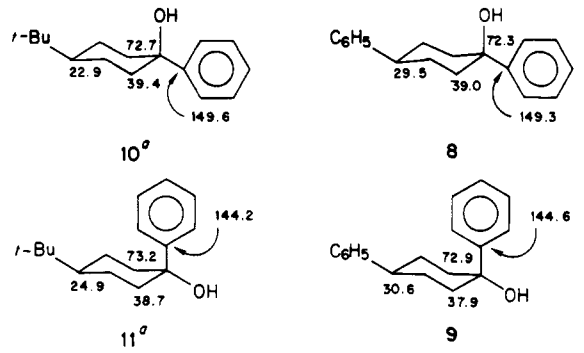
Chart I




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 ($CDCl_3$) $\delta$ 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 ($CCl_4$) $\delta$ 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 ($CCl_4$) $\delta$ 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 ($CCl_4$) $\delta$ 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 ($CCl_4$) $\delta$ 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 ($CCl_4$) $\delta$ 1.75 (4 H, m), 2.88 (1 H, m), 6.95 (5 H, m); $^{13}C$ NMR ($CCl_4$) $\delta$ 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 $\delta$ 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 $\delta$ 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.

(1) Lamson, D. W.; Sciarro, R.; Hryb, D.; Hutchins, R. O. *J. Org. Chem.* **1973**, *38*, 1952.
(2) (a) Suzuki, K.; Weisburger, E. K. *J. Chem. Soc. C* **1968**, 199. (b) *Tetrahedron Lett.* **1966**, 5409.

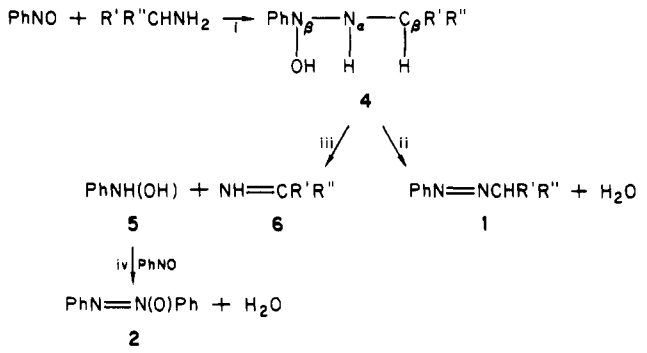
0022-3263/85/1950-0392$01.50/0 

**Table I. Products Observed from the Reactions of Nitrosobenzene with Amines[a]**

| entry | amine | amine/nitrosobenzene | solvent | % of products | | |
|---|---|---|---|---|---|---|
| | | | | (phenylazo)alkane | azoxybenzene | aniline |
| 1 | $MeNH_2$ | 1:1 | ether | 76 (39) | 23 | 1 |
| 2 | $EtNH_2$ | 1:1 | chloroform | 52 (30) | 46 | 2 |
| 3 | $n$-$PrNH_2$ | 1:1 | chloroform | 51 (30) | 49 | 0 |
| 4 | $i$-$PrNH_2$ | 0.8:1 | ether | 0 | 100 | 0 |
| 5 | $n$-$BuNH_2$ | 1:1 | methanol | 54 | 45 | 1 |
| 6 | $n$-$BuNH_2$ | 1:1 | chloroform | 50 (26) | 50 | 0 |
| 7 | $n$-$BuNH_2$ | 4:1 | chloroform | 0 | 95 | 5 |
| 8 | $t$-$BuNH_2$ | 1:1 | chloroform | 0 | 0 | 0 |
| 9 | $PhCH_2NH_2$ | 1.2:1 | ether | 0 | 100 | 0 |
| 10 | $Me_2NH$ | 1.2:1 | ether | 36 | 48 | 16 |
| 11 | $Et_2NH$ | 1:1 | ether | 12 | 85 | 23 |

[a] Each solution was prepared according to the method described in the Experimental Section. The reaction time was approximately 36 h. The yield of each product was determined by $^1H$ NMR spectroscopy. For most reactions, several runs were conducted and the average data of these runs were used. Values in the parentheses are yields isolated.

**Scheme I**




The earliest report by Gallagher[3] described the formation of (benzylazo)benzene (**1a**) from nitrosobenzene and benzylamine in alcohol. However, subsequent study by Su-

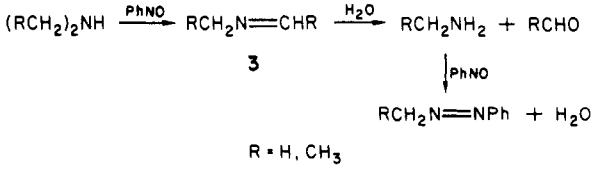
$$PhNO + RNH_2 \rightarrow PhN{=}NR + H_2O$$

