Acknowledgment. We are grateful to Dr. P. M. Collins, Birbeck College, for sending us information on the NMR spectra of **8** and **9.** Mr. W. H. Kruizinga provided synthetic assistance at various stages.

References and Notes

(1) For example (a) E. W. Meijer and H. Wynberg, *Tetrahedron Lett.*, 3997 (1979); (b) H. Wynberg and H. Numan, *J. Am. Chem. Soc.*, **99,** 603 (1977); (c) C. W. Jefford and C. G. Rimbault, *ibid.*, **100**, 6437 (1978); **100,** 295 (1979).

(2) (a) R. W. Denny and A. Nickon, *Org. React.*, **20,** 133 (1973); (b) C. S. Foote, *Acc. Chem. Res.*, **1,** 104 (1969); (c) "Singlet Oxygen", H. H. Wasserman and R. W. Murray, Eds., Academic Press, New York, 1979.

(3) (a) G. Rousseau, P. LePerchec, and J. M. Conia, *Synthesis*, 67 (1978). Also see (b) G. Rousseau and A. Lechevallier, *Tetrahedron Lett.*, 3287 (1978); (c) G. Rousseau, P. LePerchec, and J. M. Conia, *ibid.*, 2517 (1977); (d) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, **171,** 79 (1970); (e) A. A. Frimer, P. D. Bartlett, A. F. Boschung, and J. G. Jewett, *J. Am. Chem. Soc.*, **99,** 7977 (1977); (f) D. Lerdal and C. S. Foote, *Tetrahedron Lett.*, 3997 (1979).

(4) For example the presence and amount of **3a** is readily established from its characteristic absorption (C_6D_6) at δ 5.08 (s, 1, $-OOCH(OCH_3)$) and 3.00 (s, 3, OCH_3) and partial ^{13}C NMR ($CDCl_3$, relative to Me_4Si) at δ 109.0 (d, J = 177 Hz, $OOCH(OCH_3)$) and 89.5 (s, quarternary C). The allylic alcohol from **2a** and glycol from **3a** (as well as from the other products reported here) were fully characterized by spectral data and comparison with authentic samples.

(5) Partial NMR of **4**: ^1H (C_6D_6) δ 4.15 (s, 1, $CH(OCH_3)_2$) and 3.23 (s, 6, OCH_3); ^{13}C ($CDCl_3$), δ 58.0 (q, J = 166 Hz, OCH_3), 83.4 (s, quaternary C), and 108.4 (d, J = 130 Hz, $CH(OCH_3)_2$). Note that the *hemiacetal* group of **2** on reduction under basic conditions reduces to alcohol. The *acetal* group of **4** will not reduce under these conditions. The product **5** was identical in all respects with authentic material.[6]

(6) O. H. Oldenziel and A. M. van Leusen, *Tetrahedron Lett.*, 167 (1974).

(7) (a) G. Rousseau, A. Lechevallier, F. Huet, and J. M. Conia, *Tetrahedron Lett.*, 3287 (1978); (b) C. W. Jefford, *ibid.*, 985 (1979); (c) C. W. Jefford and C. G. Rimbault, *J. Am. Chem. Soc.*, **100,** 295, 6437, 6515 (1978); (d) L. B. Harding and W. A. Goddard, III, *Tetrahedron Lett.*, 747 (1978).

(8) M. Bellarmine Grdina, M. Orfanopoulos, and L. M. Stephenson, *Tetrahedron Lett.*, 4351 (1979). The dissent centers on the requirements for a *general* mechanism for the ene reaction.

(9) However, see the discussion by A. A. Frimer, *Chem. Rev.*, **79,** 359 (1979).

(10) The stereochemistries of **8** and **9** have been established and the ^{13}C NMR shifts for each carbon atom of the ring and the CH_2OH have been assigned.[11] In the product mixture resulting on reduction, the absorptions for four of the ring carbons and the CH_2OH did not overlap with those of the allylic alcohol and could be assigned. Observed ^{13}C NMR shifts (literature[11] values in parentheses): for **8,** δ 65.6 (65.7) (CH_2OH), 72.3 (72.6) (quaternary C), 35.3 (35.4) ($-CH_2C(OH)CH_2OH$), and 47.4 (47.5) (tertiary C); for **9,** δ 71.8 (71.8) (CH_2OH), 71.0 (71.2) (quaternary C), 34.0 (34.2) ($-CH_2C(OH)CH_2OH$), and 48.1 (48.2) (tertiary C). The presence of **8** and **9** was further ascertained by comparison with authentic samples.

