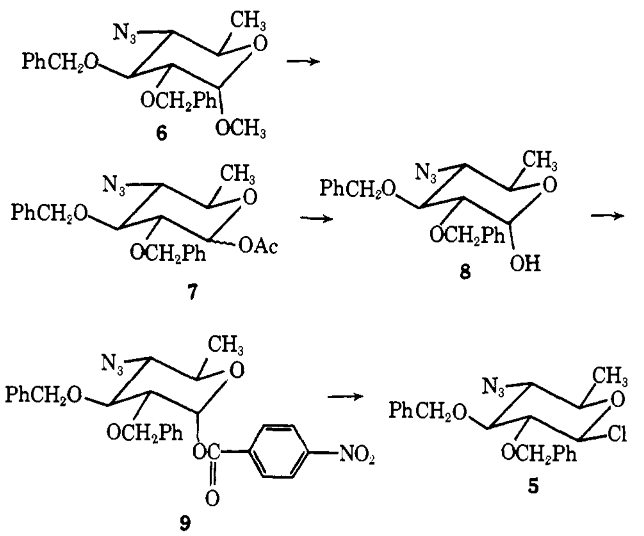


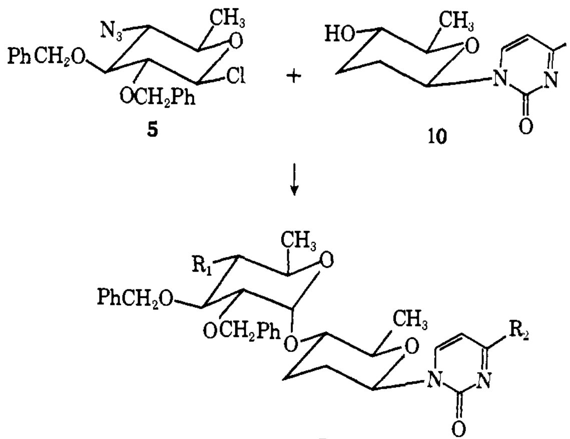
to give a 90% yield of the 1-O-acetyl derivative **7** as a syrup. Acetate **7** was deacetylated by means of sodium methoxide at room temperature for 45 min and the resulting free sugar **8** could be crystallized in the α form, mp 91–93°, in 72% yield.

Mutarotation studies in pyridine indicated that inversion to the β form occurred slowly, if at all, which allowed the free sugar to be converted to the 1-α-*p*-nitrobenzoate derivative, **9**, mp 66–67° in 58% yield. The *p*-nitrobenzoate reacted with dry hydrogen chloride to give clean inversion at the anomeric carbon and produced the crystalline β-chloro derivative, **5** (90%), mp 94.5–95.5°. The β configuration was confirmed by the rotation, $[\alpha]_D$ −155° (*c* 1.25, $CHCl_3$); the nmr spectrum (C_6D_6) showed the anomeric hydrogen as a doublet ($J_{1,2}$ = 8 Hz) at δ 4.85; and a coupling reaction with methanol in the presence of silver carbonate which cleanly gave the starting α-methyl glycoside.

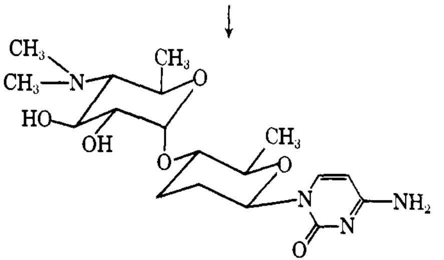
The nucleosidic alcohol **10** was available in our laboratory from the previous synthesis of **4**.[11] Coupling to form the α-disaccharide linkage and the final chemical maneuvers to synthesize cytosamine and plicacetin are shown below.

The chloro sugar **5** was treated with the nucleosidic alcohol **10** in the molten state, under diminished pressure and in the presence of Dowex 1-X2 (OH^-), to give a 64% yield of crude **11**. Preparative thin-layer chromatography (2:1 $CHCl_3$–Et_2O) and two recrystallizations from ether gave 38% 1-[2,3,6-trideoxy-4-(4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-glucopyranosyl)-β-D-erythrohexapyranosyl]-4-ethoxy-2(1*H*)-pyrimidone (**11**), mp 106–108°; $[\alpha]_D$ −199° (*c* 1.2, $CHCl_3$). The α configuration of the disaccharide linkage was confirmed by nmr (CD_3COCD_3) which showed the anomeric proton as a doublet ($J_{1,2}$ = 3 Hz) at δ 5.08.