**1a**, R = $PhCH_2$
**1b**, R = $CH_3$
**1c**, R = $CH_3CH_2$
**1d**, R = $CH_3CH_2CH_2$
**1e**, R = $CH_3CH_2CH_2CH_2$

zuki and Weisburger[2] failed to isolate any (phenylazo)alkanes (**1**) from similar reactions. The main products observed were azoxybenzene (**2**) (Scheme I) from the reduction of nitrosobenzene and aldehydes or ketones from the oxidation of the corresponding alkylamines. A reinvestigation of Gallagher's work later by Hutchins et al.[1] failed to produce **1a**, but azoxybenzene and *N*-benzylbenzaldimine, $PhCHNCH_2Ph$, were formed. Recently, we studied the same reactions at elevated temperatures and found that nitrosobenzene is reduced by alkylamines to azobenzene and aniline.[4,5] Careful monitoring of the reactions by $^1H$ NMR spectroscopy indicated that nitrosobenzene is rapidly converted to azoxybenzene which is further reduced by alkylamine to the final products. Our attempts to detect reaction intermediates provided strong evidence for the formation of **1** from nitrosobenzene and some primary alkylamines. In order to clarify the controversy concerning the formation of **1** and to explore the possibility of developing a new method for the synthesis of (arylazo)alkanes,[6] we reinvestigated the reaction of nitrosobenzene with primary alkylamines.

Addition of 1.0 equiv of methylamine to nitrosobenzene in ether at ambient temperature leads to the formation of **1b** in 76% yield, determined by NMR spectroscopy. An analytically pure product can be obtained from vacuum distillation of the reaction mixture. Other linear, primary alkylamines also react with nitrosobenzene to give the corresponding (phenylazo)alkanes **c–e**, albeit in lower yield. Vacuum distillation is also used for the purification of these products. Microanalyses and all the spectral data (see Experimental Section) of these compounds **1b–e** are in agreement with the assigned structures. It is noteworthy that all the products show a characteristic absorption at very near 4.0 ppm in the $^1H$ NMR spectra for the $\alpha$-protons of the alkyl group. In addition, the chemical shifts of the phenyl protons vary with the solvent. For example, the chemical shifts of the phenyl protons of **1e** in $CDCl_3$ appear at $\delta$ 7.45 (*m*- and *p*-H) and 7.66 (*o*-H), while the corresponding chemical shifts in $C_6D_6$ are $\delta$ 7.04 and 7.80, respectively. Other (phenyazo)alkanes also show similar variations with solvents. While the exact cause for such behavior is not known, it might arise from the interaction of the two electron pairs on the nitrogen atoms with the solvent and with the aromatic ring. The other products observed in the reaction of primary alkylamines with nitrosobenzene are azoxybenzene and aniline. The yields of these products are summarized in Table I.

While only primary amines are expected to give (phenylazo)alkanes, the reaction of secondary amines $(RCH_2)_2NH$ with nitrosobenzene also yield some of the (phenylazo)alkanes, $PhN{=}NCH_2R$ in addition to azoxybenzene (Table I). For example, addition of 1.0 equiv of $Me_2NH$ and $Et_2NH$ separately to nitrosobenzene affords **1b** and **1c** in 36% and 12% yields, respectively. These surprising results may be understood in terms of the following sequence of reactions which involve oxidation of the secondary amine to imine **3** by nitrosobenzene, hydrolysis of **3** to a primary amine, and reaction of this amine with nitrosobenzene to give phenylazoalkane.




The reaction of benzylamine with nitrosobenzene deserves special attention because of the inconsistent results reported previously and our observation of phenylazoalkanes in similar reactions. Analysis of the $^1H$ NMR spectrum of a 1:1 mixture of benzylamine and nitrosobenzene indicates that only azoxybenzene and *N*-benzyl-

(3) Gallaher, P. *Bull. Soc. Chim. Fr.* **1921**, *29*, 683.
(4) Ho, L. Y.; Wu, Y. M.; Cheng, C. H. *Proc. Natl. Sci. Counc., Repub. China, Part B* **1984**, *8*, 93.
(5) Chung, T. F.; Wu, Y. M.; Cheng, C. H. *J. Org. Chem.* **1984**, *49*, 1215.
(6) For examples of the synthesis of (arylazo)alkanes, see: (a) Bellamy, A. J.; Guthrie, R. D. *J. Chem. Soc.* **1965**, 2788. (b) Curtin, D. Y.; Ursprung, J. A. *J. Org. Chem.* **1956**, *21*, 1221.

benzaldimine ($PhCHNCH_2Ph$) are present in the mixture; this observation is completely in agreement with the report of Hutchins et al.[1] Thus, it appears that in this case, no (phenylazo)alkane **1a** is produced. Other primary amines that do not give (phenylazo)alkanes are *tert*-butylamine and isopropylamine. The former amine does not react with nitrosobenzene at ambient temperature, while the latter reduces nitrosobenzene to only azoxybenzene and a trace of aniline.

