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(6) J. M. Lalancette, M. J. Fournier-Breault, and R. Thiffault, *Can. J. Chem.*, **52**, 589 (1974). See also G. Henning, *J. Chem. Phys.*, **19**, 922 (1951).

(7) Under different conditions (heating to 70°) esterification proceeds at a fair rate. Temperature dependence of the reaction is under investigation.

(8) Polymer protected aluminum chloride serves a similar dual function in etherification: D. C. Neckers, D. A. Koolstra, and G. W. Green, *J. Amer. Chem. Soc.*, **94**, 9284 (1972).

(9) A. Casadevall, A. Commeyras, P. Paillous, and H. Collet, *Bull. Soc. Chim. Fr.*, 719 (1970).

(10) Epr spectra were recorded at 345.15 MHz on a slightly modified Alpha Scientific Laboratories Al 340 type spectrometer. For the sake of convenience, pyrocarbon was used instead of natural graphite for the spectral measurements. The known chemical properties of graphite bisulfate prepared from natural or artificial graphites (pyrocarbons) are identical.

(11) G. Henning, B. Smaller, and L. Yasaitis. *Phys. Rev.*, **54**, 1088 (1954).

(12) Associated to CNRS (ERA No. 070395).

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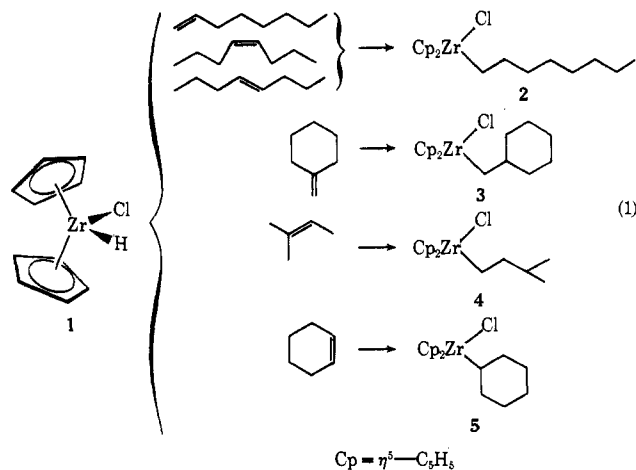*Université Paris-Sud*
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$$Cp = \eta^5\text{-}C_5H_5$$

Hydrozirconation. Organic Synthesis via Organozirconium Intermediates. Synthesis and Rearrangement of Alkylzirconium(IV) Complexes and Their Reaction with Electrophiles

Sir:

We wish to report our observations concerning the synthesis and reactivity of alkylzirconium(IV) complexes of the type $(\eta^5\text{-}C_5H_5)_2Zr(Cl)R$ which we have shown to be useful as intermediates in rational organic syntheses. These compounds are of significance in that they are inexpensive and easy to prepare, require only moderate care in their handling, and undergo a wide range of transformations to organic products under mild conditions and in high yield.

The organometallic complexes of interest herein were prepared by reaction of $(\eta^5\text{-}C_5H_5)_2Zr(Cl)H^{1-3}$ (1) with olefins (hydrozirconation). In each case, the position of attachment of the zirconium in the alkyl product obtained is that one in which the transition metal moiety is attached to the sterically least hindered, accessible[4] position of the olefin *as a whole*. Formation of this product involves either the regiospecific addition of Zr–H to a terminal olefin or addition to an internal olefin followed by rapid rearrangement *via* Zr–H elimination and readdition[5] to place the metal in the less hindered position of the alkyl chain. Whereas organoboron[6] or -aluminum[7] compounds positionally rearrange slowly at elevated temperatures, internally metalated zir-

conium analogs undergo this process rapidly at room temperature. Functionalization at this least hindered position[4] can then be effected by replacement of the zirconium moiety with various other structural groups.

Hydrozirconation proceeds as follows. Shaking a suspension of 892 mg of 1 (3.47 mmol) in 15 ml of benzene[8] with 351 mg of 1-octene (3.13 mmol) produces 2 after a few hours at room temperature (reaction 1).[9] In similar fashion, reaction of either *cis*- or *trans*-4-octene also produces 2. Zirconium migration in this system is fast and when the course of hydrozirconation is monitored by nmr, only the starting olefin and the ultimate 1-substituted alkyl are detected. This observation suggests that rearrangement of the postulated 4-substituted octane to 2 proceeds with an intrinsic rate at least as fast as olefin insertion into the Zr–H bond occurs. Other representative olefins react with 1 to yield the products shown in reaction 1.[10]

In contrast to their air-sensitive or pyrophoric boron or aluminum analogs, the alkylzirconium compounds described herein are not readily decomposed by dry air. They are susceptible to hydrolysis (to yield alkane) and are protonolyzed rapidly by dilute aqueous acid. It is by virtue of their ready reaction with a range of other electrophiles that these organometallic reagents play their role as valuable synthetic intermediates. For example, mixing a benzene solution of the alkylzirconium with Br_2, I_2, or $PhICl_2$ gives the alkyl halide as shown in Table I. In addition, the alkyl can be acylated in high yield by reaction with acetyl chloride. In each case, a $(\eta^5\text{-}C_5H_5)_2Zr(Cl)X$ species is recoverable which can be recycled to 1.