Reduction of the azido group in **11** was accomplished in a hydrogen atmosphere using 10% palladium/carbon as catalyst and gave the amine **12**, which after reductive methylation (HCHO, H_2, 10% Pd/C, EtOH) gave **13**, in 84% overall yield. Treatment of **13** with a liquid ammonia–ethanol mixture at 110° produced the cytosine derivative **14** in excellent yield (88%). Cytosamine **15** was obtained by reductive debenzylation in ethanol of **14** using hydrogen with 10% palladium/carbon and hydrochloric acid as catalysts. After recrystallization from isopropyl alcohol the synthetic cytosamine, mp 254–256° dec, was identical in all respects [ir(KBr), nmr (dihydrochloride in D_2O), $[\alpha]_D$ (0.1 *N* HCl), tlc (2:1 CH_3COCH_3–CH_3OH)] with natural product.[1] A mixture melting point was without depression. Conversion of **15** to its triacetate, mp 220.5–222° after recrystallization from benzene–hexane, was accomplished in 90% yield by treatment with acetic anhydride–pyridine (1:6) at room temperature overnight. A mixture melting point with the triacetate[1] of natural cytosamine was undepressed and ir (KBr) and nmr (CD_3CN) spectra were superimposable. The conversion of cytosamine to plicacetin has been recorded[1] previously.



	R₁	R₂
11,	N_3	OEt
12,	NH_2	OEt
13,	$N(CH_3)_2$	OEt
14,	$N(CH_3)_2$	NH_2



15. cytosamine

Acknowledgment. This investigation was made possible through Research Grant No. CA 03772 of the National Institutes of Health. The support is gratefully acknowledged.

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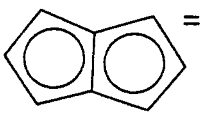
Received January 18, 1972

Bis(pentalenylnickel)

Sir:

Over the past 16 years two ideas have been formulated for making stable derivatives of unstable nonaromatic hydrocarbons. One was to make transition metal complexes, an extension of the explanation for the stability of ferrocene,[1] and was proposed originally as a way to prepare stable derivatives of cyclobutadiene.[2] The other was to make the pure reduction or oxidation products of the hydrocarbons, an extension of Hückel's theory for the stability of the cyclopentadienyl anion,[3] and was proposed originally as a way to prepare stable derivatives of planar cyclooctatetraene,[4] of cyclobutadiene,[5] and of pentalene.[6] A number of transition metal complexes of cyclobutadiene were prepared,[7,8] as was the pure reduction product of pentalene, the pentalene dianion, I.[6] However, although some transition metal complexes of pentalene are known,[9] no purely pentalene–metal complex is. Neither is a purely cyclobutadiene–metal complex, and, in fact, the only compounds that are composed simply of nonaromatic hydrocarbons and transition metals covalently bonded are bis(*as*-indacenyliron),[10] bis(*as*-indacenylnickel),[11] and 1,1′-biferrocenyl.[12]



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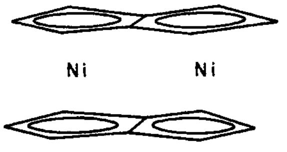

II

We have now prepared the simplest such substance, bis(pentalenylnickel) (II), a pure pentalene–metal sandwich. The compound is a red-brown solid that does not melt below 315° and is stable in air for at least a few hours. After a number of days in air it does decompose. It is slightly soluble in carbon disulfide, tetrahydrofuran, toluene, ether, and acetone, and although its solutions in carbon disulfide or tetrahydrofuran rapidly decompose in the presence of air, they do not in its absence. The compound is not hydrolyzed by aqueous tetrahydrofuran at room temperature during 2 hr, although 2 N hydrochloric acid in tetrahydrofuran–water during 6 hr destroys it. It was characterized by its proton nmr,[13] ir,[17] visible,[18] and mass spectra.[19,20] The simplicity of the proton nmr spectrum[14] implies that the molecule has D_{2h} symmetry, at least on the average over the nmr time scale.