A mechanism proposed for the reactions of nitrosobenzene with primary amines is depicted in Scheme I and involves an initial nucleophilic attack by alkylamine on nitrosobenzene to afford **4**, followed by elimination of water from **4** to produce the corresponding phenylazoalkane. Intermediate **4**[7] may also cleave to produce phenylhydroxylamine (**5**) and imine **6**. Condensation of **5** with nitrosobenzene gives azoxybenzene. As shown in entries 6 and 7 of Table I, a sharp decrease in the ratio of **1e** to azoxybenzene is obtained upon increasing the amount of *n*-butylamine employed. The result appears to indicate that step iii in the scheme is a base-catalyzed process similar to an E2 elimination reaction. In addition to the concentration of amines employed, the substituents on $C_\beta$ of **4** can also influence the rates of steps ii and iii, with the latter expected to be more affected. The product distributions revealed in Table I show that the relative amount of azoxybenzene to (phenylazo)alkane is a function of the amine and increases in the order $CH_3NH_2 < CH_3CH_2NH_2 \approx CH_3CH_2CH_2NH_2 \approx CH_3CH_2CH_2CH_2NH_2 < (CH_3)_2CHNH_2$. These results clearly demonstrate that replacement of one or two hydrogens at $C_\beta$ of **4** by alkyl groups promotes the formation of phenylhydroxylamine, consistent with an E2 mechanism of Saytzeff type[8] for step iii. While the ratio of (phenylazo)alkane to azoxybenzene is governed by the relative rates of steps ii and iii, neither one is the rate-determining step for the overall reaction in view of the fact that $^1H$ NMR monitoring of the reaction solution shows that only the reactants and the final products, (phenylazo)alkane and azoxybenzene, are present during the reaction. The presence of reactants nitrosobenzene and alkylamine indicates that the slowest step of the entire reaction is the attack of alkylamine on nitrosobenzene, i.e., step i.

## Experimental Section

**General Procedures.** $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL FX-100 spectrometer, IR spectra were recorded on a JASCO A-100 spectrometer, and mass spectra were obtained on a JEOL JMS-D100 mass spectrometer. Methylamine, ethylamine, (Merck), *n*-propylamine (Aldrich), *n*-butylamine, (Fluka), and nitrosobenzene (Tokyo Kasei) were used as purchased.

**Isolation of (Phenylazo)methane (1b).** To 1.07 g (10.0 mmol) of nitrosobenzene in 25 mL of ether was added 0.310 g (10.0 mmol) of methylamine (35% in water). The mixture was stirred at ambient temperature for 24 h and then dried over magnesium sulfate. Evaporation of the solvent followed by vacuum distillation at 45 °C and 3 torr gave 0.471 g (39%) of a pale yellow liquid. Analysis of the original mixture after solvent removal by $^1H$ NMR spectroscopy showed the yield of **1b** was 76%. Spectral data for the isolated product: $^1H$ NMR ($CDCl_3$) $\delta$ 3.98 (s, 3 H), 7.36 (m, 3 H), 7.64 (d of d, $J$ = 8, 2 Hz, 2 H); $^1H$ NMR ($C_6D_6$) $\delta$ 3.72 (s, 3 H), 7.08 (m, 3 H), 7.76 (d of d, $J$ = 8, 2 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 57.1 (q), 121.8 (d), 128.7 (d), 130.1 (d), 151.8 (s); MS, $m/e$ 120 ($M^+$), 105 ($M^+ - CH_3$), 77 ($M^+ - CH_3 - N{=}N$). Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.31. Found: C, 69.82; H, 6.78; N, 23.41.

**(Phenylazo)ethane (1c).** To 1.07 g (10.0 mmol) of nitrosobenzene in 25 mL of chloroform was added 0.45 g (10.0 mmol) of ethylamine (70% in water). The mixture was stirred at ambient temperature for 36 h. The desired product was then isolated by following the method for phenylazomethane. Vacuum distillation was conducted at 50 °C and 3 torr. Analytical data: yield, 30%; yield determined by $^1H$ NMR spectroscopy, 52%; $^1H$ NMR ($CDCl_3$) $\delta$ 1.42 (t, $J$ = 6 Hz, 3 H), 4.06 (q, $J$ = 6 Hz, 2 H), 7.38 (m, 3 H), 7.62 (d of d, $J$ = 8, 2 Hz, 2 H); $^1H$ NMR ($C_6D_6$) $\delta$ 1.20 (t, $J$ = 6 Hz, 3 H), 3.92 (q, $J$ = 6 Hz, 2 H), 7.04 (m, 3 H), 7.76 (d of d, $J$ = 8, 2 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 12.5 (q), 63.5 (t), 121.8 (d), 128.5 (d), 129.8 (d), 151.8 (s); MS, $m/e$ 134 ($M^+$), 105, 77. Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.87. Found: C, 71.74; H, 7.51; N, 20.94.

