This lesser ability of the CF_3 group to stabilize the reduced system when compared with the CO_2Et substituent may be explained by qualitative differences in their electron-withdrawing effects. Thus although CF_3 exerts a strong inductive effect, it is incapable of the kind of mesomeric stabilization (**6** ⇄ **7**) afforded by the ethoxycarbonyl group. Further, the hydrogen-bonding stabilization (**8**) available to the ethoxycarbonyl derivatives would be weak or nonexistent in the trifluoromethyl compounds.[10]

Borohydride reduction of 2-oxo-4-(ethoxycarbonyl)-pteridine, which existed as the 3,4-hydrate **9a**, was anomalous. Hydrogenation occurred in the pyrimidine rather than the pyrazine ring, with concomitant reduction of the ester group to yield the 3,4-dihydro-4-hydroxymethyl derivative **9b**. The special stability conferred by urea-type resonance on hydrated and reduced fused pyrimidines of this kind has been well documented[6] and in this case seems to outweigh the factors responsible for the stability of reduced pyrazines discussed above.

The foregoing study illustrates the effect of an electron-attracting group in stabilizing reduced pteridine derivatives. In view of the known difficulties usually experienced in the isolate and biological evaluation of hydrogenated pteridines, introduction of such substituents may represent a useful strategy in increasing the chemotherapeutic utility of analogues of reduced folates and other pterin cofactors.

Experimental Section

Melting points were determined on a Büchi capillary apparatus and are uncorrected. ^1H NMR spectra were obtained on Varian HA100, CFT-20, and T60 spectrometers. Chemical shifts (δ) are reported relative to Me_4Si (δ 0). Mass spectra were determined on a Varian MAT CH5 DF instrument at 70 eV. Analyses were performed by Atlantic Microlabs Inc., Atlanta, GA. All C, H, N and analyses not reported here were acceptable (±0.3%) and may be found with ^1H NMR data in the supplementary data section.

6,7-Dimethyl-4-(ethoxycarbonyl)pteridines 3c–j. The ethyl 2-substituted 4,5-diaminopyrimidine-6-carboxylate **5** was heated under reflux in *tert*-butyl alcohol with an excess of diacetyl. Particular reaction conditions for each compound are given in Table I. The reaction mixture was evaporated to dryness and extracted with pentane (700 mL). The pentane solution was evaporated to 70 mL, from which the products **3c–j** (40–99%) crystallized on setting aside the solution overnight in the cold. The dimethylpteridines were recrystallized from pentane or pentane/solvent mixtures as indicated.

6,7-Dimethyl-4-(ethoxycarbonyl)-5,6,7,8-tetrahydropteridines. The pteridine **3** was stirred in dry methanol with sodium borohydride, the reaction mixture was neutralized with glacial acetic acid and evaporated, and the residue was suspended in water and extracted with 2 × 20 mL of CH_2Cl_2. The residue from evaporation of the combined extracts was crystallized as indicated in Table II to yield the tetrahydro derivative **4**. A specific example is described below for the preparation of **4g**.

2-Amino-6,7-dimethyl-4-(ethoxycarbonyl)-5,6,7,8-tetrahydropteridine (4g). To a stirred solution of the pteridine **3c** (0.12 g, 0.005 mol) in dry methanol (15 mL) at room temperature was added sodium borohydride (0.15 g, 3.97 mmol). After 15 min the reaction mixture was neutralized with acetic acid and evaporated to dryness under reduced pressure at 37 °C. The residue was suspended in distilled water and extracted with 2 × 20 mL of CH_2Cl_2. The extracts were combined and evaporated to a yellow residue which was crystallized from CH_2Cl_2/pentane to give the amino compound **4g** (0.047 g, 37%): mp 206–208 °C; NMR ($CDCl_3$) (80 MHz) δ 1.16 (d, 3 H, J = 6.3 Hz), 1.19 (d, 3 H, J = 6.3 Hz), 1.40 (t, 3 H, J = 7 Hz), 3.13 (m, trans-6,7-H (16%) $J_{6,7}$ = 7.5 Hz), 3.60 (m, cis-6,7-H (84%), $J_{6,7}$ = 3.4 Hz), 4.38 (q, 2 H, J = 7 Hz), 3.34 (s, <1 H, MeOH). Anal. Calcd for $C_{11}H_{17}N_5O_2 \cdot 0.25MeOH$: C, 52.10; H, 6.99; N, 27.01. Found: C, 51.93; H, 6.82; N, 26.95.

