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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Synthesis of a [7]Paracyclophane[1,2]

Sir:

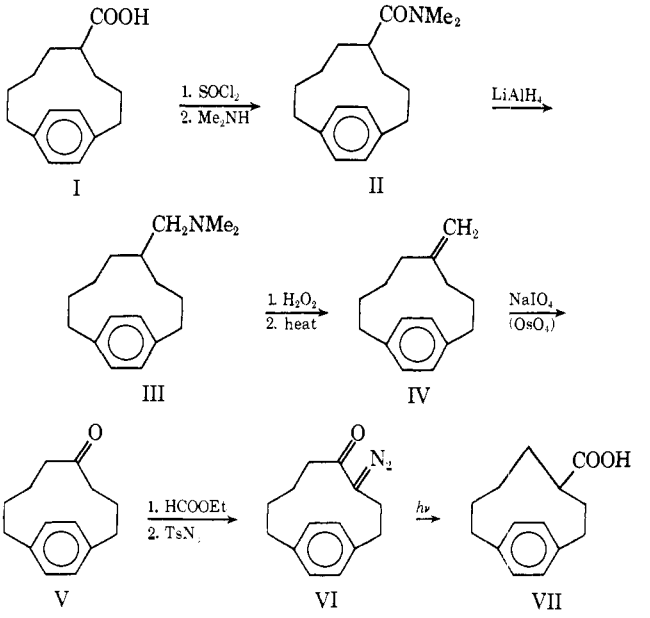
Chemists continue to be intrigued by the possibility of preparing and studying benzene rings which are still more "bent and battered" than previous examples.[3] The present report is concerned with the preparation and a preliminary study of what is believed to be one of the most highly deformed benzene 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.

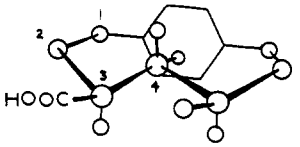
The infrared spectrum shows a broad O–H band at 2300–3500 cm^{-1} and a C=O band at 1705 cm^{-1} which are characteristic of a carboxyl group. The C–H stretching region is normal for an alkylbenzene. The mass spectrum showed the molecular ion at 218, calcd 218. The nmr spectrum showed δ 11.2 (s, 1, COOH),

(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%.

7.2 (d, 4, aromatic), 3.2–0.1 (m, 12, side-chain protons), −1.4 (m, 1, unique aliphatic proton). The highly deshielded proton at δ −1.4 is noteworthy. This is clearly one which is pushed deep into the π cloud by the constraints imposed by the ring. These data prove that VII is a carboxy[7]paracyclophane.

The compound VII has been tentatively formulated as the 3-carboxy derivative,[7] rather than the 4 isomer (which it might be, depending on which position of V was attacked in the formylation). The available pertinent information at present is that the proton at δ −1.4 is seen as a pair of doublets, with coupling constants of 11 and 15 Hz.

Models of the 4-carboxy compound show that the proton pushed into the ring should be anti to two equivalent vicinal protons, and show a triplet, perhaps further split by smaller coupling constants with the gauche vicinal protons. In the *exo*-3-carboxy compound the upfield proton is anti to one vicinal proton, but is also geminally coupled. The dihedral angles with the gauche protons are presumably large enough that no coupling is observed. The nmr spectrum of the upfield proton is thus consistent with the 3-carboxy, not the 4-. Further, when VII is reduced to the alcohol (with sodium bis(2-methoxyethoxy)aluminum hydride, the upfield proton is unchanged in coupling constant and in chemical shift. The lines from the $-CH_2OH$ protons are immersed in the complex multiplet at δ 2.95 assigned to two benzyl protons. It can be noted that the two $-CH_2OH$ protons of the 4-hydroxymethyl are equivalent (enantiotopic), and hence would appear as a doublet, which would be easily observed when superimposed on the benzyl multiplet. This is *not* found. The $-CH_2OH$ protons are much more split up and mixed into the multiplet, and cannot be separated out by visual inspection. In the 3-hydroxymethyl derivative, these $-CH_2OH$ protons are diastereotopic, and hence will give at least (to the first order) a doublet of doublets of doublets (barring accidental degeneracy). Such a situation is compatible with the observed spectrum. Accordingly, the carboxyl group in VII is tentatively assigned to the 3 position. Further discussion will be deferred to the full paper.



