

(5c). Recrystallization from methanol gave colorless plates, mp 70–71 °C.

Typical Procedure for ω,ω' -Bis(triphenylphosphine) Polyethers. A. 1,4-Bis(*p*-bromophenoxy)benzene (**2a**)¹ (2.1 g, 5 mmol) in anhydrous tetrahydrofuran (THF, 20 mL) was added dropwise at –65 °C under dry nitrogen atmosphere with stirring to 30 mL of a hexane solution containing 15 mmol of *n*-butyllithium. The reaction mixture was then allowed to warm to –10 °C and stirred at this temperature for 1 h. After the solution was recooled to –65 °C, diphenylchlorophosphine⁴ (2.21 g, 10 mmol) in THF (10 mL) was added dropwise while the temperature was kept at about –65 °C. The solution was then warmed to room temperature and dry methanol was added. The solvents were removed at reduced pressure to leave a residue. Recrystallization of the residue from petroleum ether (bp 60–80 °C)/benzene gave 1,4-bis(*p*-diphenylphosphinophenoxy)benzene (**6a**) in 52% yield as colorless plates, mp 148–149 °C.

B. **5c** (2.3 g, 5 mmol), 15 mmol of *n*-butyllithium in hexane, and 2.5 g (11 mmol) of diphenylchlorophosphine in THF (10 mL) were treated and worked up as described above. The resulting oily material was column chromatographed on silica gel with chloroform as eluent to give 3.1 g (93%) of 1,2-bis[β,β' -(*p*-diphenylphosphinophenoxy)ethoxy]ethane as a colorless viscous oil.

Spectral data of compounds **6** are summarized below:

6a: IR (KBr) 3050, 1585, 1485, 1430, 1220, 1190, 1165, 820, 740, 695 cm⁻¹; NMR (CDCl₃) δ 6.8–7.3 (m, aromatic protons).

6c: IR (KBr) 1500, 1435, 1395, 1280, 1245, 1180, 1095, 830, 740, 695 cm⁻¹; NMR (CDCl₃) δ 4.8 (s, 4 H, CH₂), 6.88 (d, *J* = 8 Hz, 4 H, aromatic protons), 9.08–7.36 (m, 24 H, aromatic protons).

6d: IR (KBr) 1595, 1500, 1430, 1280, 1245, 1175, 1120, 1095, 820, 740, 695 cm⁻¹; NMR (CDCl₃) δ 3.84 (m, 4 H, CH₂), 4.08 (m, 4 H, CH₂), 6.82 (d, *J* = 8 Hz, 4 H, aromatic protons), 7.07–7.23 (m, 24 H, aromatic protons).

6e: IR (KBr) 2925, 2875, 1590, 1495, 1435, 1280, 1245, 1180, 1120, 1095, 820, 740, 695 cm⁻¹; NMR (CDCl₃) δ 3.7 (s, 4 H, CH₂), 3.83 (m, 4 H, CH₂), 4.06 (m, 4 H, CH₂), 6.86 (d, *J* = 8 Hz, 4 H, aromatic protons), 9.14–9.30 (m, 24 H, aromatic protons).

Registry No. **1b**, 3379-41-7; **2a**, 41318-76-7; **2b**, 72659-51-9; **3**, 106-41-2; **4a**, 106-93-4; **4b**, 111-44-4; **4c**, 112-26-5; **5a**, 36506-46-4; **5b**, 72659-52-0; **5c**, 72659-53-1; **6a**, 72659-54-2; **6c**, 72659-55-3; **6d**, 72659-56-4; **6e**, 72659-57-5; diphenylchlorophosphine, 1079-66-9; β,β' -bis(phenoxyethyl) ether, 622-87-7.

(4) L. Horner, P. Beck, and V. G. Toscano, *Chem. Ber.*, **94**, 2124 (1961).