2-Ethoxy-6,7-dimethyl-5,6,7,8-tetrahydro-4-(trifluoromethyl)pteridine (4j). 2-Ethoxy-6,7-dimethylpteridine (**3h**; 0.03 g, 0.11 mmol) was suspended in 0.2 M HCl (30 mL) and sodium cyanoborohydride (1.0 g, 15.9 mmol) was added in small portions over 2 h. The reaction mixture was stirred for 1 h at room temperature, adjusted to pH 8 with 6 M NaOH, and extracted with 3 × 30 mL of methylene chloride. The combined extracts were evaporated and the residue was crystallized from methylene chloride/pentane (1:1) to yield the tetrahydro derivative (**4j**; 0.005 g, 16%); mp 154–155 °C; mass spectrum (70 eV, 115 °C), m/e 276.1213 (M^+, 100%); $C_{11}H_{15}F_3N_4O$ requires 276.1198; NMR ($CDCl_3$) δ 1.16 (d, 1 H, J = 6.3 Hz), 1.20 (d, 1 H, J = 6.3 Hz), 1.34 (t, 3 H, J = 7 Hz), 3.66 (m, 2 H) 3.99 (br s, 1 H), 4.76 (q, 2 H, J = 7 Hz) 5.71 (br s, 1 H).

6,7-Dimethyl-4-(ethoxycarbonyl)-4-hydroxy-1,2,3,4-tetrahydropteridin-2-one (9a). 4,5-Diamino-1,2-dihydro-6-(ethoxycarbonyl)pyrimidin-2-one[8] (0.5 g, 2.5 mmol) was heated under reflux with diacetyl (0.5 mL) for 15 min. The cooled solution was evaporated under reduced pressure to 3 mL, when the pteridine **9a** (0.25 g, 35%) crystallized as pale yellow prisms which decomposed gradually without melting at >200 °C: NMR (Me_2SO-d_6) δ 1.13 (t, 3 H, J = 7 Hz); 2.34 (s, 3 H), 2.38 (s, 3 H), 4.12 (q, 2 H, J = 7 Hz), 6.8 (s, 1 H), 8.30 (s, 1 H), 10.19 (s, 1 H). Anal. Calcd for $C_{11}H_{14}N_4O_4 \cdot H_2O$: C, 46.47; H, 5.67; N, 19.71. Found: C, 46.62; H 5.59; N, 19.80.

6,7-Dimethyl-4-(hydroxymethyl)-1,2,3,4-tetrahydropteridin-2-one (9b). The foregoing (ethoxycarbonyl)pteridine **9a** (0.10 g, 0.376 mmol) was stirred in dry methanol (10 mL) during the addition of sodium borohydride (0.16 g, 4.23 mmol) portionwise over 20 min. The reaction mixture was neutralized with glacial acetic acid, and the resulting solid was filtered off and washed with methanol to yield the reduced pteridine (0.051 g, 64.9%) as a white solid: mp 245–250 °C; NMR (Me_2SO-d_6, 80 mHz) δ from Me_4Si 2.34 (s, 6 H), 3.58 (q, 2 H), 4.32 (m, 1 H), 4.84 (t, 1 H), 6.95 (br s, 1 H), 9.47 (br s, 1 H). Anal. Calcd for $C_9H_{12}N_4O_2 \cdot 0.4H_2O$: C, 50.18; H, 5.99; N, 26.01. Found: C, 50.42; H, 5.88; N, 25.75.

Acknowledgment. We thank Dr. R. W. Morrison for helpful discussions and encouragement, Dr. B. S. Hurlbert, A. Ragouzeous, and R. Crouch for NMR spectra, Dr. D. Brent. B. Soltmann and R. Johnson for mass spectra, and S. K. Wrenn for technical assistance.

Registry No. **3c**, 93683-57-9; **3d**, 93683-58-0; **3e**, 93683-59-1; **3f**, 93683-60-4; **3g**, 93683-61-5; **3h**, 93683-48-8; **3i**, 93683-62-6; **3j**, 93683-63-7; *cis*-**4e**, 93683-51-3; *cis*-**4f**, 93683-52-4; *cis*-**4g**, 93683-49-9; *cis*-**4h**, 93683-50-2; *cis*-**4i**, 93683-53-5; **4j**, 93683-54-6; **5c**, 60914-72-9; **5d**, 90084-94-9; **5e**, 90769-45-2; **5f**, 18204-20-1; **5g**, 90649-37-9; **5h**, 32706-24-4; **5i**, 2927-10-8; **5j**, 32706-22-2; **9a**, 93683-55-7; **9b**, 93683-56-8; 2,3-butanedione, 431-03-8; 4,5-diamino-1,2-dihydro-6-(ethoxycarbonyl)pyrimidin-2-one, 89897-53-0.

