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Alkylation–Reduction of Carbonyl Systems. IV. The Convenient and Selective Synthesis of Simple and Complex Aromatic Hydrocarbons by Phenylation–Reduction of Aldehydes and Ketones

Stan S. Hall* and Frank J. McEnroe

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, New Jersey 07102

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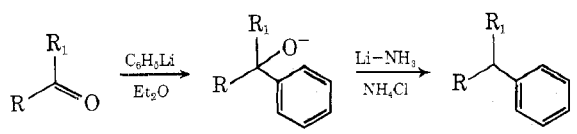
Simple and complex aromatic hydrocarbons are conveniently prepared from aldehydes and ketones by tandem phenylation–reduction. By this procedure benzyl alkoxides, generated *in situ* by phenylation, are reduced by lithium–ammonia–ammonium chloride to the corresponding aromatic hydrocarbons. Complex aldehydes and ketones, containing structural features or other functional groups which might not be compatible with the reaction conditions, were subjected to the phenylation–reduction sequence to explore the limits of this simple synthetic procedure as an efficient and selective synthesis of rather complex molecular structures. These structural features or functional groups included steric hindrance, terminal olefins, isolated double bonds, α,β-unsaturated carbonyl systems, an $\alpha,\beta,\gamma,\delta$-unsaturated ketone system, α,β-unsaturated aldehyde systems containing isolated double bonds, a cross-conjugated ketone, a cyclopropane ring, aromatic systems, and heterocycles.

This laboratory innovated the concept of tandem alkylation–reduction of aromatic carbonyl systems as a convenient method of preparing aromatic hydrocarbons by the lithium–ammonia reduction of benzyl alkoxides generated *in situ* by alkylation.[1] The mechanistic and selective synthetic utility of the procedure was then demonstrated for the synthesis of aromatic hydrocarbons and alcohols by the alkylation–reduction of benzylidene ketones and aldehydes.[2] Herein we report the extension of this convenient procedure for the selective synthesis of simple and complex aromatic hydrocarbons in excellent isolated yields by the phenylation–reduction of appropriate aldehydes and ketones.

The general procedure, which is carried out in the same reaction vessel and consumes only a few hours, is to generate a benzyl alkoxide in a metal–ammonia reaction vessel[3] by the addition of the aldehyde or ketone to phenyllithium, prepared *in situ* from bromobenzene and excess lithium, in ether. Ammonia is subsequently distilled into the vessel, and then the resulting dark blue mixture is cautiously quenched with ammonium chloride.[4]

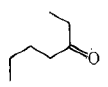
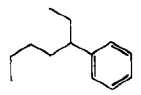
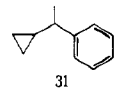
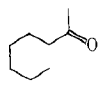
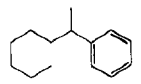
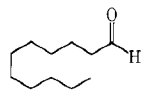
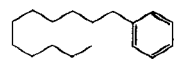
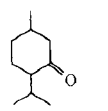
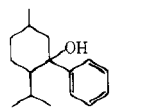
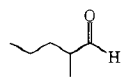
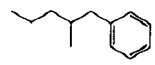
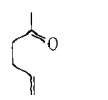
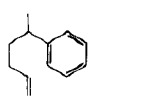
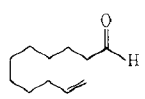
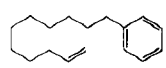
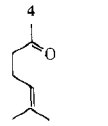
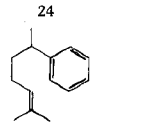
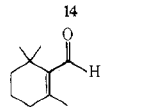
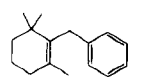
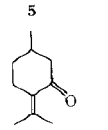
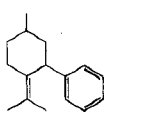
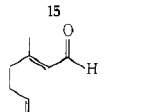
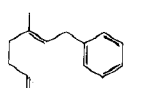
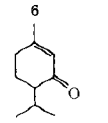
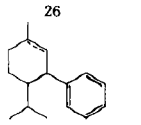
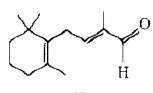
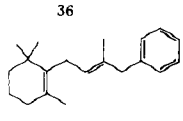
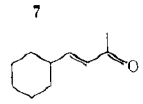
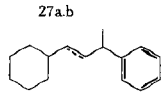
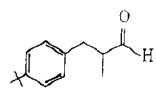
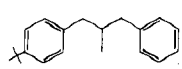
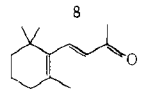
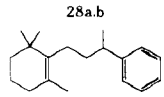
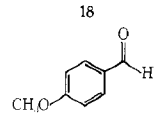
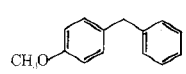
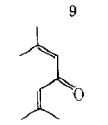
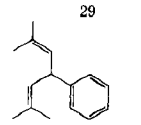
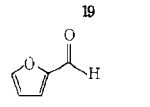
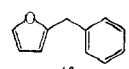


The primary objective of this study, after first demonstrating the feasibility of the procedure with simple aldehydes and ketones, was to test the method using aldehydes and ketones containing structural features or functional groups which may or may not be compatible with the conditions. By so doing, we would explore the possible limits of this simple synthetic procedure as a selective method of preparing complex aromatic hydrocarbons which might be difficult to elaborate by conventional methods.

