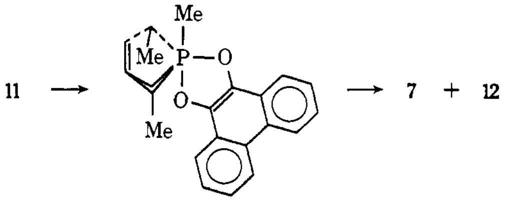
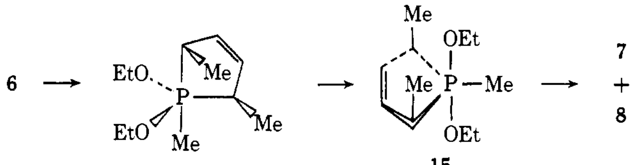
phorane by e–e departure[17] the pseudorotation **11** → **13** violates the strain rule (17–22 kcal mol^{-1} energy loss),[18] whereas the energy loss in placing the phospholene ring of **6** diequatorial by pseudorotation **6** → **15** *via* **14** is compensated for by placing two electronegative ethoxy groups in apical positions (energy gain, 10–17 kcal mol^{-1}).[18] This argument is supported by the free energy of activation for fragmentation of **11** which is very close to the energy barrier established by Gorenstein for switching of a five-membered ring from an e–a to an e–e conformation.[18a] Hence, a large part of $\Delta G^{\ddagger}$ for fragmentation probably arises from this energetically unfavorable pseudorotation.



13



14

15

Thus the evidence suggests that Hoffmann's orbital-symmetry predictions are correct. Indeed, if one accepts that attack of peroxide on trigonal phosphorus is a biphilic process, the peroxide molecule may well enter e–e (**5a,b** → **14**) which may pseudorotate rapidly to **15** and hence fragment to **7** and **8**.

Acknowledgment. Thanks are due to California State University—Long Beach for an equipment grant and to California Institute of Technology for the use of nmr facilities. The advice of Dr. D. B. Denney (Rutgers University) is also gratefully acknowledged.

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(17) a–a disposition of the five-membered ring is impossibly strained.

(18) (a) D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970); (b) D. Houlla, R. Wolf, D. Gagnoire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

(19) On leave from King's College, London.

C. D. Hall,*[19] J. D. Bramblett, F. F. S. Lin
Department of Chemistry
California State University—Long Beach
Long Beach, California 90840

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Reductive Silylation of Molecular Nitrogen *via* Fixation to Tris(trialkylsilyl)amine

Sir:

In the course of studies concerned with the reductive silylation of benzene derivatives employing a Nichrome-wire high-speed stirrer, the author found remarkably that the molecular nitrogen used as an inert atmosphere was taken up at room temperature and reductively silylated to trissilylamine.

$$6(CH_3)_3SiCl + 6Li + N_2 \xrightarrow[\text{THF}]{\text{transition metal}} 2N[Si(CH_3)_3]_3 + 6LiCl$$

In order to obtain more information on the nature of this direct transformation of molecular nitrogen into trissilylamine, a number of reactions were carried out in the presence of a variety of transition metal compounds, mainly their chlorides (Table I).

Table I. Effect of Various Catalysts on Reductive Silylation of Nitrogen

Catalyst	Mol ratio of silylamine to transition metal	Catalyst	Mol ratio of silylamine to transition metal
$TiCl_4$	0.8	$NiCl_2$	0.2
Cp_2TiCl_2	0.8	CuCl	0.0
VCl_3	0.9	$CuCl_2$	0.0
$CrCl_3$	5.4	$MoCl_5$	1.0
$MnCl_2$	1.2	WCl_6	0.2
$FeCl_3$	2.3	$PdCl_2$	0.0
$FeCl_2 \cdot 4H_2O$	0.6	$RuCl_3 \cdot H_2O$	0.0
$CoCl_2$	1.2	None	0.0