Supplementary Material Available: Elemental analyses on compounds **3c–j** and **4e–i**; ^1H NMR spectra on compounds **3c–j** and **4e–j** (3 pages). Ordering information is given on any current masthead page.

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Preparation of (*Z*)-1,4-Diphenylcyclohexane

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In line with our interest in the stereochemical properties of (arene)chromium tricarbonyl (CT) complexes,[1] we undertook to determine the conformational energy of a complexed phenyl group. This objective seemed most amenable to approach by Eliel's "counterpoise" method[2]

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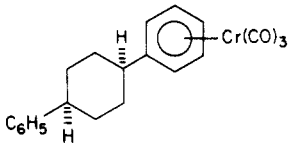
0022-3263/85/1950-0390$01.50/0

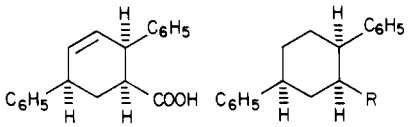
which entails the determination of conformational equilibrium for a disubstituted cyclohexane in which a second substituent is located *Z*-1,4 to the substituent under study. The second substituent must be of known conformational energy, and the two substituents should not differ greatly in size. We selected ((*Z*)-1,4-diphenylcyclohexane)CT (**1**)



1

as the most suitable compound for this purpose since it fulfills the above criteria and should be obtainable by the controlled direct complexation of (*Z*)-1,4-diphenylcyclohexane (**7**) with chromium hexacarbonyl. Access to an isomer-free sample of **7** was, however, problematical. Several procedures have been described which lead to a mixture of the isomeric 1,4-diphenylcyclohexanes from which only the *E* isomer, mp 172 °C, can be obtained pure by fractional crystallization.[3-5] We describe here two routes to pure **7**. The first is a six-step sequence in which the required stereochemistry is achieved by a Diels–Alder reaction. The second is a much more expeditious, if less systematic, approach which provides the desired product in equal purity.

The starting substance for our first synthesis was *c*-2,*c*-5-diphenyl-3-cyclohexene-*r*-1-carboxylic acid (**2**) from the [4 + 2] cycloaddition of acrylic acid and (*E*,*E*)-1,4-diphenyl-1,3-butadiene.[6]



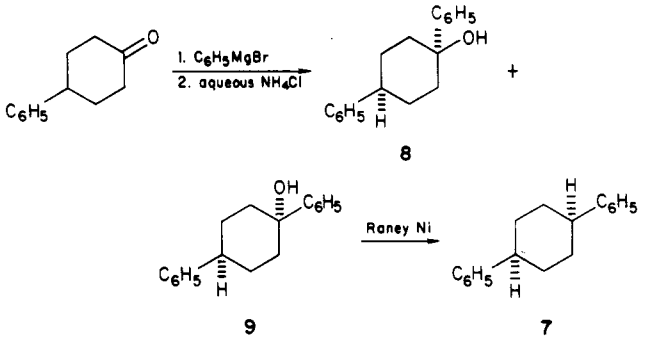
2

3, R = COOH
4, R = $COCH_3$
5, R = OH
6, R = $OCSOC_6H_5$
7, R = H

Catalytic hydrogenation of **2** provided the saturated carboxylic acid **3**. The latter with methyllithium gave methyl ketone **4** which, after Baeyer–Villiger oxidation and saponification, yielded the secondary alcohol **5**. Reductive removal of the hydroxyl group, accomplished by the action of tri-*n*-butyltin hydride on the derived phenyl thionocarbonate[7] (**6**), gave (*Z*)-1,4-diphenylcyclohexane (**7**) as an oil which could not be induced to crystallize. The sample was homogeneous by TLC, GC, and ^{13}C NMR. The ^{1}H NMR of **7** displayed the benzylic protons as a complex multiplet at δ 2.88 and was devoid of absorption in the region of δ 2.55 where the benzylic protons appear in the *E* isomer. The ^{13}C NMR spectrum of **7** shows signals at δ 29.8 and 40.1 for the benzylic and methylene carbons, respectively, and was devoid of absorption at δ 34.5 and 44.0 where these carbons appear in the *E* isomer. The overall yield was 18% for the six steps.