Just what the geometric or electronic structure is for the complex is not clear, but a simple π-allyl-π-cyclopentadienylnickel[15a,22] structure twice over would be highly strained because the distance between the five-membered ring centers in a pentalene system should be about 2.0 Å, much shorter than the distance (2.49 Å) between nickels that are bonded,[23] no-less nonbonded.[24]

Bis(pentalenylnickel) was prepared by treating dilithium pentalenide (I) in tetrahydrofuran either with

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(13) In perdeuterated toluene at 85°: τ 3.81 (t), 6.47 (d) ($|J|$ = 2.3 Hz), relative intensities 3.98:8.02, respectively. In CS_2 at ambient temperatures the triplet is at 3.80, the doublet at 6.54 ($|J|$ = 2.2 Hz). The spectrum in CS_2 was determined using fast Fourier transform nmr spectroscopy by James C. Carnahan, Jr., at the State University of New York, Albany, and we are grateful to him for it. The coupling constant is like that in other metallocenes.[9b,c,10c,14] In various π-allylnickel compounds the central proton resonates at *ca.* τ 5.3 and the outer protons at *ca.* 6.5.[9c,15] In di-π-indenylnickel the central proton resonates at τ 3.07[16] and in bis(*as*-indacenylnickel) at 3.87.[11]

(14) See also references in footnote 8 of ref 10c.

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(17) In KBr (cm^{-1}): 3097 (m), 3076 (m), 3069 (m), 1370 (m), 1265 (s), 1259 (s), 1090 (s), 1020 (m), 1012 (m), 998 (m), 882 (s), 852 (m), 822 (m), 807 (w), 780 (vs), 770 (vs), 666 (m), 644 (m), 564 (m), 444 (m), 384 (w), 361 (w).

(18) λ_{max} [nm (ϵ)]: 735 (2300), 470 (5180), 376 (11,310).

(19) The only peaks of >25% intensity after ionization by 75 eV electrons are the parent peaks, which are in the calculated intensity ratio. Other peaks of greater than 10% intensity relative to the base peak (*m/e* 320) are *m/e* 58 (10%, Ni^+), 102 (16%, $C_8H_6^+$), 160 (25%, $C_8H_6Ni^+$, not $C_{16}H_{12}Ni_2^{2+}$, as the peak at *m/e* 160.5 is only 7% as intense as that at 160), 202 (15%, $C_{16}H_{10}^+$),[21] and 260 (10%, $C_{16}H_{10}Ni^+$).

(20) We were unsuccessful in obtaining satisfactory analyses for C, H, or Ni.

(21) A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, 3847 (1964).

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(24) Bonding the nickels to allyl moieties as in di-π-allylnickel, rather than to cyclopentadienyl moieties, does not relieve the strain if the five carbon atoms of each ring remain coplanar, for in bismethylallylnickel[25] the distance from the projection of the nickel onto the allyl plane to the central carbon atom is 0.07 Å greater than the distance from the center to an apex of a regular pentagon whose sides are 1.42 Å.[26] One way to relieve the strain is to bond the nickels to allyl moieties that are not coplanar with the remaining two carbon atoms of the five-membered rings, for which there is precedent in the noncoplanarity of the terminal substituents and the allyl atoms in a number of allyl–transition metal complexes.[27] Another way is to leave the atoms in the pentalene system coplanar and push the nickel atoms further apart, for which there is precedent in two bis(benzenepalladium) complexes.[28]

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$NiCl_2 \cdot (CH_3OCH_2)_2$ or with nickelocene.[29] It was isolated by sublimation at 155° (10^{-4} mm) after extraction with either CS_2 or ether. The yield was 4% from either nickel precursor.

Thus, although pentalene must be very difficult to isolate, and never yet has been, although its 1-methyl derivative recently has at −196°,[30] two of its derivatives are easily prepared and stable under common laboratory conditions: the dianion I and the nickel derivative II.

Acknowledgments. We are grateful to the U. S. Army Research Office—Durham for its support under Grant No. DA-ARO(D)-31-124-G1119.

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[29] Allylmagnesium chloride reacts with nickelocene to give π-allyl-π-cyclopentadienylnickel.[15a]

[30] R. Bloch, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, **93**, 3071 (1971).