One of the reactions which gave the highest yield of silylamine, for example, was that under the following conditions: a mixture of 1.6 g (0.01 mol) of chromium chloride, 54.0 g (0.5 mol) of trimethylchlorosilane, and 3.5 g (0.5 g-atom) of cut lithium wire in 150 ml of dry THF was stirred at room temperature for 30 hr under 1 atm of dry nitrogen. At an initial stage of this reaction, the mixture darkened with evolution of heat, followed by fairly rapid absorption of nitrogen. The absorption of nitrogen slowed down after several hours. After separation of unreacted lithium metal, distillation of the homogeneous black filtrate gave a fraction boiling at 50–100° (26 mm). Further purification by fractional distillation gave pure tris(trimethylsilyl)amine: 10.0 g; bp 97–98° (26 mm); mp 69–71°; pmr (CCl_4), singlet at 0.19 ppm ($Si-CH_3$, no other protons present); ir, strong absorption at 915 cm^{-1} (Si–N stretching); reported[1] for $[(CH_3)_3Si]_3N$, bp 76° (12 mm), mp 70–71°. Tris(dimethylethylsilyl)amine was similarly prepared in lower yield, because of increased consumption of dimethylethylchlorosilane by coupling on lithium metal to give disilane.[2]

Whenever nitrogen was absorbed, regardless of its quantities, the system darkened and trissilylamine appeared. Not only the reaction mixtures, but also the black residues left after distillation were soluble even in benzene and *n*-hexane to give a homogeneous solution.

Although the yields were small, the silylamine was also obtained when sodium and potassium metal were used as a reducing agent with chromium(III) acetylacetonate.

The formation of nitride as a completely reduced species of fixed nitrogen, prior to ammonia by hydrolysis, has been postulated by some investigators.[3,4] This species, however, so far has not been fully characterized. The fact that insufficient reduction of molecular nitrogen on transition metals results in the formation of hydrazine by protonation[5] seems to support

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(1) J. Gaubeau and J. Jimenz-Barbera, *Z. Anorg. Allgem. Chem.*, 303, 217 (1960).

(2) H. Gilman, K. Shiina, D. Aoki, B. J. Gaj, D. Wittenberg, and T. Brennan, *J. Organometal. Chem.*, **13**, 323 (1968).

(3) M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Commun.*, 1074 (1968).

(4) E. E. van Tamelen, *Accounts Chem. Res.*, **3**, 361 (1970), and references cited therein.

(5) E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).

strongly the idea that the successive reductive silylation must take place in this first example of catalytic fixation of molecular nitrogen to tris(trialkylsilyl)amine.

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Kyo Shiina
Research Institute for Atomic Energy, Osaka City University
Sumiyoshi-ku, Osaka, Japan 558
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Synthesis of a [7]Paracyclophane[1,2]

Sir:

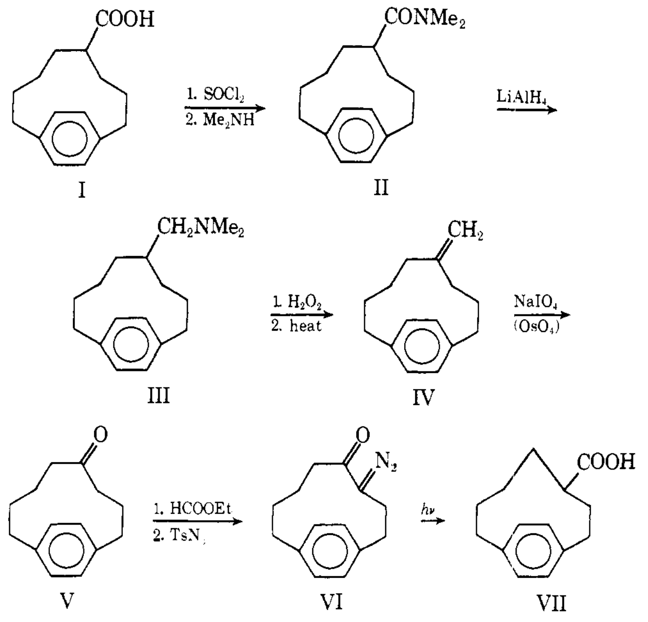
Chemists continue to be intrigued by the possibility of preparing and studying benzene rings which are still more "bent and battered" than previous examples.[3] The present report is concerned with the preparation and a preliminary study of what is believed to be one of the most highly deformed benzene rings obtained to date, which is to be found in a molecule containing the [7]paracyclophane ring system, explicitly 3-carboxy[7]-paracyclophane.