The second synthesis of **7** (Scheme I) began with the addition of phenylmagnesium bromide to 4-phenylcyclohexanone and was followed by chromatographic separation of the resulting 1,4-diphenylcyclohexanols. The earlier

Scheme I



8 **9** **7**

Table I. (Chemical Shift of Specified Carbon of the *Z* Isomer) - (Chemical Shift of That Carbon in the *E* Isomer)

carbon	4-*tert*-butyl	4-phenyl
ipso	+5.4	+4.7
1	−0.5	−0.6
2,6	+0.7	+1.1
3,5	−2.0	−1.1

eluted product, mp 185–188 °C, was obtained in 21% yield and is assigned the *Z* structure **8**; later eluants gave the second isomer, mp 116–118 °C in 49% yield which is assigned the *E* structure **9** These tertiary alcohols have apparently not previously been described. The assigned configurations are based primarily on a comparison of their ^{13}C NMR spectra with those of the known (*Z*)- and (*E*)-4-*tert*-butyl-1-phenyl-cyclohexanols[8] **10** and **11**, respectively. The pertinent ^{13}C chemical shifts for both series are given in Chart I, and chemical shift differences for corresponding carbons are summarized in Table I. It is apparent that our configurational assignments are in good agreement with the direction and approximate magnitude of the chemical shift differences, the agreement being best for those carbon atoms most distal to C–4. The configurations assigned to carbinols **8** and **9** are also in accord with the results of the following Raney nickel hydrogenolysis experiments.

Treatment of **9** with excess Raney nickel W-2 at 25 °C gave (*Z*)-1,4-diphenylcyclohexane (**7**) in 76% yield, identical in all respects with the corresponding product obtained in several steps from **2**. Hydrogenolysis of benzylic hydroxyl groups under these reaction conditions was previously known to occur with retention of configuration.[10] Similar treatment of the *E* epimer **8** led to complete recovery of starting material, a result which is not unexpected considering that axial alcohols are known to be resistant to hydrogenolysis under these conditions.[10] The most expeditious preparation of **7** (42% overall yield) consists of Raney nickel reduction of the mixed alcohols followed by the facile chromatographic separation of the desired hydrocarbon from unreacted tertiary alcohol.

The conversion of **7** to its CT complex **1** and the conformation study of **1** by low-temperature ^{13}C NMR will be reported separately[11] as part of a larger study of conformational effects in (arene)CT complexes.

Experimental Section

Melting points were taken on a Köfler micro hot stage and are uncorrected. IR spectra were recorded with a Beckman Acculab

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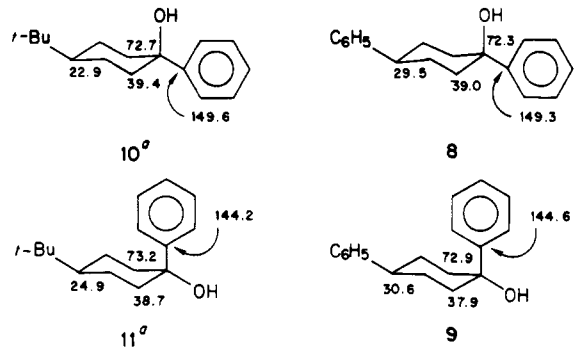
(11) Eliel, E. L.; Manoharan, M. M.; Levine, S. G.; Ng, A., manuscript in preparation.

Chart I



1 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. High-resolution ^1H NMR spectra were obtained at 250 MHz with a Bruker W.M. 250 spectrometer; chemical shifts are reported in part per million downfield from Me_4Si. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA.

***c*-2,*c*-5-Diphenylcyclohexane-*r*-1-carboxylic Acid (3).** The unsaturated carboxylic acid **2** (3.00 g, 0.0108 mol) and 5% palladium on carbon (0.400 g) were stirred in 50 mL of ethyl acetate under an atmosphere of hydrogen for 0.5 h by which time the expected volume of hydrogen had been absorbed and uptake ceased. Removal of catalyst by filtration through Celite followed by evaporation of solvent left 2.90 g (96% yield) of product, mp 141–144 °C, which was uniform by TLC. Recrystallization from toluene gave an analytical sample of **3**: mp 142–145 °C, R_f 0.65 (20% ether in CH_2Cl_2); IR ($CHCl_3$) 3500–3000, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (2 H, m), 2.13 (4 H, m), 2.60 (1 H, m) 2.90 (1 H, m), 3.60 (1 H, m), 7.20 (10 H).