(11) P. M. Collins and V. R. N. Munasinghe, *Carbohydr. Res.*, **62,** 19 (1978).

(12) R. M. Kellogg and J. K. Kaiser, *J. Org. Chem.*, **40,** 2575 (1975)

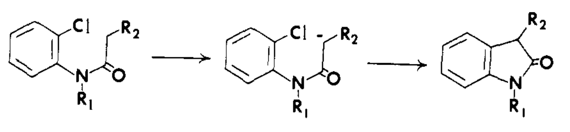
E. W. H. Asveld, Richard M. Kellogg*
Department of Organic Chemistry
University of Groningen, Nijenborgh
Groningen 9747 AG, The Netherlands

Received January 16, 1980

Photoinduced Cyclization of Mono- and Dianions of *N*-Acyl-*o*-chloranilines. A General Oxindole Synthesis

Sir:

Although a variety of methods for the synthesis of oxindoles appear in the literature,[1] one of the conceptually most attractive, i.e., cyclization of α carbanions of *N*-acyl-*o*-chloroanilines (**2**) has not proved to be efficient or general in scope.[2,3] We now report that *N*-alkyl-*N*-acyl-*o*-chloroanilines **1a–d** as well as *N*-acyl-*o*-chloranilines **1e–g** undergo smooth cyclization to afford oxindoles **3a–g** upon treatment with excess lithium diisopropylamide (LDA) in THF–hexane followed by near-UV irradiation of the resulting monoanions **2a–d** ($R_1 = CH_3, C_6H_5CH_2$) and dianions **2e–g** (R_1 = Li).



1a-g **2a-g** **3a-g**

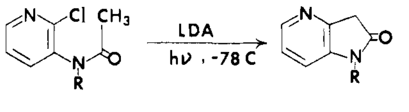
Table 1. Photoinduced Cyclization of *N*-Acyl-*o*-chloranilines **1** to Form Oxindoles **3**

starting anilide			product	isolated
no.	R_1	R_2	no.[a]	yield, %[b]
1a	CH_3	C_6H_5	**3a**[c]	64
1b	CH_3	H	**3b**[c]	82
1c	CH_3	n-C_4H_9	**3c**[d]	73
1d	$C_6H_5CH_2$	H	**3d**[e,f]	32[g]
1e	H	C_6H_5	**3e**[h]	63
1f	H	H	**3f**[i]	74
1g	H	CH_3	**3g**[j]	73

[a] ^1H NMR spectra of all products were consistent with assigned structures. Physical constants of known compounds were in agreement with published values. [b] Unless noted otherwise, irradiation was conducted for 3 h. [c] Reference 3. [d] Daisley, R. W.; Walker, J. *J. Chem. Soc. C* **1971,** 1375. [e] Satisfactory elemental analysis was obtained for this compound. [f] Yield was determined by GC. [g] Irradiated for 0.5 h. [h] Bruce, J. M.; Sutcliffe, F. K. *J. Chem. Soc.* **1957,** 4789. [i] Bayer, A. *Ber.* **1878,** *11*, 583. [j] Reference 8.

Results of a representative series of reactions are presented in Table I, where it may be seen that this mild procedure affords generally good yields of oxindoles with various alkyl substitution patterns at positions 1 and 3. Comparison of these results with those of earlier efforts[3] to effect cyclization of anilides **1b, 1e,** and **1f** through intramolecular addition of the laterial carbanions to an aryne intermediate clearly demonstrates the advantages of the photostimulated process. Moreover, the present method provides a route to oxindoles from anilides which cannot be converted into the required arynes because of substituents flanking the halogen of the benzene ring (vida infra).

2-Chloro-3-(*N*-methylacetamido)pyridine (**4a**) also underwent photocyclization to afford azaoxindole[4] **5a** (83%). In this case it was necessary to maintain the reaction mixture at −78 °C to prevent decomposition of the intermediate carbanion. Interestingly, the unmethylated pyridine **4b** was not converted into the expected **5b** under similar conditions. Instead, **4b** was recovered.



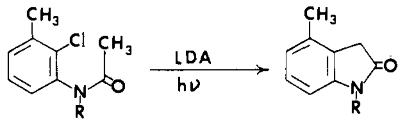
4a, R= CH3
b, R= H

5a, R= CH3
b, R= H

Photocyclization of **1d** with KNH_2 in liquid NH_3 afforded 57% oxindole **3d** along with 8% aryne-derived *N*-benzyl-*m*-aminoacetanilide. Attempted cyclizations of **1b** and **1f** under similar conditions led to much lower yields of the desired oxindoles than obtained with LDA.

