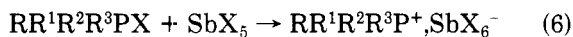
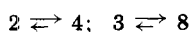


similar to those used in this investigation there is little interaction within the ion pair involved in the phosphonium salt.^{3b} In the case of a phosphorane structure 2, one should expect a dramatic change in chemical shift after addition of antimony pentachloride due to a transformation into a lower coordination state as clearly demonstrated before with the aid of suitable models⁵ (eq 6).



The phosphonium hexachloroantimonate 7 was isolated at -10°C as colorless crystals which were sensitive to air or moisture. The phosphonium hexabromoantimonate 5 and its chlorine analogue 7 are stable at ambient temperature, owing to the low P nucleophilicity of the counterion, and do not undergo subsequent changes leading to a complex mixture as is observed for 4 and 6. The compounds of the phosphonium structure 4 and 6 are also present in the reaction of 1 with halogens at room temperature. For example, in our hands the reaction between 1 and equimolar amounts of elemental bromine under this condition gave the same ^{31}P NMR spectrum as given by Tseng. After 0.5 h at 20°C two major peaks, $\delta(^{31}\text{P})$ 2.8 and $\delta(^{31}\text{P})$ -22.6 , were observed which must be ascribed to the phosphonium salt 4 and another phosphonium salt $(\text{PhO})_4\text{P}^+\text{Br}^-$ (8).⁶

For this reason the scheme of Tseng^{2g} presented in the introduction of this paper should be amended by adding to the equilibrium equation containing the phosphorane structures 2 and 3, an equilibrium reaction further illustrating the collapse of 2 and 3 into their respective phosphonium species 4 and 8. This equilibrium should be strongly shifted in favor of the phosphonium structure:



Experimental Section

General Methods. All solvents were purified by conventional methods. All reactions were carried out in sealed tubes, and standard vacuum techniques were used throughout. ^{31}P NMR spectra were recorded at 24.3 MHz with a JEOL R-60H spectrometer operating in the pulsed FT mode. A heteronuclear spin decoupler, JNM-SD-HC, was used for chemical shift determinations and integration. All spectra were recorded on samples which were approximately 0.5 M in reagent, i.e., 0.001 mol of the compound in 2 mL of a solvent. The chemical shifts downfield from the 85% phosphoric acid standard are reported as positive values and those upfield as negative values.

Chlorotriphenoxyphosphonium Hexachloroantimonate (7). To a stirred solution of triphenyl phosphite (3.1 g, 0.01 mol) in methylene chloride-ether (3:1, 6 mL) at -78°C under argon is added elemental chlorine (0.71 g, 0.01 mol). The mixture is stirred for 10 min, and then antimony pentachloride (3 g, 0.01 mol) in methylene chloride (2 mL) is added over 20 min at -78°C . The white crystals which separated at -10°C are washed with anhydrous ether to yield 7 (5.05 g, 75%). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{Cl}_7\text{O}_3\text{PSb}$: C, 31.8; H, 2.25; P, 4.55; Cl, 36.5. Found: C, 31.65; H, 3.0; P, 3.50; Cl, 36.5.

Registry No. 1, 101-02-0; 7, 18556-97-3; chlorine, 22537-15-1; bromine, 10097-32-2.

(5) For example: R, R¹ = *o*-phenylene and R² = R³ = X = Br [$\delta(^{31}\text{P})$ -189 (P^V), $\delta(^{31}\text{P})$ 20.6 (P^{IV})], J. Gloede and H. Gross, *J. Prakt. Chem.*, **320**, 140 (1978); R, R¹ = *o*-phenylene, R² = OEt, and R³ = X = Br [$\delta(^{31}\text{P})$ -104 (P^V), $\delta(^{31}\text{P})$ 37 (P^{IV})].^{3c}

(6) The chemical shift value for 8 is identical with that of the phosphonium cation described by other authors: L. Kolditz, K. Lehmann, W. Wicker, and A.-R. Grimmer, *Z. Anorg. Allg. Chem.*, **360**, 259 (1968); L. V. Nestorov, R. I. Metalopova, S. G. Salikhov, and E. I. Loginova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 414 (1971); H. Teichmann and M. Jatkowski, *J. Prakt. Chem.*, **314**, 125 (1972).

Conformational Analysis Utilizing Carbon-13-Carbon-13 Spin-Spin Coupling Constants: Diamantane (Congressane) Derivatives

James L. Marshall* and Edward D. Canada, Jr.

