

Table II. Aromatic Group Enthalpies of Transfer from Vapor to Solvents^a

Compound (substituent)	Group polarizability ^b	Group molar volume ^c	$\Delta\Delta H$			
			$v \rightarrow c\text{-C}_6\text{H}_{12}$ ^d	$v \rightarrow \text{Bz}$ ^d	$v \rightarrow \text{MeOH}$ ^d	$v \rightarrow \text{DMF}$ ^d
Benzene			(-7.15)	(-8.09)	(-7.73)	(-8.05)
Me	4.9	17.5	-1.16	-0.87	-0.90	-0.87
1,4-Me ₂	4.9	17.5	-1.06	-0.90	-0.90	-0.87
1,3,5-Me ₃	4.9		-0.99	-0.88	-0.86	-0.82
<i>c</i> -C ₆ H ₁₂			(-7.91)	(-7.01)	(-6.70)	(-6.04)
<i>c</i> -C ₆ F ₁₁ CF ₃			(-3.9)	(-2.2)	(-3.7)	(-1.7)
F	0	5.0	-0.24	-0.38	-0.73	-0.75
Cl	5.0	12.9	-2.12	-2.05	-2.27	-2.37
Br	7.2	16.2	-2.65	-2.73	-2.84	-2.97
I	13.1	23.0	-3.39	-3.56	-3.61	-4.16
CF ₃	4.6	34.1	-0.17	-0.33	-1.30	-0.94
COCH ₃	10.3	28.0	-2.90	-4.74	-4.26	-5.24
NO ₂	6.7	13.5	-3.19	-4.54	-4.46	-5.29
COOEt	16.4	53.9	-5.41	-5.96	-5.16	-5.74
NH ₂	4.4	23.0	-1.60	-3.63	-5.86	-7.60
OH	1.6 ^e		+0.07	-2.72	-6.92	-8.69

^a Values in kcal/mol. Estimated accuracy $\pm 0.1\text{--}0.2$ kcal/mol. ^b Values calculated from Lorenz-Lorentz equation. Polarizability $C_6H_5X - C_6H_6$. ^c Group molar volume (in ml) = $MV(C_6H_5X) - MV(C_6H_6)$. ^d Based on ΔH_v values from R. R. Dreisbach, *Advan. Chem. Ser.*, No. 15 (1955). Values in parentheses are for entire molecules; others are those of individual groups. ^e Calculated from polarizability of *m*-cresol - toluene.

(ΔH_v) to give enthalpies of transfer for the compounds from the vapor state to solutions in DMF, MeOH, benzene, and cyclohexane, using the relationship $\Delta\Delta H(\text{vap} \rightarrow S) = \Delta H_s(S) - \Delta H_v$. Since the transfer values from vapor to solution are at least approximately additive (see results for $-\text{CH}_3$, Table II), it is possible to discuss $\Delta\Delta H(\text{vap} \rightarrow S)$ in terms of group contributions, where $\Delta\Delta H(X) = \Delta\Delta H(C_6H_5X) - \Delta\Delta H(C_6H_6)$. Group $\Delta\Delta H_s$ values, along with values for the molecules benzene, cyclohexane, and perfluoro(methylcyclohexane) are given in Table II.

The quantity $\Delta\Delta H(\text{vap} \rightarrow S)$ is usually taken as equal to the enthalpy of solvation, although it also includes a term for the "hole" energy in that solvent. Solvation enthalpies of neutral molecules are small compared with those of typical ions, but $\Delta\Delta H_s(S_1 \rightarrow S_2)$ may be comparable. In the transfer of the reaction of a benzene derivative with an ion from one solvent to another, rate changes may result from changes in solvation of both reacting species, as well as that of the transition state.

A number of interesting conclusions regarding the solvation of functional groups can be drawn from the data in Table II. (I) A principle solvation interaction for hydrocarbon molecules and groups as solutes is dispersion interactions. These are comparable for solute benzene and cyclohexane. Dipole-induced dipole forces cause a more exothermic interaction of solute benzene with DMF than with cyclohexane. The less polarizable solute cyclohexane has a less exothermic interaction with DMF, reflecting the rather large solvent-solvent forces and "hole" energy in this solvent. This effect is still more pronounced in the case of perfluoro(methylcyclohexane). (II) The enthalpies of solvation of polar and nonpolar substituents in the nonpolar solvent cyclohexane roughly parallel the group polarizabilities and must, therefore, result largely from dispersion interactions. (III) Substituents with large dipole moments ($-\text{COCH}_3$, $-\text{NO}_2$) interact more strongly with the polarizable or polar solvents, benzene, MeOH, and DMF, than with cyclohexane. (IV) The hydrogen bond donor groups OH and NH₂ undergo large increases in solvation upon transfer

from cyclohexane to solvents of greater polarity and basicity. Nearly half of the solvation enthalpy of *m*-cresol in DMF results from the interactions of solvent with the hydroxyl group.

