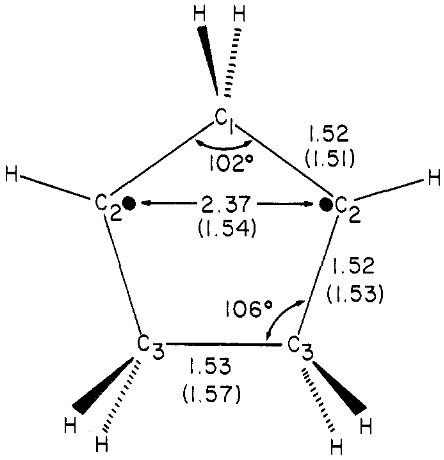


Figure 2. Predicted equilibrium geometry of Closs's diradical, 1,3-cyclopentadiyl. In parentheses is given the experimental (r_s) structure of the related closed-shell singlet molecule bicyclo[2.1.0]pentane. Bond distances are given in ångstroms. Omitted for clarity is the 113° $C_1C_2C_3$ angle.

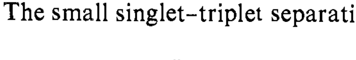
Table I. Relative Energies of Several Electron Configurations of 1,3-cyclopentadiyl. The Triplet-State Total Energy Was −193.84905 Hartrees

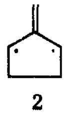
electronic confign and state	rel energy, kcal
$2a_23b_1$ $^1B_2$	142.2
$2a_2^2$ $^1A_1$	90.9
$3b_1^2$ $^1A_1$	85.6
$c_12a_2^2 + c_23b_1^2$ $^1A_1$	0.9
$2a_23b_1$ $^3B_2$	0.0

Perhaps more important, the C_2–C_2 distance is a full 0.83 Å longer than in the bicyclo species. This C_2–C_2 distance of 2.37 Å is in fact only slightly less than the separation of ~2.48 Å expected[16] for cyclopentane. Thus we see that triplet 1,3-cyclopentadiyl has a structure consistent with features classically anticipated on the basis of the known structures of these two closed-shell singlet molecules.

At the predicted triplet equilibrium geometry, an examination of the other diradical states[17] was carried out. It was found (see Table I) that the two closed-shell singlet configurations are nearly degenerate and rather high lying, at 85.6 and 90.9 kcal, respectively, above the $^3B_2$ state. However the relative energy of the lowest $^1A_1$ state is radically lowered by the more appropriate[18] two-configuration SCF treatment. There the coefficients of the . . .$2a_2^2$ and . . .$3b_1^2$ configurations are nearly equal, −0.70 and 0.71. By this criterion, Closs's singlet diradical at this geometry is almost perfectly diradical-like in character. The theoretical value of 0.9 kcal for the singlet-triplet separation $\Delta E(^3B_2-^1A_1)$ is at best reliable to ±3 kcal. Nevertheless it is impossible to deny the fact that our prediction is in remarkably close agreement with the experimental deduction (seen in Figure 1) of Buchwalter and Closs.[7]

After completing this research, it occurred to us that Closs's diradical is structurally related to the unsubstituted trimethylenemethane (TMM) (eq 1). In fact this analogy is nearly as close as that between the primitive TMM and Berson's TMM[19] (**2**). The small singlet-triplet separation for 1,3-cyclopentadiyl suggests that ΔE(S–T) for Berson's TMM might be significantly less than that for the primitive TMM. This would nicely resolve a smoldering discrepancy between theory[20] and experiment.[19]


(1)


2

Acknowledgment. We thank Professor G. L. Closs for permission to reproduce Figure 1 and Professors R. G. Bergman and J. A. Berson for helpful discussions. This research was supported by the National Science Foundation Grant CHE-762261.

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Received December 22, 1978

Nickel-Induced Conversion of Carbon–Oxygen into Carbon–Carbon Bonds. One-Step Transformations of Enol Ethers into Olefins and Aryl Ethers into Biaryls

Sir:

In connection with a general study of the Felkin reaction—the replacement of the hydroxy group of allyl alcohols by hydrogen or an alkyl function in the reaction of Grignard reagents with such alcohols in the presence of phosphine-ligated nickel dichloride[1]—a new reaction was encountered, involving the substitution of alkoxy groups bound to carbon-carbon double bonds by alkyl and aryl units.[1a,2] Hence there was undertaken an investigation of the reactions of phenylmagnesium and methylmagnesium bromides with enol and aryl ethers induced by bis(triphenylphosphine)nickel dichloride, the results of which are presented herewith.

As Table I indicates,[3] various types of enol ethers are susceptible to cleavage and arylation or alkylation, leading to olefins in high yield. The replacement of the alkoxy or aryloxy group of the aldehyde enol ethers yields mainly olefins with

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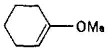
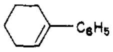
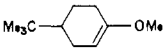
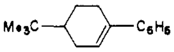
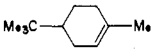
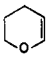
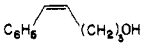
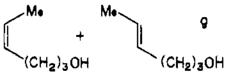
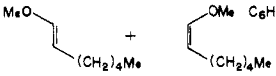
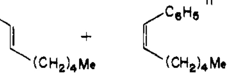
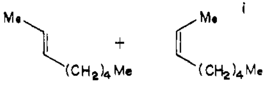
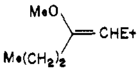
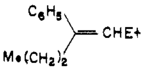
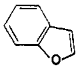
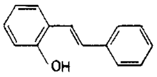
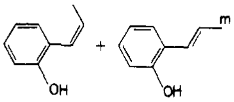
Table I. The Reactions of Enol Ethers with Phenylmagnesium and Methylmagnesium Bromides[a]