Preliminary mechanistic studies with **1d** and **1f** reveal that the LDA-mediated reactions involve initial side-chain carbanion formation, but do not proceed via nucleophilic addition to an aryne intermediate. Thus, reaction of **1d** and **1f** with excess LDA in THF without illumination, followed by quenching with D_2O, resulted in quantitative recovery of starting materials containing >0.95 deuterium atom (^1H NMR) in the respective acetyl methyl group. Isolation of oxindoles **7a**[4] (87%) and **7b**[5] (76%) from 3-substituted 2-chloroanilides **6a** and **6b**, respectively, rule out an aryne mechanism. The requirement for Pyrex-filtered light and the inhibitory action of di-*tert*-butyl nitroxide indicate that the present reactions may represent one of the few reported examples of an intramolecular $S_{RN}1$ mechanism.[6,7] Additional studies concerning the mechanistic details of these reactions are in progress.

0002-7863/80/1502-3646$01.00/0



6a, R = CH_3 7a, R = CH_3
b, R = H b, R = H

A typical reaction procedure follows. To a solution of LDA (10 mmol) in 30 mL of THF, maintained at −78 °C under an argon atmosphere, was added a solution of 0.46 g (2.5 mmol) of *N*-propionyl-*o*-chloroaniline (**1g**) in 20 mL of THF. After addition was complete, the solution of the dianion was allowed to come to 25 °C and then irradiated for 3 h in a Rayonet Model RPR-240 photoreactor equipped with four 12.5-W lamps emitting at 350 mm. The reaction mixture was quenched with H_2O, acidified to pH 1 with 6 M HCl, and extracted with ether. The extracts were dried ($MgSO_4$), filtered, and concentrated. Purification of the crude product by medium pressure chromatography (1:3 diisopropylamine-hexane) followed by recrystallization from ether-hexane afforded 0.27 g (73%) of **3g**, mp 120-121 °C (lit.[8] mp 124 °C).

Acknowledgment. This work was supported by the National Science Foundation (CHE 77-13317) and the National Institutes of Health (NS 10197).

References and Notes

(1) For reviews see: (a) Sumpter, W. C. *Chem. Rev.* **1945**, *37*, 443. (b) Elderfield, R. C. "Heterocyclic Compounds"; Wiley: New York, 1952; p 128. (c) Sundberg, R. J. "Chemistry of Indoles"; Academic Press: New York, 1970; p 357. For recent examples of oxindole syntheses see: (d) Gassman, P. G.; van Bergen, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 5508, and references cited therein. (e) Mori, M.; Ban, Y. *Tetrahedron Lett.* **1979**, 1133. (g) Schultz, A. G.; Hagmann, W. K. *J. Org. Chem.* **1978**, *43*, 3391, 4231.
(2) Bunnett, J. F.; Hrutfiord, B. F. *J. Am. Chem. Soc.* **1961**, *83*, 1691.
(3) Bunnett, J. F.; Kato, T.; Flynn, R. R.; Skorcz, J. A. *J. Org. Chem.* **63**, *28*, 1.
(4) Satisfactory ^1H NMR and analytical data were obtained for this compound.
(5) Wright, W. B., Jr.; Collins, K. H. *J. Am. Chem. Soc.* **1956**, *78*, 221.
(6) Semmelhack, M. F.; Chong, B. P.; Stauffer, R. D.; Rogerson, T. D.; Chong, A.; Jones, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 2507.
(7) Semmelhack, M. F.; Bargar, T. M. *J. Org. Chem.* **1977**, *42*, 1481.
(8) Endler, A. S.; Becker, E. I. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 657.
(9) Abstracted in part from the Ph.D. dissertation of M. C. Sleevi, Virginia Polytechnic Institute and State University, July 1979.

James F. Wolfe,* Mark C. Sleevi,[9] R. Richard Goehring
Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Received October 22, 1979

Unsymmetrical Cleavage of Boranes by Bis(trimethylphosphine)-Diborane(4). Formation of a Triboron Cation.