Anal. Calcd for $C_{19}H_{20}$: C, 81.45; H, 7.14, Found: C, 81.24; H, 7.22.

***r*-1-Acetyl-*c*-2,*c*-5-diphenylcyclohexane (4).** A solution of methyllithium (0.141 mol) in ether (88 mL) was added dropwise and with vigorous stirring to a cold (0 °C) solution of carboxylic acid **3** (19.75 g, 0.0705 mol) in ether (500 mL). After 16 h at 25 °C, the reaction mixture was slowly added to a stirred mixture of ice and dilute hydrochloric acid. The organic layer was washed in sequence with 10% Na_2CO_3 and water, dried over $MgSO_4$, and filtered. Removal of solvent at reduced pressure left 8.60 g (44% yield) of ketone **4**: R_f 0.79 (30% methyl *tert*-butyl ether in hexane); IR (CCl_4) 3030–3010, 2930, 2860, 1710, 1600, 1500, 1450–850, 690 cm^{-1}; ^1H NMR (CCl_4) δ 1.62 (2 H, m), 1.85 (3 H, s), 2.11 (4 H, m), 3.68 (2 H, m), 3.75 (1 H, m), 7.18 (10 H, m). Characterization of ketone **4** was accomplished by preparing its (2,4-dinitrophenyl)hydrazone which was recrystallized from hot EtOAc–hexane: mp 183–185 °C. Anal. Calcd for $C_{26}H_{26}O_4N_4$: C, 68.12, H, 5.67; N, 12.22. Found: C, 67.88; H, 5.73; N, 12.16.

***c*-2,*c*-5-Diphenylcyclohexan-*r*-1-ol (5).** A solution of *m*-chloroperoxybenzoic acid (6.71 g of 85% reagent, 0.033 mol) and ketone **4** (9.00 g, 0.032 mol) in 50 mL of chloroform was kept in the dark at room temperature for 9 days. Benzoic acid was removed by filtration, and the filtrate was washed, in sequence, with aqueous $NaHSO_3$, aqueous $NaHCO_3$, and water. Evaporation of solvent from the dried ($MgSO_4$) ether solution left 8.89 g of the liquid acetate ester of **5**: IR (CCl_4) 1737 cm^{-1}; ^1H NMR (CCl_4) δ 5.12 (1 H, m, CHOAc). A solution of this ester in methanol (180 mL) containing KOH (18 g) was stored under nitrogen in the dark for 21 h at 25 °C. After removal of solvent, the residue was partitioned between water and CH_2Cl_2–hexane (1:3). The dried organic extract was freed of solvent leaving 6.30 g of liquid alcohol **5** (82% yield): R_f 0.16 (15% EtOAc in petroleum ether); IR (CCl_4) 3600, 1480, 1450, 680 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (1 H, s), 1.80 (6 H, m), 2.70 (1 H, m), 3.19 (1 H, m), 3.95 (1 H, m), 7.22 (10 H, m). With 3,5-dinitrobenzoyl chloride, **5** gave an ester, mp 151–157 °C (freom EtOAc– hexane). Anal. Calcd for $C_{25}H_{22}O_6N_2$: C, 67.11; H, 5.14. Found: C, 67.09, H; 4.99.

***(Z)*-1,4-Diphenylcyclohexane (7).** A solution of the secondary alcohol **5** (0.410 g, 0.001 68 mol), 4-dimethylaminopyridine (0.387 g, 0.001 63 mol), and phenyl chlorothionocarbonate (0.40 g, 0.0022 mol) in dry dichloromethane (2.0 mL) was stored at 25 °C for 18 h. After dilution with additional dichloromethane, the solution was washed, in sequence, with 10% aqueous citric acid, 10% aqueous $NaHCO_3$, and saturated NaCl—the dried ($MgSO_4$) and filtered. Removal of solvent left 0.641 g (97% yield) of liquid thionocarbonate **6**: R_f 0.72 (15% EtOAc in petroleum ether); IR (CCl_4) 1200 cm^{-1}; ^1H NMR (CCl_4) δ 2.10 (6 H, m), 2.88 (1 H, m), 3.62 (1 H, m) 5.58 (1 H, m), 6.82 (2 H, m), 7.20 (13 H, m).