Department of Chemistry, North Texas State University,
Denton, Texas 76203

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Ever since the suggestion was made that ^{13}C - ^{13}C coupling constants might parallel geometrically equivalent proton-proton coupling constants,^{1,2} a natural goal was to establish such a correlation between vicinal carbon-carbon and proton-proton couplings³ and to proceed to conformational analysis by utilizing carbon-carbon J values.⁴ Employing carbon-carbon coupling constants, instead of proton-proton coupling constants,⁵ would have the advantage in conformational analysis of utilizing a phenomenon that involves the four-carbon chain in question throughout its length. Accordingly, it might be anticipated that carbon-carbon couplings would give more accurate information regarding the conformation of the carbon chain. Also, a successful correlation of J_{CC} and the dihedral angle⁶ could be used in the conformational analysis of systems that would not be amenable to proton NMR analysis (whether because of no hydrogens, too many hydrogens, or hydrogens substituted in the wrong places). However, because of additional bonding electrons, carbon-13 couplings might be susceptible to a greater number of complications; and, indeed, some difficulties were noted⁷ in an attempt to establish a J_{CC} /dihedral angle correlation, particularly in adamantane derivatives.^{8,9} It therefore became of interest to see if these "anomalous" results were unique or were characteristic of certain cage-like molecules. Accordingly, in the present study we synthesized analogous diamantane (*two* fused adamantanes) derivatives 2 and 3 (see Table I) and determined the corresponding carbon-carbon coupling constants.

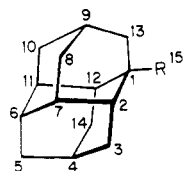
Results and Discussion

Synthesis of 1-diamantanecarboxylic acid- ^{15}C (2) was accomplished by recycling carbon- ^{13}C monoxide through 1-bromodiamantane dissolved in sulfuric acid. Compound 2 was then carried on to 1-(hydroxymethyl)diamantane- ^{15}C (3) by lithium aluminum hydride reduction.

Carbon-13 chemical shift assignments for 2 were made by integration (one carbon vs. two carbons), comparison of δ values with the parent compound diamantane (1), by use of CW off-resonance decoupling, and observation of carbon-carbon splitting; and, fortunately, through this combination of methods all assignments could be made unambiguously and securely. For the utilization of the δ values of 1, misassignments in the literature¹⁰ had to be

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Table I. Carbon-13 NMR Chemical Shifts and Coupling Constants for 1-Diamantane Derivatives 1-3



1, R = H
 2, R = $^{13}\text{COOH}$
 3, R = $^{13}\text{CH}_2\text{OH}$

carbon no.	1 (R = H) ^a		2 (R = $^{13}\text{COOH}$)		3 (R = $^{13}\text{CH}_2\text{OH}$)	
	δ , ppm ^b	δ , ppm ^b	J_{CC} , Hz ^c	δ , ppm ^b	J_{CC} , Hz ^c	
4	26.1	25.3		25.8		
9	26.1	26.3	2.82 (3J)	27.2	2.40 (3J)	
2, 12	37.7	37.1		38.2		
7, 11	37.7	37.5	2.8 ^d (3J)	38.2	<i>e</i>	
6	37.7	36.7		39.7		
1	37.7	40.2	55.4 (1J)	<i>f</i>		
3, 14	38.5	35.3		32.7		
8, 10	38.5	37.5		37.3		
5	38.5	38.0		38.8		
13	38.5	42.0	1.70 (2J)	39.9		
15		183.4		68.3		

^a Assignments of 1 made by CW off-resonance decoupling and by reversing the media and secondary assignments of ref 10. ^b Referenced to internal Me_4Si , accurate to 0.1 ppm. Chemical shifts of 2 are certain; for 3, C-5, C-6, and C-13 might be exchanged, and C-2,12 and C-8,10 might be reversed. See text. ^c Accurate to 0.1 Hz, except where noted. Where an entry is not made, splitting could not be discerned, either because of no coupling or overlap with other signals. ^d Accuracy of ± 0.5 Hz, owing to overlap of signals with that of C-8,10. ^e Broadening observed, but no discernible splitting, owing to overlap of signal with that of C-2,12; it appears that broadening of both C-7,11 and C-2,12 is occurring. Rough estimates of J_{CC} are difficult. ^f Signal never observed; compare with geometrically similar 1-(hydroxymethyl)-adamantane¹⁸ where the C-1 signal also is not observed.

corrected (see Table I). Splittings of the labeled carbon in 2 to four other carbons were measured.

In contrast, chemical shift assignments for compound 3 were rendered difficult by the tighter spectral pattern, and only one splitting could be measured. Table I lists chemical shifts (δ values) and carbon-13 couplings (J_{CC} values) for 2 and 3.