Ether	Olefinic Products		% Yield
		b	71
		c	75
		d	59[e]
			64[f]
	 3.1 : 1	g	74[f]
 1.3 : 1	 1.7 : 1	h	79
	 1.4 : 1	i	66
		j	86
$C_6H_5OCH{=}CH_2$	$C_6H_5CH{=}CH_2$		93[k]
		l	61
	 4.0 : 1	m	75

[a] A benzene solution of ~2 mol of Grignard reagent and 0.1 mol of bis(triphenylphosphine)nickel dichloride/mol of enol ether was refluxed for 15–48 h. Isolated olefin yields are based on the initial enol ether quantity. [b] P. Markov, L. Dimitrova, and C. Ivanov, *Monatsh. Chem.*, **107**, 619 (1976). [c] P. Geneste, J. M. Kamenka, P. Herrmann, and J. Moreau, *Recl. Trav. Chim. Pay-Bas*, **95**, 116 (1976). [d] Y. Kitagawa, S. Hashimoto, S. Iemura, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **98**, 5030 (1976). [e] Reaction time 168 h. [f] 1:2 Grignard reagent-ether. [g] B. Chantegrel and S. Gelin, *Bull. Soc. Chim. Fr.*, 2639 (1975). [h] T. H. Chan and E. Chang, *J. Org. Chem.*, **39**, 3264 (1974). [i] R. B. Bates and W. A. Beavers, *J. Am. Chem. Soc.*, **96**, 5001 (1974). [j] I. I. Lapkin and M. N. Rybakova, *Zh. Obshch. Khim.*, **30**, 1227 (1960). [k] GC yield; GC yield of phenol 62%. [l] W. E. Truce and C.-I. M. Lin, *J. Am. Chem. Soc.*, **95**, 4426 (1973). [m] P. Golborn and F. Scheinmann, *J. Chem. Soc., Perkin Trans. 1*, 2870 (1973).

Table II. The Reactions of Aryl Ethers with Phenylmagnesium Bromide[a]

ether	products	% yield
1-methoxynaphthalene	1-phenylnaphthalene	70
2-methoxynaphthalene	2-phenylnaphthalene	77[b]
2,3-dimethoxynaphthalene	2,3-diphenylnaphthalene[c]	45
m-dimethoxybenzene	*m*-methoxybiphenyl	23 (79)
p-dimethoxybenzene	*p*-methoxybiphenyl,	33 (37)
	p-terphenyl	24 (27)
p-methoxybiphenyl	*p*-terphenyl	30 (55)
m-cresyl methyl ether	*m*-methylbiphenyl	16 (74)
p-cresyl methyl ether	*p*-methylbiphenyl	20 (60)

[a] A benzene solution of 2–4 mol of Grignard reagent and 0.1 mol of bis(triphenylphosphine)nickel dichloride/mol of aryl ether was refluxed for 72 h. Isolated product yields are based on the initial ether quantity, whereas those listed in parentheses take into account recovered ether. [b] Reaction time 24 h. [c] H. M. Crawford, *J. Am. Chem. Soc.*, **61**, 608 (1939).

retention of configuration.[4] The reactions of phenylmagnesium bromide with highly substituted enol ethers, with enolates, and with enamines, as exemplified by 2,6-dimethyl-1-methoxycyclohexene, magnesium 2-methyl-1-propenyl oxide, and 1-(*N*-pyrrolidino)cyclohexene, respectively, do not take place, whereas the reaction with 1-trimethylsilyloxycyclohexene yields the arylation product, albeit in low (35%) yield.

As in the experience of the Felkin reaction with alkylmagnesium halides bearing labile β hydrogens,[1a,c] the reaction of dihydropyran and ethylmagnesium bromide affords alkylation product (*Z*)-4-hepten-1-ol, accompanied by reduction product 4-penten-1-ol (in 1.5:1 ratio and 55% yield). The efficiency of alkylation is enhanced by the use of bis(1,3-diphenylphosphino)propanenickel dichloride as catalyst (5.7:1 ratio, 74% yield).

Although aryl ethers are inert to methylmagnesium bromide, they are attacked by phenylmagnesium bromide in the presence of bis(triphenylphosphine)nickel dichloride. As revealed by Table II, the substitution of methoxy groups is more efficient in the naphthalene nucleus than in the benzene ring. Not only does the reaction take place faster on methoxynaphthalenes than methoxybenzenes, but it even occurs on a vicinal dimethoxynaphthalene in the face of the inertness of *o*-dimethoxybenzene and *o*-cresyl methyl ether. Exposure of β-naphthyl *p*-toluenesulfonate[5] and even magnesium β-naphthoxide to phenylmagnesium bromide in the presence of the nickel catalyst leads to β-phenylnaphthalene in 60 and 16% yield, respectively.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(3) New compounds gave satisfactory elemental and spectral analyses.

(4) Whereas the product of the ring opening of benzofuran is one of inversion of configuration, it may be the outgrowth of the isomerization of an initially formed *cis*-stilbene under the reaction conditions.

(5) The isolation of *p*-methylbiphenyl indicates the attack of the Grignard reagent to occur also at the site of the aryl–sulfur bond.

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Received November 20, 1978

Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 4. Chiral Silylcyclopentadienes: New Evidence for a 1,2 (1,5) Metallotropic Shift

Sir:

Over the course of the past 20 years, the fluxional nature of *monohapto*cyclopentadienyl derivatives of a range of both transition and nontransition metals has been clearly established through application of variable-temperature NMR techniques.[1] While such dynamic behavior has been thoroughly characterized as metallotropic[2] and intramolecular,[3,4] the mechanism of the degenerate rearrangement has remained

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