reaction Mixture			
	temp	time[d]	solvent	$LiAlH_4$	$(Ph)_3SnCl$	I	IIa	IIb	III[e]
1[a]	80	1.5	glyme	2.73g	.93g	25	52	3	20
2[b]	80	1.5	glyme	2.73g	.93g	28	69	3	-
3[c]	25	12	diglyme	0.74g	-	-	97	3	-
4[b]	25	54	diglyme	3.67g	-	-	94	6	-

---

a) 48 ml of solvent and 5 g of unpurified I were employed.
b) 48 ml of solvent and 5 g of purified I were employed.
c) 20 ml of solvent and 1 g of purified I were employed.
d) Time recorded in hrs. e) unidentified olefin.

Thus, reduction of 1 g of purified, olefin-free 7-chloro-7-phenylnorcarane[5] employing four equivalents of lithium aluminum hydride in diglyme (glyme requires longer reaction times) at 25° for 12 hrs. resulted in complete reduction of I, affording a 65% yield of the 7-phenylnorcaranes (97% IIa, 3% IIb by vpc[4]) and no olefin; the reduction of larger samples required longer reaction times.

EXPERIMENTAL

Preparation and Purification of 7-Chloro-7-Phenylnorcarane (I).

7-Chloro-7-phenylnorcarane was prepared by the procedure of Hodgkins[1] from 58 g of potassium *tert*-butoxide, 20.77 g of benzal chloride, and 320 ml of cyclohexene. The resulting 7-chloro-7-phenylnorcarane was then distilled, furnishing 20 g of I, bp. 83-86°/0.2 mm, lit.[2] bp. 80-85°/0.15 mm; lit.[4] 88-92°/0.05 mm. Analysis by nmr revealed the presence of an olefin; it was smoothly removed by bubbling a stream of 3% ozone through a 250 ml gas wash bottle containing a magnetically-stirred mixture of 20 g of I in 150 ml of 95% acetic acid. The gas was then passed through a 2% solution of potassium iodide, and the reaction allowed to proceed for 15 min. after iodine first appeared in the potassium iodide trap (total ozonization time was 40 min.). Then 10 ml of 30% H_2O_2 were added and the whole allowed to stir overnight. The reaction mixture was extracted with ether, washed in succession with water, 10% sodium hydroxide, saturated sodium chloride solution, and dried over calcium chloride. Removal of the solvent *in vacuo* furnished 15.98 g (60% based on benzal chloride) of I, with an isomeric ratio of 2:1[4] (nmr).

Reduction of 7-Chloro-7-Phenylnorcarane (I).-Lithium aluminum hydride (0.74 g, 0.0195 mol) was added to 20 ml of dry diglyme in a three-necked 100 ml flask equipped with a dropping funnel, thermometer, $CaCl_2$ drying tube, and magnetic stirrer and the whole cooled to 25° by means of an ice bath. Then 1.0 g (0.0048 mol) of purified I, mixed with twice its volume of diglyme, was added to the solution dropwise, not allowing the temperature to rise above 25°. After the reaction had proceeded 12 hrs., the excess $LiAlH_4$ was destroyed by the slow, sequential addition of 0.8 ml H_2O, 0.8 ml 15% NaOH and 2.4 ml H_2O.[6] The mixture was filtered, the filtrate taken up in ether, and the etheral solution washed with H_2O and dried over $CaCl_2$. The ether was evaporated *in vacuo* and the residue distilled, providing 0.54 g (65%) of II, bp. 133-136°/15 mm, lit.[1] 127-128°/13 mm; lit.[2] 68-70°/0.2 mm, which analyzed, by vpc,[4] as 97% IIa and 3% IIb.

Acknowledgment.-The authors wish to acknowledge the financial support (Grant AE-361) of the Robert A. Welch Foundation.

REFERENCES

* To whom correspondence should be addressed.

1. J. E. Hodgkins, J. D. Woodyard, and D. L. Stephenson, J. Am. Chem. Soc., 86, 4080 (1964).
2. F. R. Jensen and D. B. Patterson, Tetrahedron Lett., 3837 (1966).
3. H. G. Kuivila and L. W. Menapace, J. Org. Chem., 28, 2165 (1963).

4. Analysis by vpc was accomplished on a 6 ft. by 0.25 in. 10% Ucon 50 HB 2000 (polar) column operated at 175°.

5. A 2:1 mixture of the 7-chloro-7-phenylnorcaranes as determined by the method of Closs. G. L. Closs and J. J. Coyle, J. Org. Chem., **31**, 2759 (1966).

6. V. M. Mićović and M. Lj. Mihailović, ibid., **18**, 1190 (1953).

(Received July 20, 1973; in revised form October 9, 1973)