Table I contains a listing of the aldehydes and ketones that were subjected to this procedure. The carbonyl compounds were carefully selected to include the following structural features or functional groups: steric hindrance,[5] terminal olefins,[6] isolated double bonds, α,β-unsaturated carbonyl systems, an $\alpha,\beta,\gamma,\delta$-unsaturated ketone system (a 1,3-diene system[7] after phenylation–reduction), α,β-unsaturated aldehyde systems containing isolated double bonds (one of which is a 1,4-diene system[8] after phenylation–reduction), a cross-conjugated ketone, a cyclopropane ring,[9] aromatic systems,[10] and heterocycles[9a,11]—features and groups that might interfere with or be vulnerable to these metal–ammonia conditions.

Careful inspection of the products listed in Table I reveals that almost all of these structural features or functional groups were compatible with the conditions of the procedure. The only carbonyl compound that resisted reduction, after phenylation, was menthone (**3**), which is probably due to steric interactions.[5,12] An example of overcohol,[13] a 1,3-diene system still remains which is vulnerable and reduces, as one would predict,[7] by 1,2-addition to the less substituted double bond. The phenylation–reduction of two α,β-unsaturated ketones, piperitone (**7**) and 4-cyclohexyl-*trans*-3-buten-2-one (**8**), led to mixtures of the corresponding olefin and aromatic hydrocarbon, a result hexyl-*trans*-3-buten-2-one (**8**), led to mixtures of the corresponding olefin and aromatic hydrocarbon, a result which did not change substantially by varying the amount of lithium used for the reduction step. The only carbonyl compound found to be completely incompatible with the reductive conditions was methyl 2-thienyl ketone. Phenylation–reduction of this ketone, which is not included in Table I,

Table I
Phenylation-Reduction of Aldehydes and Ketones

Carbonyl compd	Phenylation–reduction product	% Yield: Analytical[a]	% Yield: Isolated[b]	Comments	Carbonyl compd	Phenylation–reduction product	% Yield: Analytical[a]	% Yield: Isolated[b]	Comments
 1	 21	98	96		 11	 31	100	91	
 2	 22	95	88		 12	 32	100	91	
 3	 23	100	99	*c*, *d*	 13	 33	99	83	
 4	 24	100	94		 14	 34	100	99	
 5	 25	100	90		 15	 35	100	99	
 6	 26	98	85		 16	 36	99	90	*h*
 7	 27a,b	83	78	*c*, *e*	 17	 37	99	93	
 8	 28a,b	99	94	*f*	 18	 38	99	99	
 9	 29	100	98	*g*	 19	 39	100	96	
 10	 30	93	93		 20	 40	100	93	*c*

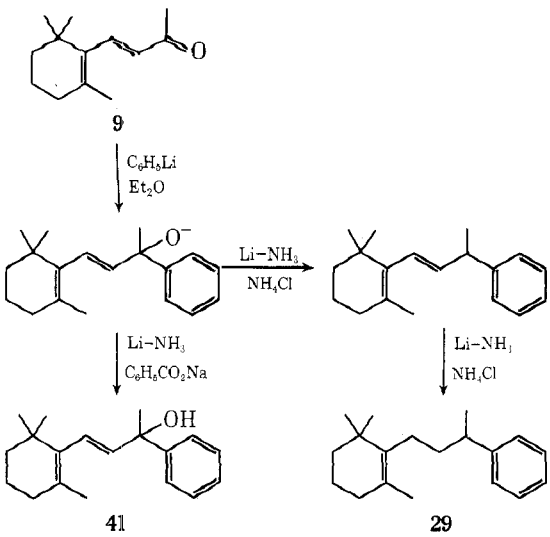
[a] Analyzed by glpc (% of volatiles). [b] Isolated by column chromatography. [c] The phenylation step was performed at *ca.* −78°. [d] This result was not altered by using an enormous excess of lithium (560 mg, 80 mg-atoms). [e] Using the normal amount of lithium (280 mg, 40 mg-atoms) or a large excess (560 mg, 80 mg-atoms) yielded an aromatic hydrocarbon fraction (83%) and 3-phenyl-1-*p*-menthen-3-ol (17%). The aromatic hydrocarbon fraction was an inseparable mixture (60:40) of 3-phenyl-1-*p*-methene (**27a**) and 3-phenyl-*p*-menthane (**27b**). Less lithium (140 mg, 20 mg-atoms) yielded the same aromatic hydrocarbon mixture (30%) and 3-phenyl-1-*p*-menthen-3-ol (70%). [f] The use of various amounts of lithium (140 mg, 20 mg-atoms; 280 mg, 40 mg-atoms; 420 mg, 60 mg-atoms; or 560 mg, 80 mg-atoms) yielded the same product **28** which was an inseparable mixture (65:35) of 1-cyclohexyl-3-phenyl-*trans*-1-butene (**28a**) and 1-cyclohexyl-3-phenylbutane (**28b**). [g] Using the normal amount of lithium (280 mg, 40 mg-atoms) yielded a mixture (30:70) of 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-phenyl-*trans*-1-butene and **29**. Less lithium (140 mg, 20 mg-atoms) resulted in the above mixture (60%) as well as the alcohol **41** (40%). Excess lithium (420 mg, 60 mg-atoms) led to **29** exclusively. [h] The aldehyde was a commercial sample of citral.