Table II compares the $^3J_{\text{CC}}$ values (vicinal carbon-carbon couplings) of 2 and 3 with values of other compounds for dihedral angles near 180° . The advantage of comparing compounds with a dihedral angle $\approx 180^\circ$ is that C1-C4 through-space interactions are minimal,¹¹ and substituent conformational contributions are small.¹² The immediately apparent feature of Table II is that the $^3J_{\text{CC}}$ values of 2 and 3 are remarkably small. Further, a comparison of the compounds of Table II shows J_{CC} values that range virtually twofold for each of the substituent categories. Thus, the $^3J_{\text{CC}}$ values seem to be imprecise indicators of the involved dihedral angle through this series of compounds. It is to be concluded that even when substituents remain the same along a carbon chain and when the involved dihedral angle remains the same, as the organic framework bearing the four-carbon chain changes, indirect (nonbonded) contributions¹³ can vary considerably.¹⁵

(11) M. Barfield, *J. Am. Chem. Soc.*, **102**, 1 (1980).

(12) Substituent conformational effects should affect $^3J_{\text{CC}}$ (180°) by much less than 1 Hz for both the alcohols¹⁸ and the carboxylic acids.¹⁴

Table II. Vicinal Carbon-Carbon Couplings ($^3J_{\text{CC}}$) with Dihedral Angles Near 180° for Various Compounds^a

compd	$^3J_{\text{CC}}$, Hz	
	R = $^{13}\text{COOH}$	R = $^{13}\text{CH}_2\text{OH}$
	5.6 ^b	4.2 ^c
	5.2 ^b (alkane)	4.5 ^c (olefin)
	4.0 ^b	4.2 ^c
	4.2 ^b	3.5 ^d
	3.6 ^b	3.3 ^c
	2.8 ^e	2.4 ^e

^a Dihedral angles estimated to be in the range 165 – 180° .^{7,18} ^b Reference 7. ^c Reference 18. ^d Reference 19. ^e This work.

In view of the additional complications involved in $^3J_{\text{CC}}$ couplings as the dihedral angle moves from 180° and becomes less than 90° (because of nonbonded interactions between terminal groups and conformational dependencies of terminal substituents), extreme care must be exercised in using $^3J_{\text{CC}}$ values in conformational analysis—even more so than when using $^3J_{\text{HH}}$ values, which also have been shown¹⁶ to rely heavily upon the nature of the associated molecular framework.

Experimental Section

Carbon-13 NMR spectra were recorded on a JEOL PFT-100 NMR spectrometer, using tetramethylsilane as an internal standard; J_{CC} values were determined by measuring the splitting of the natural carbon signals of ^{13}C -labeled compounds and utilizing 8K data points over a 500-Hz spectral window, and they are considered to be accurate within 0.1 Hz. ^1H NMR spectra were recorded on a PE-24B NMR spectrometer, using tetramethylsilane as an internal standard. NMR samples were prepared in chloroform-*d*. Infrared spectra were recorded on a Beckman IR-33 infrared spectrophotometer. Melting points were determined by using a Thomas-Hoover apparatus. Mass spectra were obtained from a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer.

1-Diamantanecarboxylic acid- ^{15}C (2) was synthesized by a procedure previously described⁷ by adding a solution of 1-bromodiamantane (1.59 g, prepared from norbornadiene as previously described¹⁷) in 10 mL of cyclohexane to 150 mL of concentrated sulfuric acid and then recycling 134 mL of $>90\%$ carbon- ^{13}C monoxide (Monsanto Chemical Corp.) until completely reacted to give 0.850 g (60%) of white crystals: mp 192 – 193°C (lit.¹⁰ mp 201.5 – 202.2°C); IR 3500 – 2300 , 1740 (1670 for unlabeled compound); ^1H NMR δ (CDCl_3) 2.13 (br, 2 H), 1.70 (br, 15 H),

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1.45 (br, 2 H); ^{13}C NMR, see Table I; mass spectrum, m/e 233 (M; 232 for unlabeled compound), B 187 (M - COOH).

1-(Hydroxymethyl)diamantane-15- ^{13}C (3) was synthesized by reacting 2 (0.380 g) with lithium aluminum hydride in a manner previously described¹⁸ to give a quantitative yield of product which was chromatographed (F-20 Alcoa alumina, *n*-pentane) to give 0.137 g (38%) of 3: mp 206-209 °C (sealed); IR 3400, 1210; ^1H NMR δ (CDCl_3) 3.17 (d, 2 H, $J = 136$ Hz; s for unlabeled compound), 2.85 (s, 1 H), 2.12 (br, 2 H), 1.90 (br, 2 H), 1.5-1.2 (br, 13 H), 0.92 (br, 2 H); ^{13}C NMR, see Table I; mass spectrum, m/e 219 (M; 218 for unlabeled compound), B 188 (M - CH_2O).