A sample of thionocarbonate **6** (0.100 g, 0.000 257 mol), azobis(isobutyronitrile) (0.10 g, 0.000 61 mol), and tri-*n*-butyltin hydride (0.32 g, 0.001 12 mol) in deoxygenated toluene was heated at reflux under nitrogen for 13 h. Removal of solvent left a residue which was chromatographed on 10 g of silica gel. Elution with hexane and evaporation of the early eluates gave 0.033 g (53% yield) of **7**: R_f 0.35 (hexane); IR (CCl_4) 1480, 690 cm^{-1}; ^1H NMR (CCl_4) δ 1.75 (4 H, m), 2.88 (1 H, m), 6.95 (5 H, m); ^{13}C NMR (CCl_4) δ 2.98 (C-2, C-3, C-5, C-6), 40.1 (C-1, C-4), 125.3 (C-para), 126.3 (C-ortho), 127.9 (C-meta), 150.0 (C-ipso).

***t*-1,*c*-4-Diphenyl-*r*-1-cyclohexanol (8) and *t*-1,*t*-4-Diphenyl-*r*-1-cyclohexanol (9).** A solution of 4-phenylcyclohexanone (1.000 g, 0.005 75 mol) in 25 mL of ether was added to a solution of phenylmagnesium bromide in ether prepared from bromobenzene (1.491 g, 0.0095 mol) and magnesium (0.220 g, 0.0091 mol). The reaction mixture was kept under nitrogen at 25 °C for 19 h. The cooled reaction mixture was then quenched with saturated aqueous ammonium chloride solution. Evaporation of solvent from the dried organic solution left 1.250 g of epimeric tertiary alcohols. Separation was accomplished with a column of 80 g of silica gel (HF-254) which was eluted with methyl *tert*-butyl ether in hexane (1:4).

The early eluates yielded alcohol **8** (0.299 g, 21% yield): mp 185–188 °C (from EtOAc–hexane); R_f 0.19 (20% methyl *tert*-butyl ether in hexane); ^1H NMR δ 2.5–2.8 (1 H, m, benzylic H). Later eluates provided **9** (0.679 g, 47% yield): mp 116–118 °C (from EtoAc–hexane); R_f 0.11 (20% methyl *tert*-butyl ether in hexane); ^1H NMR δ 2.4–2.9 (3 H, m, benzylic H and C-2,6 equatorial protons). Anal. Calcd for $C_{18}H_{20}O$: C, 85.71; H, 8.33. Found: (**8**) C, 85.64; H, 8.31. (**9**) C, 85.62; H, 8.01.

***(Z)*-1,4-Diphenylcyclohexane from 4-Phenylcyclohexanone.** A sample of 4-phenylcyclohexanone (3.00 g) was converted to a mixture of tertiary alcohols **8** and **9** (3.43 g) by the procedure given above. A 1.50-g sample of this mixture was stirred overnight at 25 °C with Raney nickel (28.0 mL) and sodium ethoxide (from 0.080 g of Na) in 50 mL of ethanol. Removal of catalyst and evaporation of solvents left 1.25 g of residue. A 1.00-g portion was chromatographed on a column of 60 g of silica gel which was eluted with 30% methyl *tert*-butyl ether in hexane. The early eluates provided 0.749 g (53% yield) of (*Z*)-1,4-diphenylcyclohexane (**7**) with spectral and chromatographic properties identical with those described above. Later eluates gave 0.190 g (12% yield) of recovered **8**.

Registry No. **2**, 93782-94-6; **3**, 93782-95-7; **4**, 93782-96-8; **4** 2,4-DNP deriv, 93782-97-9; **5**, 93782-98-0; **5** acetate ester, 93782-99-1; **5** 3,5-dinitrobenzoate, 93783-00-7; **6**, 93783-01-8; **7**, 21072-41-3; **8**, 93783-02-9; **9**, 93783-03-0; methyllithium, 917-54-4; phenyl chlorothionocarbonate, 1005-56-7; 4-phenylcyclohexanone, 4894-75-1; bromobenzene, 108-86-1.

(Phenylazo)alkanes from Reaction of Nitrosobenzene with Alkylamines

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Reactions of nitrosobenzene with alkylamines were investigated by several groups[1-4] with contradictory results.

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