led to a complex mixture which was difficult to purify and characterize, but the data on the crude product material did indicate that the thiophene ring was being destroyed.[11b-e]

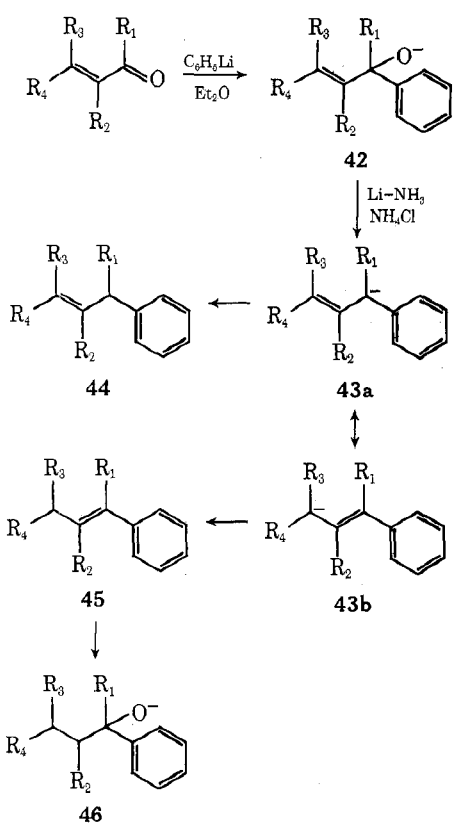
The yields, analytical (glpc) and isolated (column chromatography), listed in Table I are impressive. Generally, the only side product of the sequence is the benzyl alcohol which seems to result when the intermediate benzyl alkoxide is splattered on the walls of the reaction vessel and is not in solution during the quench. The contaminant benzyl alcohol, when present, is efficiently removed by column chromatography. In a few examples minor products were detected which stemmed from the phenylation step; these side reactions were effectively minimized by performing this operation at low temperature[14] (*ca.* −78°) and are noted in Table I.

Perhaps the most interesting mechanistic implications of this study are those involving the phenylation–reduction of the α,β-unsaturated carbonyl compounds. With these systems the reduction of the intermediate benzyl alkoxide **42** (see Scheme II) must proceed through the anion **43** which in almost every example protonates exclusively at the ben-

Scheme I



Scheme II



zylic position, trapping anion **43a**, yielding the olefin **44**. The net result is the selective introduction of a double bond β to an aromatic ring, a difficult task using classical methods. Only in two examples, **7** and **8**, does some protonation of anion **43b** occur yielding the styrene **45** which would be rapidly reduced[15] to the aromatic hydrocarbon **46**.

As a result of this study it appears that phenylation–reduction is a uniquely viable procedure for the efficient and selective synthesis of rather complex aromatic hydrocarbons. By the proper selection of the requisite carbonyl system, challenging organic structures can be rapidly assembled.