A Novel Route to 1-Alkynyl Ethers via Organocopper(I)-Induced 1,3-Substitution in 1-Iodo-1-methoxypropadiene

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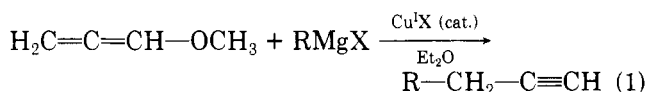
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Hitherto 1-alkynyl ethers have been obtained via base-induced dehydrohalogenation of 2-haloalkenyl ethers, alkylation of metalated ethynyl ethers, substitution of halogen by alkoxides in 1-halo-1-alkynes, and substitution of iodine by organocopper(I) reagents in 2-iodo-1-ethoxyacetylene.^{1,2}

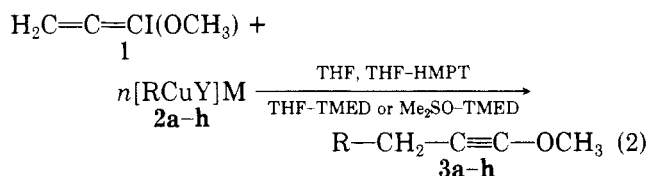
At the time this work was initiated, 1-alkynyl ethers had not been prepared via a 1,3-substitution reaction in ap-

propriately substituted allenyl ethers. In view of the smooth copper(I)-promoted 1,3-substitution in methoxypropadiene (eq 1)³ we anticipated that starting from α -



haloallenyl ethers the reaction principle depicted in eq 1 could also be of synthetic value for the preparation of 1-alkynyl ethers.

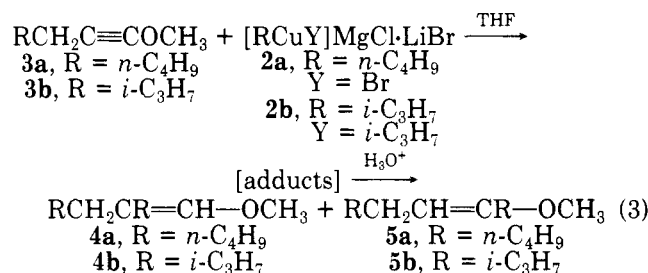
To investigate this potential route we allowed 1-iodo-1-methoxypropadiene (**1**) to react with various cuprates **2**, and we can report that under suitable conditions the reaction led to the desired 1-alkynyl ethers **3** in good yields



R = alkyl, vinyl, Ph, or C \equiv CR'
Y = Br (*n* = 1.0) or R (*n* = 0.5)
M = Li or MgX·LiBr

(eq 2; yield of **3** after distillation 65–85%). In Table I the applied reaction conditions and the composition of cuprates **2** are given. Attempts to realize a similar reaction with Grignard reagents under copper(I) bromide catalysis (5 mol % of CuBr was used) were not successful.

The choice of the reaction medium for the conversion depicted in eq 2 appeared to be very important. It was found that tetrahydrofuran (THF) was a suitable solvent to convert **1** into ethers **3c** and **3e** by the heterocuprates **2c** and **2e**. On the other hand, when this solvent was chosen for the reaction of **1** with the heterocuprate **2a** or the homocuprate **2b**, **3** was contaminated with substantial amounts of the vinylic ethers **4** and **5**, even when the reaction was carried out at –85 °C. The origin of these vinylic ethers is conceivable by assuming a subsequent attack of unreacted **2a** and **2b** on the initially formed 1-alkynyl ethers **3a** and **3b**, respectively (eq 3; see also remarks *c* and *d* in Table I).⁴



Interestingly, ethers **3a** and **3b** were not contaminated with adducts **4** and **5** when **1** was treated with cuprates **2a** and **2b** in hexamethylphosphoric triamide (HMPT) containing THF. The conversion of **1** into 1-alkynyl ethers **3d** and **3f–h** by cuprates **2d** and **2f–h** appeared to be very slow in pure THF. Acceptable reaction rates were observed in these cases when the conversion was performed in the solvent mixtures THF–tetramethylethylenediamine

(3) J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **93**, 183 (1974).