Sir:

Certain Lewis bases are known to react with diborane(6) and/or tetraborane(10) to give unsymmetrical cleavage[1] products of the boranes:

$$B_2H_6 + 2L \rightarrow H_2BL_2^+ + BH_4^-$$

$$B_4H_{10} + 2L \rightarrow H_2BL_2^+ + B_3H_8^-$$

where L represents the Lewis base. Ammonia,[2] mono- and dimethylamine,[3] tetrahydrofuran,[4] and dimethyl sulfoxide[5] are typical of the bases that can effect the unsymmetrical cleavage of the boranes, and extensive work has been reported in the literatures[6] on the chemistry of the boronium cation $H_2BL_2^+$. Many other Lewis bases cleave the boranes "symmetrically"[1] to give the base adducts of borane(3) and triborane(7).

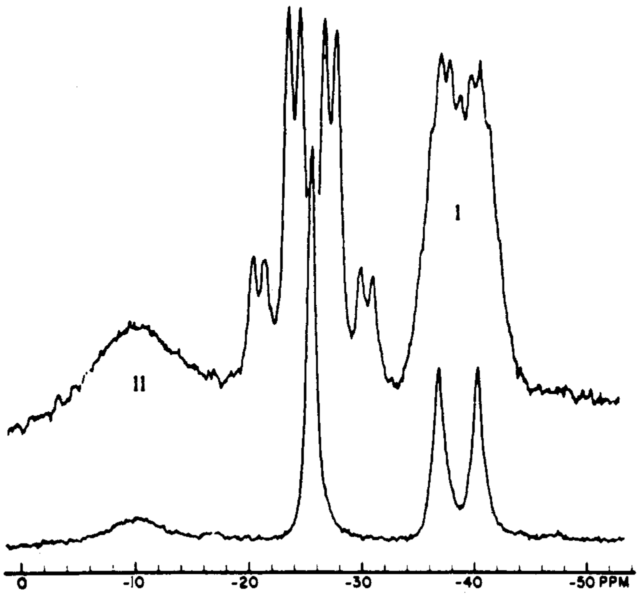


Figure 1. ^{11}B NMR spectra of $B_3H_6[P(CH_3)_3]_2^+B_2H_7^-$ $\{1.5B_2H_6 + 1.0B_2H_4[P(CH_3)_3]_2\}$ in dichloromethane at −20 °C: upper, normal spectrum; lower, proton spin decoupled spectrum.

We now report that the reactions of an unconventional base bis(trimethylphosphine)-diborane(4) with B_2H_6 and B_4H_{10} result in the unsymmetrical cleavage of the boranes, and that the cation produced by the reaction is a previously unreported *triboron* complex cation. The equations for the reactions are

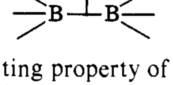
$$\tfrac{3}{2}B_2H_6 + B_2H_4[P(CH_3)_3]_2 \xrightarrow[\text{in } CH_2Cl_2]{-20\ ^\circ C} B_3H_6[P(CH_3)_3]_2^+ + B_2H_7^-$$

$$B_4H_{10} + B_2H_4[P(CH_3)_3]_2 \xrightarrow[\text{in } CH_2Cl_2]{\text{room temp}} B_3H_6[P(CH_3)_3]_2^+ + B_3H_8^-$$

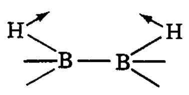
The ^{11}B NMR spectra of the reaction products are shown in Figure 1 and 2. In addition to the signals of the $B_2H_7^-$ ion at −25.8 ppm[7] [$BF_3{\cdot}O(C_2H_5)_2$ standard] and the $B_3H_8^-$ ion at −30.5 ppm,[8] a doublet signal (I, J_{BP} = 114 Hz) and a broad singlet signal (II) are seen at −39.0 and −10.5 ppm, respectively. The two signals are attributed to the new $B_3H_6[P(CH_3)_3]_2^+$ cation. The $B_3H_8^-$ salt can be isolated as a fairly stable solid at room temperature. The $B_2H_7^-$ salt, however, is unstable at room temperature and decomposes according to the equation

$$B_3H_6[P(CH_3)_3]_2^+B_2H_7^- \rightarrow (CH_3)_3PBH_3 + (CH_3)_3PB_3H_7 + \tfrac{1}{2}B_2H_6$$

On the basis of the established donor property of boron-boron single bonds[9]



and the known chelating property of two terminal hydrogen atoms attached to adjacent boron atoms[10]



the structure[11] shown in Figure 3 is proposed for the cation. Signals I and II are then assigned to the B(1,2) and B(3) atoms,

0002-7863/80/1502-3647$01.00/0