Experimental Section[16]

General Comments. The entire reaction sequence was performed under a static prepurified nitrogen atmosphere which is connected by a T tube to the assembly and to a soda-lime drying trap (then on to an oil bubbler). All glassware was oven-dried, cooled to room temperature in a large box desiccator, and then quickly assembled. Phenyllithium was generated *in situ* in the metal–ammonia reaction vessel[3] from bromobenzene and lithium in ether. Anhydrous ether was used directly from freshly opened containers. Lithium wire (0.125 in., 0.01% Na, Ventron Corp.) was hammered to a foil, cut into small pieces, and rinsed in petroleum ether just prior to use. Anhydrous ammonia was distilled into the reaction vessel. Gas chromatographic analyses (glpc) were performed on a Hewlett-Packard Model 7610A high-efficiency chromatograph (flame detector) using a 4 ft × 6 mm (all glass) 4% silicone gum rubber UCC-W-982 (methylvinyl) on 80–100 HP Chromosorb W (AW, DMCS) column. Purification of the product by column chromatography was accomplished on Woelm neutral aluminum oxide (activity grade I or II) by elution with petroleum ether. Further purification, sometimes necessary for satisfactory elemental analyses, was accomplished using a Büchi kugelrohr bulb-to-bulb distillation apparatus at reduced pressure. All boiling points are uncorrected. The assigned structure of each product is consistent with the spectral data and composition analysis. The phenylation–reduction of 3-heptanone (**1**) is described, in detail, to illustrate the general procedure.

Phenylation–Reduction of 3-Heptanone (1). 3-Phenylheptane (21). Into a metal–ammonia reaction vessel[3] containing a stirred mixture of 280 mg of lithium (40 mg-atoms, *ca.* 25 pieces which had been hammered to a foil) in 10 ml of anhydrous ether was slowly added a solution of 790 mg (5.0 mmol) of bromobenzene in 7 ml of ether. After 1 hr a solution of 285 mg (2.5 mmol) of 3-heptanone (**1**) in 8 ml of ether was slowly added and the mixture was stirred for an additional 1 hr. Ammonia (*ca.* 25 ml) was carefully, to prevent excessive splattering, distilled into the mixture and, once the dark blue color of the mixture was established,[17] *ca.* 3 g of ammonium chloride was cautiously added[18] (*ca.* 5 min) to discharge the blue color and the ammonia was allowed to evaporate. After the residue had been partitioned between aqueous NaCl and ether, the organic phase was dried ($MgSO_4$), filtered, concentrated at water aspirator pressure at 40–50°, and then analyzed (glpc). Following column chromatography 422 mg (96%) of 3-phenylheptane (**21**) was obtained as a colorless oil: bp 69–71° (1.2 mm); ir (film) 3030, 2960, 2930, 1450, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.37–6.84 (5 H, m), 2.61–2.09 (1 H, m), 1.88–1.35 (4 H, m), 1.35–0.99 (4 H, m), and two overlapping perturbed triplets centered at 0.82 (3 H, t, J = 7 Hz) and 0.73 (3 H, t, J = 7 Hz); mass spectrum *m/e* (relative intensity) 176 (M^+, 13), 147 (20), 119 (30), 105 (8), 91 (100), and 77 (5).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.31; H, 11.37.

2-Phenyloctane (22). Treatment of 2-octanone (**2**) as described above yielded **22** (88%) as a colorless oil: ir (film) 3030, 2960, 2930, 1450, and 695 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.18 (5 H, apparent s), 2.66 (1 H, apparent sextet, J = 7 Hz), 1.83–1.38 (2 H, m), a doublet centered at 1.22 (3 H, d, J = 7 Hz) superimposed on an apparent broad singlet with fine splitting centered at 1.24 (8 H, broad s), and a perturbed triplet centered at 0.87 (3 H, t); mass spectrum *m/e* (relative intensity) 190 (M^+, 9), 175 (10), 105 (100), 91 (13), 77 (6), and 43 (6).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.29; H, 11.49.

3-Phenyl-*p*-menth-3-ol (23). Treatment of menthone (**3**) as described above, except that the phenylation step was run at *ca.* −78°, yielded **23** (99%) as a colorless oil: bp 97–98° (1.2 mm); ir (CCl_4) 3625, 3500, 3035, 2925, 1600, 1490, 1445, and 690 cm^{-1}; nmr (60 MHz, $CDCl_3$) δ 7.58–7.11 (5 H, m), 2.22–1.82 (1 H, m), 1.82–1.46 (7 H, m) on which is superimposed two broad singlets (which disappear when D_2O is added) centered at 1.60 (0.66 H, –OH) and 1.46 (0.34 H, –OH) which represent two geometric isomers, an apparent triplet centered at 1.28 (1 H, t, J = 7 Hz), and a complex set of lines from 0.97 to 0.62 (9 H, m) which appears to be three major overlapping doublets (J = 7 Hz) and three minor overlapping doublets (J = 7 Hz) representing two geometric isomers present in a ratio of about 2:1; mass spectrum *m/e* (relative intensity) 232 (M^+, 26), 217 (2), 214 (2), 147 (100), 120 (12), 105 (18), 91 (6), 77 (9), and 41 (9).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.77; H, 10.37.