(4) For the formation of vinylic ethers from 1-alkynyl ethers and organocopper(I) compounds see (a) J. F. Normant, A. Alexakis, A. Commerçon, G. Cahiez, and J. Villieras, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **279**, 763 (1974); (b) A. Alexakis, G. Cahiez, J. F. Normant, and J. Villieras, *Bull. Soc. Chim. Fr.*, 693 (1977).

(1) L. Brandsma, H. J. T. Bos, and J. F. Arens, "Chemistry of Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, 1969, Chapter 11.

(2) W. Verboom, H. Westmijze, H. J. T. Bos, and P. Vermeer, *Tetrahedron Lett.*, 1441 (1978).

Table I. Reaction Conditions for the Conversion of $H_2C=C=C(I)OMe$ (1) by $n[RCuY]M$ (2a-h) into $RCH_2C\equiv COMe$ (3a-h)

2	[RCuY]M				n	solvent ^f	reaction temp, °C	reaction time, h	product 3a-h ^{a,b} yield, %
	R	Y	M						
a	Bu	Br	MgCl·LiBr		1.0	THF-HMPT	-85	1.0	80 (3a) ^c
b	<i>i</i> -Pr	<i>i</i> -Pr	MgCl·LiBr		0.5	THF-HMPT	-85	0.8	65 (3b) ^d
c	<i>t</i> -Bu	Br	MgCl·LiBr		1.0	THF	-85	1.0	70 (3c)
d	$H_2C=CH$	Br	MgCl·LiBr		1.0	THF-TMED	-50	1.0	67 (3d)
e	Ph	Br	MgCl·LiBr		1.0	THF	-50	1.0	77 (3e) ^e
f	$Me_2SiC\equiv C$	Br	Li		1.0	THF-HMPT	+25	3.5	75 (3f)
g	$H_2C=C(Me)C\equiv C$	Br	Li		1.0	Me_2SO -TMED	+20	1.0	85 (3g)
h	$BuC\equiv C$	$BuC\equiv C$	Li		0.5	Me_2SO -TMED	+25	3.0	71 (3h)

^a Yields refer to distilled products. In a number of cases considerable loss of product occurred during distillation. The purity of 3 was at least 97% (based on GLC and ¹H NMR analysis). ^b All compounds 3 exhibited spectral data in accordance with the proposed structure and showed the expected peaks in the mass spectra. ^c Purification of crude 3a by chromatography (SiO_2 /hexane- Et_2O (4:1 (v/v))) instead of distillation gave 95% yield of 3a. In pure THF a mixture of 3a and the 1-alkynyl ethers 4a and 5a (eq 3) was obtained in a ratio 65:35. ^d In pure THF the 1-alkynyl ether was contaminated with the 1-alkynyl ethers 4b and 5b (eq 3); 3b/(4b + 5b) 55:45. Reaction of 1 with the corresponding heterocuprate (Y = Br, n = 1.0) in THF-HMPT at -85 °C led to a mixture of 3b and 4b + 5b in a ratio 88:12; in pure THF this ratio was much lower, viz. 34:66. ^e Purification of crude 3e by chromatography (SiO_2 /hexane- Et_2O (4:1 (v/v))) instead of distillation gave 86% yield of 3e. ^f See Experimental Section for solvent ratios and concentration of reactants.

(TMED, cuprate 2d), THF-HMPT (cuprate 2f), or dimethyl sulfoxide (Me_2SO)-TMED (cuprates 2g-h). It is noteworthy in this connection that the 1,3-substitution induced by 2g and 2h in 1 proceeded considerably faster in Me_2SO -TMED than in THF-HMPT or THF-TMED. This observation may be of interest for reactions of 1-alkynylcopper(I) compounds with other electrophiles.

In summary, organocopper(I)-induced 1,3-substitution in 1-iodo-1-methoxypropadiene is a convenient route to various 3-substituted 1-methoxy-1-propynes, especially to 1-alkynyl ethers 3 with an alkenyl or alkynyl group in the 3-position, which are not easily accessible by other methods.