[8]Paracyclophane and derivatives thereof have been previously obtained.[4–6] From a detailed study of the ultraviolet spectrum of such compounds, it was estimated[6] that [8]paracyclophane probably would have the ring distorted from planarity by approximately 20°. This number has not been firmly established, and it is now suspected that it is somewhat too large.[7] It was also predicted at that time that [7]paracyclophane would contain about the same strain energy as does cyclopropane, and it should therefore be thermodynamically stable enough to isolate, if an appropriate synthetic method for it could be devised.

In devising the synthesis of such a compound, one might attempt a ring closure, or a ring contraction. The latter method will be discussed here.

For a ring contraction, when one is going to a thermodynamically rather unstable compound, one needs a clean process with a large driving force. The Wolff rearrangement seems to meet those criteria, since the nitrogen molecule evolved during the course of the reaction is extremely stable thermodynamically. The synthetic scheme involved beginning with 4-carboxy[8]-paracyclophane, the synthesis of which is somewhat tedious, but reasonably straightforward,[5,6] and conversion of the carboxyl function to an α-diazo ketone function. This was successfully accomplished through the steps outlined in Chart I.

Chart I



4-Carboxy[8]paracyclophane (I) was converted to the acid chloride, and then to the dimethylamide (II), a viscous colorless oil, bp 148–153° (0.1 mm), by reaction of the acid with thionyl chloride, and treatment of the acid chloride with dimethylamine. Reduction of the amide gave the corresponding (hygroscopic) amine. The latter was converted to the amine oxide, which was pyrolyzed to give a methylene derivative IV, a colorless liquid, bp 86.5–88° (0.6 mm). This was cleaved with $NaIO_4$ using a catalytic amount of OsO_4. The ketone V, mp 44.5–46°, was treated with ethyl formate and base to give the hydroxymethylene derivative, which was converted to the diazo ketone (VI) by treatment with tosyl azide. Photolysis of the latter produced a yellowish semisolid, which was purified by chromatography on silica gel with hexane–ethyl acetate. The material isolated was assigned the structure 3-carboxy[7]-paracyclophane (VII), mp 130.5–132.5°, characterized in the following way.[8]

The ultraviolet spectrum of a benzene ring as a function of bending of the type anticipated here has been studied by SCF–CI methods applicable to π systems,[6] and the observed spectrum for VII is in good agreement with that predicted[6] for [7]paracyclophane (Table I).

Table I. Ultraviolet Spectra of Some [*n*]Paracyclophanes, λ_{nm} (Log ϵ)

p-Diethylbenzene	193 (4)	193 (4)	214 (3)	265 (2)
[10]Paracyclophane			223 (3)	268 (2)
[9]Paracyclophane			224 (3)	271 (3)
[8]Paracyclophane[a]	200 (4)	205 (4)	230 (3)	275 (2)
[7]Paracyclophane (calcd)	196 (4)	210 (4)	247 (3)	288 (2)
[7]Paracyclophane (found[a])		207 (4)	237 (4)	284 (2)

[a] Actually for a carboxy derivative, in ethanol.

The infrared spectrum shows a broad O–H band at 2300–3500 cm^{-1} and a C=O band at 1705 cm^{-1} which are characteristic of a carboxyl group. The C–H stretching region is normal for an alkylbenzene. The mass spectrum showed the molecular ion at 218, calcd 218. The nmr spectrum showed δ 11.2 (s, 1, COOH),

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(1) Supported in part by a grant from Eli Lilly and Co., and in part by Grant No. GP 15263 from the National Science Foundation.

(2) This is paper LXXXVII in the series "Conformational Analysis." For paper LXXXVI, see N. L. Allinger and J. Siefert, *J. Amer. Chem. Soc.*, **94**, 8082 (1972).

(3) D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971), review the field thoroughly, and give many references.

(4) D. J. Cram and G. R. Knox, *J. Amer. Chem. Soc.*, **83**, 2204 (1961); D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

(5) N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **27**, 1490 (1962).

(6) N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Amer. Chem. Soc.*, **85**, 1171 (1963).

(7) An X-ray crystal-structure study in progress will settle this point shortly.

(8) All of the compounds assigned a Roman numeral II–VII gave ir and nmr spectra consistent with the assigned structures, and II, IV, V, and VII gave carbon and hydrogen analyses with no value different from theory by more than 0.22%.