5-Phenyl-1-hexene (24). Treatment of 5-hexen-2-one (**4**) as described above yielded **24** (94%) as a colorless oil: ir (film) 3070, 3030, 2960, 2930, 1642, 1603, 1492, 1450, 985, 900, 750, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.20 (5 H, apparent s), 6.18–5.48 (1 H, m), 5.18–4.97 (1 H, m), 4.92–4.75 (1 H, m), 2.72 (1 H, apparent sextet, J = 7 Hz), 2.20–1.52 (4 H, m), and 1.23 (3 H, d, J = 7 Hz); mass spectrum m/e (relative intensity) 160 (M^+, 7), 145 (5), 118 (58), 105 (100), 91 (31), and 77 (13).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.79; H, 10.34.

2-Methyl-6-phenyl-2-heptene (25). Treatment of 6-methyl-5-hepten-2-one (**5**) as described above yielded **25** (90%) as a colorless oil: ir (film) 3030, 2960, 2930, 1600, 1495, 1450, 750, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.21 (5 H, apparent s), 5.30–4.92 (1 H, m), 2.69 (1 H, apparent q, J = 7 Hz), a broad singlet at 1.68 (3 H, s) superimposed on a broad multiplet at 2.15–1.58 (4 H, m), 1.51 (3 H, broad s), and 1.23 (3 H, d, J = 7 Hz); mass spectrum m/e (relative intensity) 188 (M^+, 65), 118 (100), 105 (93), 91 (47), 77 (14), 69 (17), 55 (23), and 41 (26).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 88.98; H, 10.66.

3-Phenyl-4(8)-*p*-menthene (26). Treatment of (+)-pulegone (**6**) as described above yielded **26** (85%) as a colorless oil: ir (film) 3070, 3035, 2925, 1603, 1490, 1450, and 690 cm^{-1}; nmr (100 MHz, $CDCl_3$) δ 7.37–6.98 (5 H, m), 4.13-4.00 (0.3 H, m Ph–C*H*–, equatorial proton), 3.84–3.60 (0.7 H, m, Ph–C*H*–, axial proton), *ca.* 2.60–2.10 (2 H, complex m), *ca.* 2.10–1.10 (5 H, complex m) on which are superimposed three sharp singlets at 1.73, 1.72, and 1.71 (3 H, CH_3C=, configurational and conformational isomers), and three sharp singlets at 1.45, 1.44, and 1.42 (3 H, CH_3C=, configurational and conformational isomers), and 0.86 (3 H, d, J = 5.5 Hz); mass spectrum m/e (relative intensity) 214 (M^+, 100), 199 (42), 171 (35), 157 (16), 143 (47), 129 (29), 115 (14), 91 (30), and 77 (8).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.39; H, 10.20.

Mixture 27. 3-Phenyl-1-*p*-menthene (27a) and 3-Phenyl-*p*-menthane (27b). Treatment of piperitone (**7**) as described above, except that the phenylation step was run at *ca.* −78°, yielded **27** (78%) as a colorless oil: bp 120–121° (1.2 mm). Careful analysis of the 100-MHz nmr spectrum of this oil indicated that it was a 60:40 mixture of 3-phenyl-1-*p*-menthene (**27a**) and 3-phenyl-*p*-menthane (**27b**). The mass spectrum confirmed this conclusion. The mixture, which indicated one peak by glpc analysis, could not be separated by column chromatography or distillation. The third product of this reaction was 3-phenyl-1-*p*-menthen-3-ol (17%). The above results were not altered by using an enormous excess of lithium (560 mg, 80 mg-atoms). Less lithium (140 mg, 20 mg-atoms) yielded the mixture **27** (30%) and the above alcohol (70%).

Mixture 28. 1-Cyclohexyl-3-phenyl-*trans*-1-butene (28a) and 1-Cyclohexyl-3-phenylbutane (28b). Treatment of 4-cyclohexyl-*trans*-3-buten-2-one (**8**) as described above yielded **28** (94%) as a colorless oil: bp 95–97° (1.1 mm). Careful analysis of the 60-MHz nmr spectrum of this oil indicated that it was a 65:35 mixture of 1-cyclohexyl-3-phenyl-*trans*-1-butene (**28a**) and 1-cyclohexyl-3-phenylbutane (**28b**), which was confirmed by the mass spectrum. The mixture, which indicated one peak by glpc analysis, could not be separated by column chromatography or distillation. Various quantities of lithium (140 mg, 20 mg-atoms; 420 mg, 60 mg-atoms; or 560 mg, 80 mg-atoms) did not alter the above result.