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Edge Participation by a β -Cyclobutene Ring in a 7-Norbornenyl System

Sir:

Edge participation by a cyclobutene ring at an incipient carbonium ion has been demonstrated in the 7-norbornenyl system.^{1,2} Product studies indicate an intermediate trishomocyclopropenyl type cation. However, because of degenerate rearrangements of the intermediate species, conclusive evidence about the nature of the developing carbonium ion could not be given.^{1,2} In a previous communication we described the capability of a methoxy group attached to the cationic center to cancel neighboring group participation and consequently suppress rearrangement of the cation.³ We now wish to report the generation and direct observation of the 9-ethoxy-*endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl carbonium ion, III (Figure 1).

9-Ethoxy-9-chloro-*endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene, prepared from diethoxy compound I⁴ and PCl_5 or SOCl_2 , was dissolved in liquid SO_2 at -60° and observed by nmr. The downfield shift of the methylene protons of the ethoxy group (δ 5.11) indicates a posi-

(1) M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970).

(2) M. A. Battiste and J. W. Nebzydoski, *J. Amer. Chem. Soc.*, **92**, 4450 (1970).

(3) P. Schipper, W. A. M. Castenmiller, J. W. de Haan, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 574 (1973).

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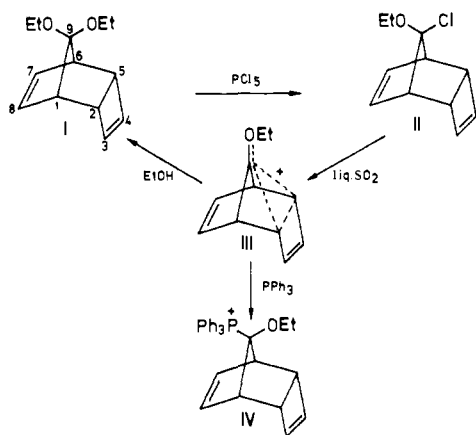


Figure 1.

tively charged structure, caused by ionization of the C-Cl bond. The structure of 9-ethoxy-*endo*-tricyclo-[4.2.1.0^{2,5}]nona-3,7-dien-9-yl cation is assigned to ion III on the basis of its nmr data compared to those of the 7-methoxy-7-norbornenyl cation, V.⁵ Furthermore, addition of ethanol gives exclusively the starting material I, indicating no rearrangement reactions. This communication presents evidence that cation III has a nonclassical structure as depicted in the appropriate figure with the positive charge partially delocalized over the 9 and 2,5 positions.

The nmr spectral data for ion III are given in Figure 2 together with the data for the related ion V and the ketal I. The proton pairs H_{1,6} and H_{2,5} of III are, similar to the bridgehead protons of ion V, nonequivalent on each side of the ion because of restricted rotation around the C-O bond.⁵

The chemical shift of the vinyl protons H_{7,8} (δ 5.97) of III indicates little charge delocalization on these positions. However, the downfield shift of the cyclobutenyl protons H_{2,5} (δ 4.14-4.4) with respect to the ketal I seems too large to be caused by a localized charge at C₉, especially since the charge at this center is stabilized by a strong electron donating group like the ethoxy group. A further indication is obtained from the considerable changes within the H₂-H₅ four-spin system, where a triplet is found for the olefinic protons H_{3,4} ($J = 2.4$ Hz) instead of the broad singlet which is usually found for the olefinic absorptions of cyclobutenyl systems.⁶ We prefer to ascribe this phenomenon to rehybridization, intrinsic charge effects, or both as a consequence of charge delocalization.⁷

Additional evidence concerning charge delocalization is provided by product studies of nucleophilic reactions on ion III. We used PPh₃ as a nucleophile

(5) R. K. Lustgarten, M. Brookhart, and S. Winstein, *Tetrahedron Lett.*, 141 (1971).

(6) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972); R. M. Coates and K. Yano, *ibid.*, **95**, 2203 (1973); E. W. Turnblom and T. J. Katz, *ibid.*, **95**, 4292 (1973).

(7) In spite of the molecular asymmetry caused by the alkoxy group (*vide supra*), chemical shifts of H₃ and H₄ turn out to be equivalent, the same applies to H₇ and H₈. As a result, the olefinic part of the spectrum of III shows two triplets. The separation between the outer two lines of a triplet is given by the absolute value of the sum of four different coupling constants. In many cyclobutenyl systems a broad singlet is observed indicating almost equal absolute values and different signs of the allylic and vicinal couplings. Correlations between $J_{3,4}$ (J_{23}) and stereochemistry are rather difficult because of the dual-pathway character of this interaction.