Experimental Section

General Procedures. Infrared spectra were recorded on a Perkin-Elmer 457 IR spectrometer using a thin film on sodium chloride. ¹H NMR spectra were determined on a Varian EM-390 spectrometer using CCl_4 as solvent and Me_4Si as internal standard. Mass spectra were recorded on a AEI-MS-902 mass spectrometer. GLC analyses were carried out on a F & M 720 chromatograph (conditions SE-33, 10% on Chromosorb W). All reactions were carried out in an atmosphere of dry nitrogen.

Materials. THF was distilled from $LiAlH_4$, Me_2SO was distilled from CaH_2 , and HMPT was purified according to ref 5. TMED was purified by distillation and stored over 4A molecular sieves. Copper(I) bromide was obtained according to the method of Keller.⁶ Methyl lithium was prepared as a 1.10 M solution in ether from methyl iodide and lithium. *n*-Butyllithium was obtained as a 1.55 M solution in *n*-hexane from Metallgesellschaft A.G., Frankfurt am Main. The Grignard reagents were prepared in THF from the corresponding alkyl halides and magnesium; their molarity was determined using Watson's titration method.⁷ Lithium bromide was dried at 220 °C in high vacuum and was used as a 2.0 M solution in THF. Methoxypropadiene was prepared from 1-methoxy-2-propyne,⁸ (trimethylsilyl)acetylene from ethynylmagnesium bromide and trimethylsilyl chloride,⁹ and 1-hexyne from lithium acetylide and *n*-butyl bromide,⁵ while isopropenylacetylene was obtained from Aldrich-Europe.

1-Iodo-1-methoxypropadiene (1). To a stirred solution of 15.40 g of methoxypropadiene (220.0 mmol) in 30 mL of dry ether

was added 200 mL of methyl lithium (1.10 M) in ether at 0 °C. After the solution was stirred for 1 h at 0 °C, 50.8 g of iodine (200.0 mmol) was added at -15 °C and stirring at -15 °C was continued for 15 min. Subsequently, the reaction mixture was poured into water (220 mL), the upper layer was separated, the aqueous layer was extracted twice with 50 mL of ether, the combined extracts were dried with K_2CO_3 , and the solvent was stripped off on an ice bath in vacuo, yielding 37.80 g of 1 (95%). Compound 1—which was used without further purification—appeared to be rather thermally unstable but could be stored at least a few weeks at -80 °C: IR 1255, 1945 cm^{-1} ; NMR (CCl_4) δ 3.50 (s, 3 H), 5.10 (s, 2 H).

General Procedure for the Preparation of 1-Alkynyl Ethers 3a-e. To a stirred suspension of 4.30 g of copper(I) bromide (30.0 mmol; cuprates 2a, 2c-e) or 2.15 g of copper(I) bromide (15.0 mmol; cuprate 2b) in 90 mL of dry THF was added, at +25 °C, 15.0 mL of lithium bromide in THF (2.0 M) to yield a clear solution. This solution was cooled to -50 °C and 30.0 mmol of $RMgX$ in about 30 mL of THF was carefully added followed by 5.37 g of HMPT (30.0 mmol; cuprates 2a and 2b) or 3.48 g of TMED (30.0 mmol, cuprate 2d). Stirring was continued for 0.5 h at -50 °C. Subsequently, at the temperatures indicated in Table I, 5.88 g of 1 (30.0 mmol) was added dropwise to the cuprates 2a-e thus obtained. After the addition of 1, the resulting reaction mixture was stirred for an additional period (see Table I) at the same temperature. The products 3a-e were isolated by pouring the respective reaction mixtures into 200 mL of a saturated aqueous NH_4Cl solution containing 2 g of NaCN, extracting the aqueous layer with pentane (3 × 50 mL), washing the combined extracts with water (6 × 100 mL), and drying the extract with K_2CO_3 . The solvent was distilled off and the residue was distilled under diminished pressure.