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-phenylbutane (29). Treatment of β-ionone (**9**) as described above, except that excess lithium (420 mg, 60 mg-atoms) was used to avoid a mixture of **29** and 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-phenyl-*trans*-1-butene, yielded **29** (98%) as a colorless oil: bp 95–98° (1.2 mm), ir (film) 3070, 3035, 2930, 1605, 1495, 1450, 755, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.21 (5 H, apparent s), 2.98–2.34 (1 H, apparent sextet, J = 7 Hz), and two broad multiplets from *ca.* 2.10 to 1.60 (6 H, m) and from *ca.* 1.60 to 1.20 (4 H, m) on which are superimposed a singlet at 1.48 (3 H, s) and a doublet at 1.27 (3 H, d), and 0.91 (6 H, s); mass spectrum m/e (relative intensity) 256 (M^+, 12), 241 (5), 123 (100), 118 (92), 105 (34), 95 (27), 91 (23), 81 (32), and 41 (25).

Anal. Calcd for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 88.96; H, 11.07.

2,6-Dimethyl-4-phenyl-2,5-heptadiene (30). Treatment of phorone (**10**) as described above yielded **30** (93%) as a colorless oil: bp 80–84° (1.2 mm), ir (film) 3070, 3030, 2975, 2925, 2730, 1600, 1488, 1445, 870, 730, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.09 (5 H, apparent s), 5.21 (2 H, d, J = 9 Hz, with fine splitting of *ca.* 1.2 Hz), 4.30 (1 H, t, J = 9 Hz), and four overlapping singlets at 1.73 (3 H, s), 1.72 (3 H, perturbed s), 1.70 (3 H, s), and 1.69 (3 H, perturbed s); mass spectrum m/e (relative intensity) 200 (M^+, 100), 185 (68), 157 (65), 145 (48), 143 (68), 129 (34), and 91 (37).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.95; H, 10.01.

1-Cyclopropyl-1-phenylethane (31). Treatment of cyclopropyl methyl ketone (**11**) as described above yielded **31** (91%) as a colorless oil: bp 119–121° (760 mm); ir (film) 3080, 3035, 3010, 2970, 2930, 2880, 1605, 1490, 1450, 1015, 810, 750, and 690 cm^{-1}; nmr (220 MHz, CCl_4, with and without TMS) δ 7.25–7.00 (5 H, m), 1.95 (1 H, quintet, J = 7 Hz), 1.32 (3 H, d, J = 7 Hz), 1.02–0.73 (1 H, m), 0.61–0.30 (2 H, m), and 0.25–0.02 (2 H, m); mass spectrum m/e (relative intensity) 146 (M^+, 27), 131 (31), 118 (98), 117 (76), 105 (100), 91 (70), 77 (42), 51 (34), and 39 (42).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.26; H, 9.71.

1-Phenylundecane (32). Treatment of 1-undecanal (**12**) as described above yielded **32** (91%) as a colorless oil: bp 92–94° (1.1 mm); ir (film) 3035, 2970, 2930, 2860, 1455, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.08 (5 H, apparent s), 2.55 (2 H, perturbed t, J = 7 Hz), 1.9–1.4 (2 H, m), 1.27 (16 H, broad s), and 0.89 (3 H, perturbed t); mass spectrum m/e (relative intensity) 232 (M^+, 8), 92 (50), 91 (100), 69 (62), 55 (34), 43 (42), and 41 (53).

Anal. Calcd for $C_{17}H_{28}$: C, 87.86; H, 12.14. Found: C, 87.86; H, 12.07.

1-Phenyl-2-methylpentane (33). Treatment of 2-methyl-1-pentanal (**13**) as described above yielded **33** (83%) as a colorless oil: bp 60–62° (1.2 mm); ir (film) 3035, 2960, 2930, 2880, 1604, 1495, 1450, 720, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.09 (5 H, apparent s), 2.64 (1 H, d of d, J = 13 and 6 Hz), 2.27 (1 H, d of d, J = 13 and 7 Hz), a broad multiplet from *ca.* 2.0 to 1.4 (1 H, m), 1.4–1.05 (4 H, m), and a doublet at 0.82 (3 H, d, J = 6.5 Hz) superimposed on a perturbed triplet at 0.88 (3 H, t); mass spectrum m/e (relative intensity) 162 (M^+, 24), 119 (2), 92 (100), 91 (48), and 43 (44).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.08.