(9) National Science Foundation Trainee, 1971–1972.

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Alkyl Group Isomerization in the Cross-Coupling Reaction of Secondary Alkyl Grignard Reagents with Organic Halides in the Presence of Nickel–Phosphine Complexes as Catalysts

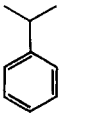
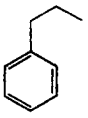
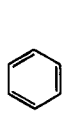
Sir:

We recently reported[1] that nickel–bisphosphine complexes exhibit extremely high catalytic activity for selective cross coupling of Grignard reagents with aromatic and olefinic halides and showed that *n*-alkyl Grignard reagents lead to *n*-alkyl derivatives without any isomerization of the alkyl group.

We now wish to report that a secondary alkyl Grignard reagent also undergoes the cross coupling very easily with chlorobenzene, but the coupling reaction is accompanied by alkyl group isomerization from secondary to primary, the extent of which is strongly dependent upon the electronic nature of the phosphine ligand in the catalyst.

The results of the reaction between isopropylmagnesium chloride and chlorobenzene using nickel(II) complexes containing various phosphines are summarized in Table I.

Table I. Products from the Reaction of i-C_3H_7MgCl with PhCl in the Presence of NiL_2Cl_2[a]

L_2 in catalyst	Total yield,[b] %	Products distribution,[b] %		
				
$Ph_2PCH_2CH_2PPh_2$	74	96	4	0
$Me_2PCH_2CH_2PMe_2$	84	9	84	7
$Ph_2PCH_2CH_2CH_2PPh_2$	89	96	4	0
dmpf[c]	48	8	74	18
dmpc[d]	7	12	88	0
dppc[e]	18	78	1	21
$Ph_2PCH{=}CHPPh_2$	8	92	8	0
$2PEt_3$	9	1	11	88
$2PBu_3$	8	2	16	82
$2PPh_3$	44	16	30	54

[a] To a mixture of chlorobenzene (5 mmol) and a nickel complex (0.05 mmol) in 5 ml of ether was added an isopropyl Grignard solution (6.9 mmol) at 0°. The mixture was refluxed for 20 hr, hydrolyzed, and then analyzed by glpc. [b] Determined by glpc using an internal standard. [c] 1,1′-Bis(dimethylphosphino)ferrocene. [d] Bis(dimethylphosphino)-*o*-carborane. [e] Bis(diphenylphosphino)-*o*-carborane.

$$i\text{-}C_3H_7MgCl + PhCl \xrightarrow{\text{catalyst}} i\text{-}C_3H_7Ph + n\text{-}C_3H_7Ph + HPh$$

The catalysts which give rise to the preferential formation of isopropylbenzene contain, as the ligand, $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2PPh_2$ (dpp), $Ph_2PCH{=}CHPPh_2$, and bis(diphenylphosphino)-*o*-carborane.[2] The complexes which induce the alkyl group isomerization to afford *n*-propylbenzene preferentially comprise $Me_2PCH_2CH_2PMe_2$ (dmpe), 1,1′-bis(dimethylphosphino)ferrocene,[3] bis(dimethylphosphino)-*o*-carborane,[2b] PEt_3, and PBu_3.

This classification does not relate to the catalytic activity of the complexes but suggests that, in general, the more electron donating the phosphine ligand on nickel, the greater is the extent of the alkyl isomerization from secondary to primary. Particularly, it should be noted that with the dmpe ligand (which is good electron donating) the formation of *n*-propylbenzene is predominant, while with the dpp ligand (which appears to be sufficiently electron accepting) isopropylbenzene is formed preferentially.

The complex Ni (dmpe)Cl_2 catalyzes also the isomer-

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(2) (a) R. P. Alexander and H. Schroeder, *Inorg. Chem.*, 2, 1107 (1963); (b) M. Kumada, K. Sumitani, Y. Kiso, and K. Tamao, *J. Organometal. Chem.*, in press.

(3) Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, *ibid.*, in press.