1-Methoxy-1-heptyne (3a). Distillation gave 3.02 g of pure material: bp 88-89 °C (63 mmHg); n_D^{20} 1.4290; IR 965, 1258, and 2278 cm^{-1} ; NMR (CCl_4) δ 0.90 (t, 3 H), 1.13-1.60 (m, 6 H), 2.03 (t, 2 H), 3.78 (s, 3 H); mass spectrum, m/e 126 (M^+).

1-Methoxy-4-methyl-1-pentyne (3b). Distillation gave 2.18 g of pure material: bp 59-60 °C (55 mmHg); n_D^{20} 1.4310; IR 975, 1253, 2270 cm^{-1} ; NMR (CCl_4) δ 0.92 (d, 6 H), 1.38-1.85 (m, 1 H), 1.90 (d, 2 H), 3.75 (s, 3 H); mass spectrum, m/e 112 (M^+).

1-Methoxy-4,4-dimethyl-1-pentyne (3c). Distillation gave 2.65 g of pure material: bp 68-69 °C (60 mmHg); n_D^{20} 1.4234; IR 972, 1260, 2275 cm^{-1} ; NMR (CCl_4) δ 0.93 (s, 9 H), 1.92 (s, 2 H), 3.78 (s, 3 H); mass spectrum, m/e 126 (M^+).

1-Methoxy-4-penten-1-yne (3d). Distillation gave 1.93 g of pure material: bp 57-58 °C (84 mmHg); n_D^{20} 1.4395; IR 960, 1242, 1640, 2275 cm^{-1} ; NMR (CCl_4) 2.83 (ddd, 2 H), 3.82 (s, 3 H), 4.90-6.00 (m, 3 H, vinylic pattern); mass spectrum, m/e 96 (M^+).

1-Methoxy-3-phenyl-1-propyne (3e). Distillation gave 3.37 g of pure material: bp 55-56 °C (0.2 mmHg); n_D^{20} 1.5368; IR 962, 1255, 1500, 1605, 2278 cm^{-1} ; NMR (CCl_4) 3.48 (s, 2 H), 3.82 (s, 3 H), 7.01-7.40 (m, 5 H); mass spectrum, m/e 146 (M^+).

(5) L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971.

(6) R. N. Keller and H. D. Wycoff in "Organic Syntheses", Vol. II, 1st ed., McGraw-Hill, New York-London, 1946, p 1.

(7) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

(8) S. Hoff, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **87**, 916 (1968).

(9) H. Westmijze and P. Vermeer, *Synthesis*, 390 (1979).

1-Methoxy-5-(trimethylsilyl)-1,4-pentadiyne (3f). To a stirred solution of 3.25 g of (trimethylsilyl)acetylene (33.0 mmol) in 90 mL of dry THF were successively added, at -40°C , 19.3 mL of *n*-butyllithium in *n*-hexane (1.55 M), 5.37 g of HMPT (30.0 mmol), and 4.30 g of copper(I) bromide (30.0 mmol). The temperature of the reaction mixture was allowed to rise to -5°C , at which temperature stirring was continued for 15 min. To the resulting clear solution was added 5.88 g of **1** (30.0 mmol), followed by stirring for 3.5 h at $+25^{\circ}\text{C}$. The product was isolated as described for compounds **3a-e**. Distillation of the crude product gave 3.74 g of pure material: bp $90-91^{\circ}\text{C}$ (19 mmHg); n_{D}^{20} 1.4630; IR 950, 1250, 2180, 2290 cm^{-1} ; NMR (CCl_4) δ 0.15 (s, 9 H), 3.08 (s, 2 H), 3.92 (s, 3 H); mass spectrum, m/e 166 (M^+).