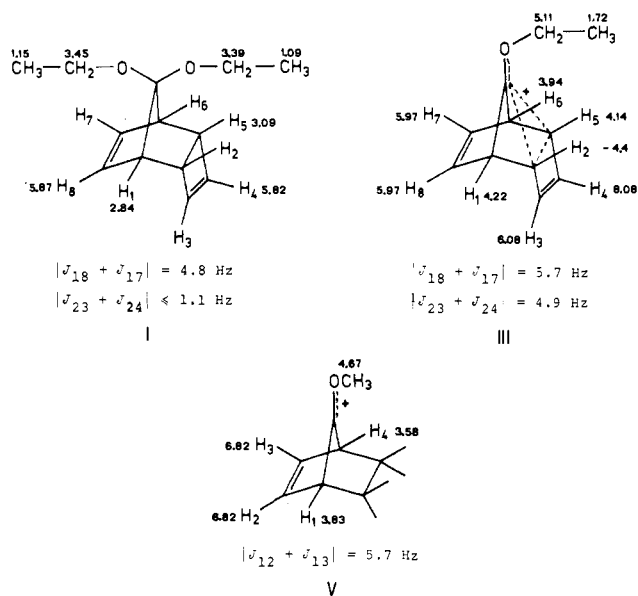


Figure 2. Nmr spectral data for cations III and V⁵ and ketal I in liquid SO₂ at -50° with TMS as internal standard.

because long range P-H couplings allow easy identification of the resulting phosphonium salt and also in order to make a comparison with earlier work.³ It appeared that ion III yields only a product with the substituent in anti position to the cyclobutene moiety, whereas ion V, a classical ion, yields a mixture of the two isomers.³

Edge participation by the cyclobutene ring is also indicated by the relative ease with which cation III is formed, with respect to other comparable cations like the 7-methoxy-7-norbornenyl cation, V, and the 7-methoxy-7-norbornadienyl cation, VI. Ion V was not observed when its 7-chloro-7-methoxy substituted precursor was dissolved in liquid SO₂. Under these conditions an exchange takes place between the two isomers of 7-chloro-7-methoxynorbornene which indicates the existence of cation V as an intermediate species. Thus cation V is insufficiently stabilized to be a long-lived species under these conditions. Recently, we made the same observations for cation VI. The carbonium ion stabilizing ability of methoxy and ethoxy groups appeared to be equal.⁸ From this we may conclude that in 7-methoxy-substituted norbornyl cations the charge is more stabilized by an endo fused cyclobutene ring than by a double bond.

The explanation can be found in the difference in orbital orientation of these functional groups. The bent-bond orbitals of cyclobutene are, similar to cyclopropane,⁹ more directed toward the cationic center than the p orbitals of the double bond in V. The structure of VI has been established to be symmetric. In this configuration there is a maximum overlap between the orbitals at C₇ and the methoxy group,¹⁰ The resulting minimum overlap between the orbitals at C₇ and the double bond permits little charge delocalization onto the

(8) Replacement of the ethoxy group by a methoxy group in ion III yields similar results. However, we describe here the ethoxy substituted compound because in this case ion III is generated in a more pure state.

(9) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969).

(10) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **94**, 2347 (1972).

olefinic group. In ion III the same arguments are valid for interaction with the $C_{7,8}$ double bond. However, the bent-bond orbitals of cyclobutene in III turn out to be more suitable to overlap with C_7 in an unbridged configuration.

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A New Method for the Reductive Coupling of Carbonyls to Olefins. Synthesis of β -Carotene¹

Sir:

The reactivity of $LiAlH_4$ as a reducing agent can be greatly modified by addition of metal salts. It is well known, for example, that a reagent prepared from $LiAlH_4$ and $AlCl_3$ is capable of reducing α,β -unsaturated ketones to olefins.² We have recently been involved in a study of $TiCl_3$ as a reducing agent in organic synthesis,³⁻⁵ and we therefore thought it would be of interest to examine the reactivity of a $LiAlH_4$ - $TiCl_3$ reagent.

One equivalent of powdered $LiAlH_4$ was added to a stirred slurry of 2 equiv of $TiCl_3$ under nitrogen in dry THF. Instantaneous reaction occurred accompanied by the evolution of heat and gas and by a rapid color change to deep black. After addition of a THF solution of 1 equiv of benzophenone, followed by 4 hr of reflux, we isolated a 95% yield of tetraphenylethylene (mp 220-221°; lit.⁶ 220°). This remarkable result is preceded only by the recent report of Sharpless⁷ on the reductive coupling of aromatic ketones using low-valency tungsten complexes.⁸ Our reaction, however, appears to work equally well for both saturated and unsaturated ketones. Some results are given in Table I.