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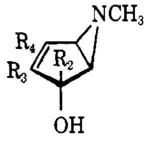
Received February 4, 1972

Photohydration of Pyridinium Ions[1]

Sir:

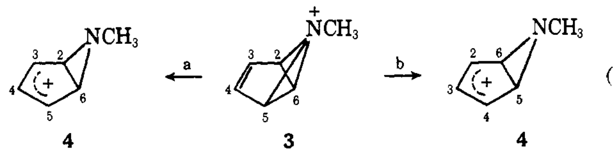
We wish to report that irradiation of methylpyridinium chloride in water at 254 nm yields 6-methylazabicyclo[3.1.0]hex-3-en-2-*exo*-ol (**1a**) with a quantum yield of about 0.1. Its methyl ether **2** is formed by irradiation in methanol. The methochlorides of the picolines and of 3,5-lutidine yield analogous products, **1b–e**. The alcohols are readily isolated by gas chromatography[2] of ethereal extracts. Since the photohydrations occur with appreciable quantum yields and can be carried to completion in basic solutions they provide a convenient route to the 6-azabicyclo[3.1.0]hexenyl system, only one example of which has been reported.[3]

The products are evidently formed by hydration of an azabicyclohexenyl cation **4**, but 1,2 shifts of nitrogen appear to precede formation of this ion in some cases. These shifts are in accord with the intervention of a 1-methylazoniabenzvalene (**3**) (eq 1). Photohydration of the pyridinium ion, perforce originating in π–π* excitation, is thus completely different from that of pyridine in which n–π* excitation[4] leads to a bicyclic valence isomer ("Dewar pyridine")[5] that is converted by hydration to an open-chain aminoaldehyde.[4,5] It instead resembles that of benzene,[6] in which hydration of the initially formed benzvalene[7–10] yields bicyclo[3.1.0]hex-3-en-2-*exo*-ol (**5**). Unlike the case of benzene, however, there is no indication that the azoniabenzvalene has an appreciable lifetime or that it rearomatizes.[7]



1

	R_2	R_3	R_4
a	H	H	H
b	CH_3	H	H
c	H	H	CH_3
d	H	CH_3	H
e	CH_3	H	CH_3



4 **3** **4**

In a typical photolysis, 40 ml of a solution 0.04 *M* in methylpyridinium chloride and 0.05 *M* in KOH was irradiated at room temperature in an annular vessel (2-mm path) with a G8T5 Hg resonance lamp. The uv absorption at 259 nm was reduced to one-half in 1 hr and to one-tenth in 2 hr. An ether extract showed a single gc product peak.[2] The product, **1a**, exhibits only end absorption in the uv; its mass spectrum shows a parent mass of 111 (C_6H_9NO) with a base peak at *m/e* 94. Its nmr spectra in D_2O[11] and CCl_4 are summarized in Table I. The assignment of its structure follows from the observations that there are only two olefinic protons, that the magnitude of the coupling between them is characteristic of a double bond in a C_5 ring, and that the chemical shifts of the bridge protons correspond to those in fused aziridine rings.[12] The stereochemistry at C_2 and the assignment of R_3 and R_4 follow from the similarity of the resonances to those,[13] δ 4.30, 5.47, and 6.13, in the corresponding carbocyclic compound **5**. The structures of the other products are readily deduced from the nmr data in Table I.

Table I. 100-MHz Nmr Spectra

		Chemical shifts, δ^a				
Compd	Solvent	NCH_3	Aziridine	R_2	R_3	R_4
1a	D_2O	2.29	2.61, 2.74^b	4.47	5.86^c	6.32
1b	D_2O	2.28	2.43, 2.63^b	(1.40)	5.67^c	6.16
1c	D_2O	2.28	2.55, 2.55	4.44	5.42	(1.89)
1d	D_2O	2.22	2.50, 2.50	4.21	(1.68)	5.84
1e	D_2O	2.29	2.38, 2.51^b	(1.37)	5.25	(1.85)
1a	CCl_4	2.32	~2.3	4.30	5.78	6.15
2^d	CCl_4	2.23	~2.2	4.00	5.71	6.12

^{a} Relative to internal $(CH_3)_3SiCD_2CD_2COONa$ in alkaline D_2O and to TMS in CCl_4; CH_3 resonances in parentheses. ^{b} $J_{1,5}$ = 5 Hz. ^{c} $J_{3,4}$ = 6 Hz. ^{d} OCH_3 resonance at δ 3.28.

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[1] Based on work performed under auspices of the U. S. Atomic Energy Commission.

[2] Retentions relative to aniline at 100° on Chromosorb G coated with Carbowax 750 (5%) and KOH (2%) are: **1a**, 1.35; **1b**, 0.48; **1c**, 1.57; **1d**, 1.96; **1e**, 0.59; **2**, 0.16.

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