1-Methoxy-6-methyl-6-heptene-1,4-diyne (3g). To a stirred solution of 2.18 g of isopropenylacetylene (33.0 mol) in 100 mL of dry Me_2SO were successively added, at $+20^{\circ}\text{C}$, 3.48 g of TMED (30.0 mmol), 19.3 mL of *n*-butyllithium in *n*-hexane (1.55 M), and 4.30 g of copper(I) bromide (30.0 mmol). After the solution was stirred for 15 min at $+20^{\circ}\text{C}$, 5.88 g of **1** (30.0 mmol) was added; this was followed by stirring for 1.0 h at $+20^{\circ}\text{C}$. The crude product was isolated as described for compounds **2a-e**. Distillation gave 3.42 g of pure material: bp $44-45^{\circ}\text{C}$ (0.5 mmHg); n_{D}^{20} 1.4920; IR 955, 1248, 1615, 2280 cm^{-1} ; NMR (CCl_4) δ 1.82 (d, 3 H), 3.12 (s, 2 H), 3.85 (s, 3 H), 5.05-5.27 (m, 2 H); mass spectrum, m/e 134 (M^+).

1-Methoxy-1,4-nonadiyne (3h). To a stirred solution of 2.70 g of 1-hexyne (33.0 mmol) in 100 mL of dry Me_2SO were successively added, at $+20^{\circ}\text{C}$, 3.48 g of TMED (30.0 mmol), 1.93 mL of *n*-butyllithium in *n*-hexane (1.55 M), and 2.15 g of copper(I) bromide (15.0 mmol). After the reaction mixture was stirred for 15 min at $+20^{\circ}\text{C}$, 5.88 g of **1** (30.0 mmol) was added. The resulting reaction mixture was stirred for 3.0 h at $+25^{\circ}\text{C}$. The product was isolated following the procedure given for **3a-e**. Distillation gave 3.20 g of pure material: bp $57-58^{\circ}\text{C}$ (0.5 mmHg); n_{D}^{20} 1.4660; IR 955, 1245, 2270 cm^{-1} ; NMR (CCl_4) δ 0.91 (t, 3 H), 1.18-1.65 (m, 4 H), 2.09 (tt, 2 H), 2.91 (t, 2 H), 3.80 (s, 3 H); mass spectrum, m/e 150 (M^+).

Registry No. **1**, 72610-28-7; **2a**, 60101-72-6; **2b**, 60101-89-5; **2c**, 60101-70-4; **2d**, 72610-03-8; **2e**, 72610-01-6; **2f**, 72610-00-5; **2g**, 72609-99-5; **2h**, 72609-98-4; **3a**, 72610-29-8; **3b**, 72610-30-1; **3c**, 72610-31-2; **3d**, 72610-32-3; **3e**, 72610-33-4; **3f**, 72610-34-5; **3g**, 72610-35-6; **3h**, 72610-36-7. **4a**, 72610-37-8; **4b**, 72610-38-9; **5a**, 72610-39-0; **5b**, 72610-40-3; methoxypropadiene, 13169-00-1; (trimethylsilyl)acetylene, 1066-54-2; isopropenylacetylene, 78-80-8; 1-hexyne, 693-02-7.

Empirical Force-Field-Extended Hückel Molecular Orbital Conformational Analysis of 1-Phenyl-3,3-dimethylbutane

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One of the principal goals of empirical force-field (EFF) calculations is the computation of both reliable molecular geometries and relative conformational energies. By use of numerous currently available force fields, the former goal can, in general, be readily accomplished while the latter goal is not as often attainable.^{1,2} The recent combination of empirical force-field (EFF) and extended

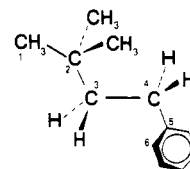


Figure 1. Numbering scheme for **3**.