11-Phenyl-1-undecene (34). Treatment of 10-undecen-1-al (**14**) as described above yielded **34** (99%) as a colorless oil: ir (film) 3075, 3040, 2920, 2865, 1640, 1605, 1495, 1450, 900, and 690 cm^{-1}; nmr (220 MHz, CCl_4) δ 7.23–6.91 (5 H, m), 5.82–5.59 (1 H, m), 5.00–4.77 (2 H, m), 2.55 (2 H, t, J = 7 Hz), 2.00 (2 H, apparent q, J = 7 Hz), 1.68–1.48 (2 H, m), and 1.45–1.14 (12 H, broad s); mass spectrum m/e (relative intensity) 230 (M^+, 11), 131 (16), 117 (16), 104 (63), 105 (18), 92 (48), 91 (100), 69 (37), 55 (19), and 41 (27).

Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.36; H, 11.63.

α-(2,6,6-Trimethyl-1-cyclohexen-1-yl)toluene (35). Treatment of β-cyclocitral (**15**) as described above yielded **35** (99%) as a colorless oil: ir (film) 3070, 3035, 2965, 2935, 2870, 1605, 1495, 1450, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.17 (5 H, broad s), 3.49 (2 H, broad s), 2.30–1.92 (2 H, broad m), a complex multiplet at 1.91–1.60 (2 H, m), 1.53 (3 H, broad s), 1.28 (3 H, t, J = 7 Hz), and 0.92 (6 H, s); mass spectrum m/e (relative intensity) 214 (M^+, 75), 199 (100), 143 (14), 123 (43), 105 (15), and 91 (46).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.35; H, 10.34.

1-Phenyl-3,7-dimethyl-2,6-octadiene (36). Treatment of citral (**16**), which is a mixture of neral and geranial, as described above yielded **36** (90%) as a colorless oil: ir (film) 3070, 3035, 2970, 2925, 1445, 715, and 685 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.19 (5 H, broad s), 5.57–4.97 (2 H, complex m), 3.33 (2 H, broad d, J = 7.4 Hz), 2.23–1.98 (4 H, m), 1.69 (6 H, broad s), and 1.60 (3 H, broad s); mass spectrum m/e (relative intensity) 214 (M^+, 91), 199 (4), 145 (98), 129 (49), 123 (83), 91 (69), 69 (100), and 41 (49).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.30; H, 10.27.

4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-2-methyl-1-phenyl-*trans*-2-butene (37). Treatment of C_{14}-aldehyde (**17**) as described above yielded **37** (93%) as a colorless oil: bp 95–97° (1.1 mm); ir (film) 3035, 2965, 2920, 2860, 1601, 1492, 1450, 720, and 690 cm^{-1}; nmr (220 MHz, CCl_4) δ 7.25–6.93 (5 H, m), 5.09 (1 H, t, J = 12 Hz), 3.21 (2 H, s), 2.69 (2 H, d, J = 12 Hz), 2.00–1.86 (2 H, m), 1.68–1.36 (4 H, m) on which are superimposed two singlets at 1.53 (3 H, s) and 1.51 (3 H, s), and 0.95 (6 H, s); mass spectrum m/e (relative intensity) 268 (M^+, 100), 253 (17), 225 (8), 198 (4), 177 (92), 123 (46), 121 (38), 107 (35), and 91 (60).

Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.31; H, 10.49.

1-(4-*tert*-Butylphenyl)-3-phenyl-2-methylpropane (38).

Treatment of 3-(4-*tert*-butylphenyl)-2-methyl-1-propanol (**18**) as described above yielded **38** (99%) as a colorless oil: ir (film) 3090, 3070, 3035, 2975, 2925, 2860, 1601, 1490, 1450, 1260, 722, and 689 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.18 (5 H, broad s) superimposed on an AB pattern with the first doublet centered at 7.31 (2 H, d, J = 8.5 Hz) and the second at 7.06 (2 H, d, J = 8.5 Hz), 2.92–2.54 (1 H, m), 2.44 (2 H, d, J = 7.5 Hz), 2.26–1.78 (2 H, m), 1.29 (9 H, s), and 0.82 (3 H, d, J = 6.2 Hz); mass spectrum m/e (relative intensity) 266 (M^+, 58), 251 (67), 175 (34), 162 (13), 147 (48), 132 (13), 119 (28), 105 (12), 92 (47), 91 (100), 57 (5), and 41 (25).

Anal. Calcd for $C_{20}H_{26}$: C, 90.17; H, 9.84. Found: C, 89.89; H, 9.75.

***p*-Methoxydiphenylmethane (39).** Treatment of *p*-anisaldehyde (**19**) as described above yielded **39** (96%) as a colorless oil: ir (film) 1610, 1586, 1510, 1495, 1240, 1172, 1030, 830, 790, 760, 718, and 690 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.19 (5 H, s), an AB pattern with the first doublet centered at 7.07 (2 H, d, J = 9 Hz) and the second at 6.76 (2 H, d, J = 9 Hz), 3.86 (2 H, s), and 3.65 (3 H, s); mass spectrum m/e (relative intensity) 198 (M^+, 100), 197 (40), 183 (12), 167 (30), 121 (28), and 91 (12).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.83; H, 7.10.