Acknowledgment. The authors are indebted to the Robert A. Welch Foundation (Grant No. B-325) and to North Texas State University Faculty Research for financial support of this research.

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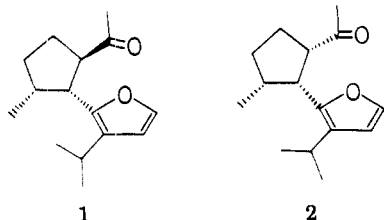
An Approach to the Synthesis of *dl*-Furopelargones¹

Akira Takeda,* Koichi Shinhama, and Sadao Tsuboi

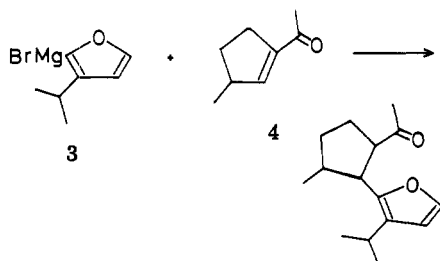
Department of Synthetic Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700, Japan

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Furopelargones A (1) and B (2),^{2,3} ketonic constituents



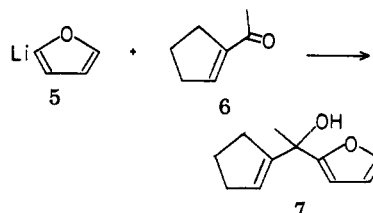
of Geranium Bourbon Oil, have been synthesized by Büchi and Wüest⁴ through several steps from citral. A survey of the structures reveals that the furan ring moiety of these compounds may be introduced by the Michael addition of 3-isopropyl-2-furylmagnesium bromide (3) to the conjugated system of 1-acetyl-3-methylcyclopentene (4).⁵ As



a part of our work on the synthetic approach to the carbon skeleton of natural products by means of Michael addi-

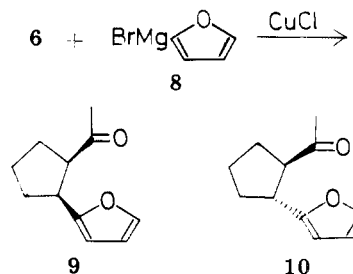
tion,^{5,6} we carried out the reaction of the Grignard reagent 3 with the α,β -unsaturated ketone 4 in the presence of copper(I) chloride (CuCl) in order to prepare furopelargones. This paper deals with the isolation and structural identification of the diastereomeric mixture obtained in this reaction. The stereochemistry of these isomers has been confirmed principally on the basis of IR and NMR spectral data.

The use of 2-lithiofuran (5)⁷ in the appropriate Michael



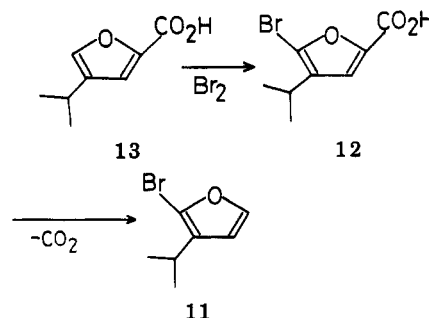
addition was abandoned, since the preliminary experiment has shown that the reaction of 5 with 1-acetylcyclopentene (6)⁵ proceeds only in the mode of 1,2-addition to give 1-(1-cyclopentenyl)-1-(2-furyl)ethanol (7), either in the presence or in the absence of CuCl.

To the contrary, the reaction of 2-furylmagnesium bromide (8)^{8,9} with the ketone 6 afforded a mixture (isomer



ratio ca. 1:1) of *cis*- and *trans*-*dl*-2-(2-acetylcyclopentyl)-furans (9 and 10), although the yield was as low as 15% as a result of the formation of an intractable material. The structural assignment of 9 and 10 is based on the chemical shift of the acetyl methyl protons, which are thought to be affected by the shielding effect of furan ring current more in the *cis* isomer (δ 1.70) than in the *trans* isomer (δ 2.04). The same effect has been observed in the chemical shift of the acetyl methyl protons of furopelargones A and B.²

The starting material of the present synthesis, 2-bromo-3-isopropylfuran (11) was prepared in a 48% yield



by the pyrolysis of 4-isopropyl-5-bromofuran-2-carboxylic

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