Hückel molecular orbital (EHMO) calculations, generating a hybrid (EFF-EHMO) method, has been successfully utilized for the calculation of relative orders of conformational energies.^{1,2}

We had previously calculated the geometries and conformational energies of bibenzyl (**1**) and of 1,2-diphenylpropane (**2**), employing the EFF program BIGSTRN.³ Both **1** and **2** are known, experimentally, to exist predominantly in the phenyl-phenyl anti conformation,^{4,5} yet the EFF calculations indicate that both molecules prefer a phenyl-phenyl gauche conformation.³ The hybrid method (EFF-EHMO)⁶ reverses the EFF conclusions and, further, provides conformational energies in qualitative agreement with the experimental results.^{1,3,5}

1-Phenyl-3,3-dimethylbutane (**3**), a compound whose conformational analysis was originally reported by Whitesides and co-workers,⁷ was the key compound in the exposition of the stereochemistry of the hydroboration-protonation reaction sequence.⁸ This reaction was demonstrated to proceed in a predominantly overall cis fashion, i.e., (*E*)-1-phenyl-3,3-dimethyl-1-butene [(*E*)-**4**], upon reaction with BD_3 and acetic acid- d_4 , yielded *threo*-1-phenyl-3,3-dimethylbutane-1,2- d_2 (*threo*-**3-d₂**); the corresponding *Z* diastereomer [(*Z*)-**4**] yielded the erythro diastereomer (*erythro*-**3-d₂**). The deuterium-decoupled proton spectra of *threo*-**3-d₂** and *erythro*-**3-d₂** exhibit vicinal proton-proton coupling constants ($^3J_{\text{HH}}$) of 12.5 and 5.0 Hz, respectively, at 30°C in neat solution.⁹ From the temperature dependence of the vicinal coupling constants of **3** the energy difference between the anti and gauche conformers was determined to be 1.70 ± 0.09 kcal/mol in CCl_4 solution, the anti conformer being favored.⁷

Thus, **3** appears to be an excellent candidate to further test the hybrid conformational energy approach (EFF-EHMO). The starting geometries for EFF minimization are presented in Table I, as are the final geometries and relative conformational energies. The following dihedral angles are required to define a single conformation of **3**: the 1234 angle, the 2345 angle, and the 3456 angle (Figure 1). A complete description of any of these conformers would require description of the dihedral angle made by the protons of the *tert*-butyl methyl groups with respect to the contiguous carbon atom and atoms 2 and

(3) (a) J. Jacobus, *Tetrahedron Lett.*, 2927 (1976). (b) The program BIGSTRN is available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN 47401.

(4) For bibenzyl, see: K. K. Chiu, H. H. Huang, and L. H. L. Chia, *J. Chem. Soc., Perkin Trans. 2*, 286 (1972); A. M. North, R. A. Pethrick, and A. D. Wilson, *Spectrochim. Acta, Part A*, **30**, 1317 (1974).

(5) For 1,2-diphenylpropane, see: S. L. Spassov, A. S. Orahovats, S. M. Mishev, and J. Schraml, *Tetrahedron*, **30**, 365 (1974); ref 3a.

(6) The extended Hückel program [R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963)] employed was EXTHUC, available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN 47401.

(7) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Am. Chem. Soc.*, **89**, 1135 (1967).

(8) G. W. Kabalka, R. J. Newton, Jr., and J. Jacobus, *J. Org. Chem.*, **44**, 4185 (1979).

(9) For **3** in CCl_4 solution Whitesides and co-workers⁷ report $^3J_{\text{HH}}$'s of 13.7 and 4.2 Hz. These data were obtained by iterative calculations on the AA'XX' spin system exhibited by **3**. The dependence of these coupling constants on solvent is expected to be small; the coupling constants reported herein were obtained directly.⁸

(1) D. A. Dougherty and K. Mislow, *J. Am. Chem. Soc.*, **101**, 1401 (1979).

(2) (a) D. A. Dougherty, K. Mislow, J. W. Huffman, and J. Jacobus, *J. Org. Chem.*, **44**, 1585 (1979); (b) S. G. Baxter, H. Fritz, G. Hellman, B. Kitschke, H. J. Linder, K. Mislow, C. Ruchardt, and S. Weinter, *J. Am. Chem. Soc.*, **101**, 4493 (1979).