One result in particular requires comment. Adamantylideneadamantane (**8**) was produced in 85% yield from 2-adamantanone. This olefin is of current interest,⁹⁻¹¹ and our synthesis is an improvement over the multistep methods which now exist for its preparation.^{12,13}

(1) The material covered in this communication is the subject of a U. S. Patent Application filed by the Regents of the University of California.

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(3) L. C. Blaszcak and J. E. Mc Murry, *J. Org. Chem.*, **39**, 258 (1974).

(4) J. E. Mc Murry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).

(5) J. E. Mc Murry and J. Melton, *J. Org. Chem.*, **38**, 4367 (1973).

(6) A. Orekhoff, *Bull. Soc. Chim. Fr.*, **25**, 86 (1919).

(7) K. B. Sharpless, M. A. Umbreit, M. T. Nich, and T. C. Flood, *J. Amer. Chem. Soc.*, **94**, 6538 (1972).

(8) Two alternate procedures for reductively coupling aromatic ketones to olefins with titanium-based reagents have recently appeared: S. Tyrlik and I. Wolochowicz, *Bull. Soc. Chim. Fr.*, 2147 (1973); T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, 1041 (1973). Neither of these procedures appears capable of coupling aliphatic ketones, however.

(9) A. P. Schaap and G. R. Faler, *J. Amer. Chem. Soc.*, **95**, 3381 (1973).

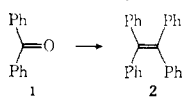
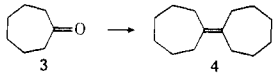
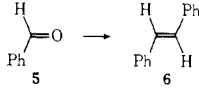
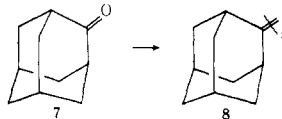
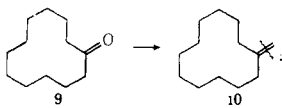
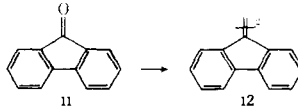
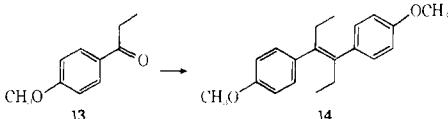
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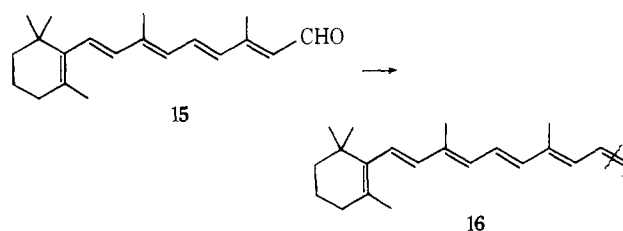
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(13) H. W. Geluk, *Synthesis*, 652 (1970).

Table I. Some Reactions of Carbonyl Compounds with $LiAlH_4$ - $TiCl_3$

	% yield
	95
	95
	85
	85
	80
	95
	85

The coupling reaction is probably limited to the synthesis of symmetrical olefins but even so should prove valuable. β -Carotene (**16**) for example is a symmetrical



polyolefin of commercial importance as a food coloring agent and is generally prepared by a multistep route from vitamin A.¹⁴ We therefore subjected retinal (**15**) to treatment with the $LiAlH_4$ - $TiCl_3$ reagent and isolated β -carotene in 85% yield (mp 180-182°; lit.¹⁵ 183°). Multiple unsaturation in the substrate is clearly compatible with the reaction.

A detailed understanding of the reaction mechanism must await knowledge of the nature of the reagent. The course of the reaction can be readily accounted for, however, if one assumes that Ti(II) species are involved.¹⁶ Ti(II) is a strong reducing agent [$Ti^{2+} = Ti^{3+} + e^-$; 0.37 V] and should be capable of effecting a pinacol reduction to an intermediate diol. Further reduction, either through formation of a cyclic Ti(II)

(14) For a listing of β -carotene syntheses, see O. Isler, Ed., "Carotenoids," Birkhauser Verlag, Basel, 1971, Chapter 6.

(15) "The Merck Index," 8th ed, Merck and Co., Rahway, N. J., 1968, p 213.

(16) $TiCl_3$ alone is not responsible for the reaction as we determined in a control reaction on cycloheptanone.