**(Phenylazo)-*n*-propane (1d).** To 1.07 (10.0 mmol) of nitrosobenzene was added 0.55 g (10.0 mmol) of *n*-propylamine in 25 mL of chloroform. The solution was left at ambient temperature for 35 h. The product was isolated by the same method used for (phenylazo)methane. Vacuum distillation was conducted at 50 °C and 1 torr: yield, 30%; yield determined by NMR spectroscopy, 51%; $^1H$ NMR ($CDCl_3$) $\delta$ 1.02 (t, $J$ = 6 Hz, 3 H), 1.92 (m, $J$ = 6 Hz, 2 H), 4.00 (t, $J$ = 6 Hz, 2 H), 7.36 (m, 3 H), 7.62 (d of d, $J$ = 8, 2 Hz, 2 H); $^1H$ NMR ($C_6D_6$) $\delta$ 0.8 (t, $J$ = 6 Hz, 3 H), 1.78 (m, $J$ = 6 Hz, 2 H), 3.92 (t, $J$ = 6 Hz, 2 H), 7.08 (m, 3 H), 7.80 (d of d, $J$ = 8, 2 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 12.1 (q), 21.3 (t), 71.2 (t), 121.9 (d), 128.7 (d), 130.0 (d), 151.9 (s); MS, $m/e$ 148 ($M^+$), 105, 77. Anal. Calcd for $C_9H_{12}N_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.83; H, 8.11; N, 19.08.

**(Phenylazo)-*n*-butane (1e).** This compound is prepared by a procedure similar to that of (phenylazo)-*n*-propane. Analytical data: yield, 26%; yield determined by NMR spectroscopy, 50%; $^1H$ NMR ($CDCl_3$) $\delta$ 1.00 (t, $J$ = 7 Hz, 3 H), 1.46 (m, $J$ = 7 Hz, 2 H), 1.90 (m, $J$ = 7 Hz, 2 H), 4.06 (t, $J$ = 7 Hz, 2 H), 7.40 (m, 3 H), 7.64 (d of d, $J$ = 8, 2 Hz, 2 H); $^1H$ NMR ($C_6D_6$) $\delta$ 0.82 (t, $J$ = 7 Hz, 3 H), 1.28 (m, $J$ = 7 Hz, 2 H), 1.76 (m, $J$ = 7 Hz, 2 H), 3.98 (t, $J$ = 7 Hz, 2 H), 7.04 (m, 3 H), 7.80 (d of d, $J$ = 8, 2 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.8 (q), 20.6 (t), 29.9 (t), 69.1 (t), 121.8 (d), 128.6 (d), 129.8 (d), 151.8 (s); MS, $m/e$ 162 ($M^+$), 105, 77. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.69; N, 17.26. Found: C, 73.85; H, 8.54; N, 17.71.

**Acknowledgment.** We thank the National Science Council of the Republic of China for support of this work.

**Registry No.** **1b**, 4406-66-0; **1c**, 935-08-0; **1d**, 84113-60-0; **1e**, 940-55-6; **2**, 495-48-7; ONPh, 586-96-9; $MeNH_2$, 74-89-5; $EtNH_2$, 75-04-7; $PrNH_2$, 107-10-8; $BuNH_2$, 109-73-9; *i*-$PrNH_2$, 75-31-0; $PhCH_2NH_2$, 100-46-9; $Me_2NH$, 124-40-3; $Et_2NH$, 109-89-7; aniline, 62-53-3.

(7) **4** was suggested as an intermediate for the formation of phenylhydroxylamines by Hutchins et al. A Cope-type elimination was employed. See ref 1.
(8) Ford, W. T. *Acc. Chem. Res.* **1973**, *6*, 410.

## Reduction of Aromatic Rings by 2-Propanol with Raney Nickel Catalysis

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2-Propanol is a reducing agent in certain environments that include photochemical and basic conditions as well as the presence of Raney nickel. This catalyst has been employed in some instances to reduce ketones to alcohols[1] in 2-propranol and to study the equilibration of epimeric alcohols[2] in the presence of some acetone.

In another connection, we were interested in the equilibrium position of the *syn*- and *anti*- 5-phenyladamantan-2-ols and attempted to measure it by treating

(1) (A) Fieser, M.; Fieser, L. F. "Reagents for Organic Synthesis"; Wiley: New York, 1967; p 723 ff. (b) Augustine, R. L. "Catalytic Hydrogenation"; Marcel Dekker: New York, 1965; p 24, 71.
(2) Eliel, E. L.; Schroeder, S. H. *J. Am. Chem. Soc.* **1965**, *87*, 5031.

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