Applications are apparent of the reactions described herein in which 1 adds to an olefin and then rapidly migrates along the alkyl chain thereby produced to generate a versatile synthetic handle at an unhindered part of the alkyl

Table I

Olefin	Electrophile	Product	Yield,[a] %
1-Octene or 4-octene	H^+ [b]	Octane	100
	Br_2[c]	1-Bromooctane	96
	I_2[d]	1-Iodooctane	91
	$PhICl_2$[e]	1-Chlorooctane	65
	$CH_3C(O)Cl$[f]	2-Decanone	80
2-Methyl-2-butene	Br_2	1-Bromo-3-methylbutane	100
	$CH_3C(O)Cl$	5-Methyl-2-hexanone	72
Cyclohexene	Br_2	Bromocyclohexane	95

[a] Yields were determined by vpc and are based on $(\eta^5\text{-}C_5H_5)_2Zr(R)Cl$ species. [b] Dilute HCl at 0° (instantaneous). [c] Br_2 added slowly at 0° (instantaneous). [d] Alkyl added to I_2–CCl_4 at room temperature (fast). [e] Solid $PhICl_2$ added at room temperature (fast). [f] As 1.5 equiv of $CH_3C(O)Cl$ in C_6H_6 added at room temperature (slow).

chain. Hydrozirconation may thus prove to be an attractive alternate to published synthetic procedures employing hydroboration or hydroalumination, especially when facile rearrangement of the functionalization unit in the alkyl intermediate is desired.

References and Notes

(1) B. Kautzner, P. C. Wailes, and H. Weigold, *Chem. Commun.*, 1105 (1969).
(2) Vitride, 0.5 mol, is added slowly to a solution of 1.0 mol of Cp₂ZrCl₂ in THF. The white precipitate of 1 is filtered, washed with THF, benzene, and ether and then vacuum dried. It reacts with moisture and is slightly light sensitive.
(3) A reaction of 1 with three olefins was reported, but the alkylzirconium products were not properly characterized, and the product of reaction of 1 with 2-methyl-2-pentene was incorrectly assigned: (P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, **43**, C32 (1972).
(4) We have not observed metal migration past a 3° (or 4°) carbon at room temperature.
(5) For example, see C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971), and references cited therein.
(6) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **89**, 561 (1967), and references cited therein.
(7) L. I. Zakharkin and O. Y. Okhlobystin, *Bull. Acad. Sci. USSR*, 1236 (1958).
(8) Solvents were distilled from sodium benzophenone ketyl under argon. For benzene, this was made possible by admixing 5% tetraglyme. All reactions were performed under an argon atmosphere.
(9) Products, which were pale yellow oils, were characterized by nmr (δ_{Cp} = 5.9; δ_{Zr-CH_2} = 0.9–1.2; an impurity, arising in the preparation of 1 has δ_{Cp} = 6.1) and by comparison of bromination products with known materials. Yields of alkyl in excess of 90% have been obtained.
(10) Relative rates for olefin reaction with 1 at room temperature are: 1-octene > *cis*-4-octene ≳ *trans*-4-octene > methylenecyclohexane > cyclopentene > cyclohexene ≫ 2-methyl-2-butene. Hydrozirconation of hindered olefins can be facilitated by reaction at 40°. The order of reactivity of various olefins with 1 may reflect relative ease of fitting bulky olefins into a somewhat sterically crowded bent "sandwich" structure. Indeed, 1-methylcyclohexene and tetramethylethylene fail to react with 1 even when heated to 40° overnight. Cyclooctene also fails to react with 1 under these conditions.

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1H-Cyclobuta[de]naphthalene
**(1,8-Methanonaphthalene)**

Sir:

The interatomic distance between the hydrogen atoms at the C_1 and C_8 positions in naphthalene is 2.40 Å.[1] There are as yet few examples in which the peri positions of naphthalene or its analogs have been bridged by one atom. Naphth[1,8-*bc*]oxete (**1**, 1,8-monoxynaphthalene) is reported to be a product of dehydration of 1,8-naphthalenediol;[2a] however, its synthesis cannot be repeated.[2b] Naphtho[1,8-*bc*]thiete 1,1-dioxide (**2**, 1,8-sulfononaphthalene) has been prepared and gives products of 1,8-dehydronaphthalene upon thermolysis.[3] We now report synthesis of 1-bromo-1H-cyclobuta[*de*]naphthalene (**3**) and 1H-cyclobuta[*de*]naphthalene (**4**, 1,8-methanonaphthalene), the first examples of naphthalene bridged in its 1,8-positions by single carbon atom moieties.[4]
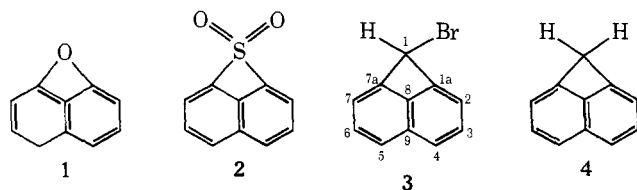
Irradiation (450-W mercury lamp through Pyrex, N₂) of the sodium salt (**6**) of 8-bromo-1-naphthaldehyde *p*-tosylhydrazone (mp 193–195°)[5] or (8-bromo-1-naphthyl)diazomethane (**7**)[6] in ethyl ether yields **3** (45%) along with *trans*-bis(8-bromo-1-naphthyl)ethylene (**5**, 15%, mp 203–204°).[7] Strained bromide **3** is possibly formed from (8-bromo-1-naphthyl)methylidene (**8**) as in eq 1. Bromide **3** is
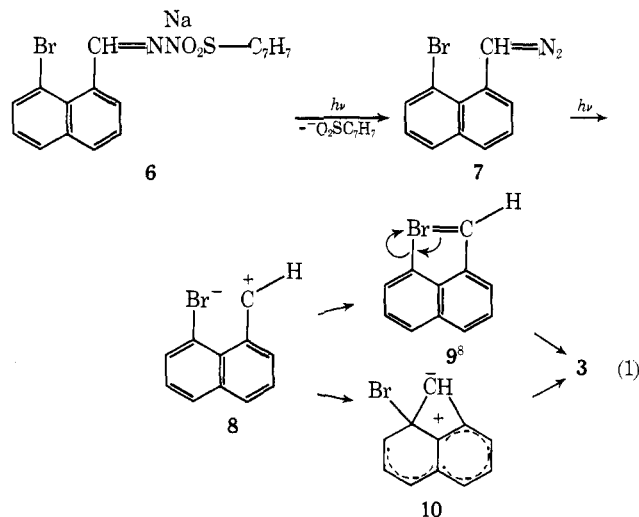
white (mp 102–104° from ethanol after chromatography on silica gel)[5] and of the following properties:[9a] *m/e* 218, 220 (M⁺, theory 218), 139 (M⁺ − Br); mol wt (osmometry) 215 (CHCl₃); nmr (CDCl₃) δ 6.76 (s, 1 H, H at C_1), 7.18 (d of d, 2 H, H at $C_{2,7}$, J = 5 and 2 Hz), 7.30–7.68 (m, 4 H, H at C_{3-6}); ¹³C nmr (CDCl₃) δ 51.9 (1 C, C_1), 115.8 (2 C, $C_{2,7}$), 122.9 (2 C, $C_{4,5}$), 126.3 (1 C, C_9), 131.4 (2 C, $C_{3,6}$), 143.6 (2 C, $C_{1a,7a}$), 145.1 (1 C, C_8). The structure of **3** is confirmed by its rapid reaction with silver nitrate in aqueous dioxane at 40° to give 1-naphthaldehyde (**12**, 25%), 1-(1H-cyclobuta[*de*]naphthyl) nitrate (*m/e* 201, theory 201; ir (KBr) 1630, 1275, 865, 790 cm⁻¹), and silver bromide; **12** apparently arises by isomerization (eq 2) of 1-hydroxy-1H-cyclobuta[*de*]naphthalene (**11**). Alcohol **11** is an (expletive deleted) unstable compound.
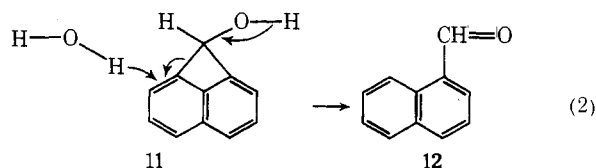
Reaction of **3** with magnesium in ethyl ether, hydrolysis with aqueous ammonium chloride, and gas chromatography at 135° yields **4** (60%), a colorless liquid:[9b,10] *m/e* 140.0628 (M⁺, theory 140.0626); nmr (CDCl₃) δ 4.80 (s, 2 H, H at C_1), 7.1 (d of d, 2 H, H at $C_{2,7}$, J = 5 and 2 Hz), 7.25–7.65 (m, 4 H, H at C_{3-6}); ¹³C nmr (CDCl₃) δ 47.31 (1 C, C_1, $J_{C^{13}-H}$ = 143.4 Hz), 117.08 (2 C, $C_{2,7}$), 121.29 (2 C, $C_{4,5}$), 125.44 (1 C, C_9), 130.57 (2 C, $C_{3,6}$), 141.57 (2 C, $C_{1a,7a}$), and 146.27 (1 C, C_8). The 90-MHz pmr spectrum of **4** reveals that its apical protons do not display an AB pattern. Further the proton-coupled ¹³C nmr spectrum of **4** shows the apical carbon to be a triplet rather than a doublet of doublets, indicating that its C_1 protons are magnetically equivalent. The strained hydrocarbon, **4**, is thus essentially planar or of a rapidly equilibrating puckered conformation. The uv spectra of **3** and **4** are compared in Table 1 with naphthalene (**13**). The slight shift to longer wavelengths and the significant decrease in the extinction coefficient of the E_1 bands of **3** and **4** are indicative of perturbed π electron systems.