2-Benzylfuran (40). Treatment of furfural (**20**) as described above, except that the phenylation step was run at *ca.* −78°, yielded **40** (93%) as a colorless oil: ir (film) 1595, 1505, 1492, 1450, 1065, 1001, 710, and 690 cm^{-1}; nmr (60 MHz, CCl_4) a multiplet at δ 7.22–6.97 (1 H, m) on which is superimposed a singlet at 7.14 (5 H, s), 6.22–6.05 (1 H, m), 5.92–5.77 (1 H, m), and 3.86 (2 H, s); mass spectrum m/e (relative intensity) 158 (M^+, 100), 129 (65), 115 (23), 103 (4), 91 (9), and 81 (19).

Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.76; H, 6.51.

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Registry No.—**1,** 106-35-4; **2,** 111-13-7; **3,** 89-80-5; **4,** 109-49-9; **5,** 110-93-0; **6,** 89-82-7; **7,** 89-81-6; **8,** 41437-84-7; **9,** 14901-07-6; **10,** 504-20-1; **11,** 765-43-5; **12,** 112-44-7; **13,** 123-15-9; **14,** 112-45-8; **15,** 432-25-7; **17,** 14398-40-4; **18,** 80-54-6; **19,** 123-11-5; **20,** 98-01-1; **21,** 2132-85-6; **22,** 777-22-0; **23,** 18368-90-6; **24,** 30134-52-2; **25,** 53210-18-7; **26,** 53210-19-8; **27a,** 53210-20-1; **27b,** 53210-21-2; **28a,** 53210-16-5; **28b,** 53210-22-3; **29,** 53210-23-4; **30,** 53210-24-5; **31,** 16510-30-8; **32,** 6742-54-7; **33,** 39916-61-5; **34,** 53210-25-6; **35,** 53210-26-7; **36,** 53210-27-8; **37,** 53210-15-4; **38,** 53210-28-9; **39,** 834-14-0; **40,** 37542-92-0; bromobenzene, 108-86-1; neral, 106-26-3; geranial, 141-27-5.

References and Notes

(1) (a) Part I: S. S. Hall and S. D. Lipsky, *J. Chem. Soc., Chem. Commun.*, **1242** (1971). (b) Part II: S. S. Hall and S. D. Lipsky, *J. Org. Chem.*, **38**, **1735** (1973). (c) S. S. Hall and S. D. Lipsky, *Org. Syn.*, in press.

(2) Part III: S. S. Hall, *J. Org. Chem.*, **38**, 1738 (1973).

(3) For a useful general discussion of metal–ammonia experimental techniques see M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N.Y. 1968, pp 98–105.

(4) For a discussion of the mechanism of the reduction see (a) S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); (b) S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, **36**, 2588 (1971).

(5) In previous unpublished work (S. S. Hall and G. H. Small) certain sterically hindered benzyl alcohols were found resilient to these reducing conditions.

(6) H. Greenfield, R. A. Friedel, and M. Orchin, *J. Amer. Chem. Soc.*, **76**, 1258 (1954).

(7) W. Hückel and H. Bretschneider, *Justus Liebigs Ann. Chem.*, **540**, 157 (1939).

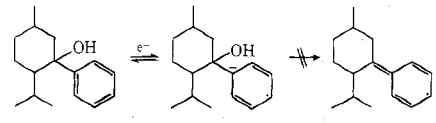
(8) A. J. Birch, *J. Chem. Soc.*, 1642 (1947).

(9) (a) A. J. Birch, *J. Chem. Soc.*, 809 (1945); (b) R. van Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **71**, 3595 (1949); (c) H. M. Walborsky, M. S. Aronoff, and M. F. Schulman, *J. Org. Chem.*, **36**, 1036 (1971), and the references cited therein.

(10) A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

(11) (a) H. Gilman and C. W. Bradley, *J. Amer. Chem. Soc.*, **60**, 2333 (1938); (b) S. F. Birch and D. T. McAllan, *Nature (London)*, **165**, 899 (1950); (c) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (d) W. Hückel and I. Nabih, *Chem. Ber.*, **89**, 2115 (1956); (e) A. J. Birch and D. Nasipuri, *Tetrahedron*, **6**, 148 (1959).

(12) During the reduction of the benzyl alcohol intermediate, the benzyl carbon must assume an sp^2 configuration.



(13) That no reduction occurs until the ammonium chloride quench was established by repeating the experiment using sodium benzoate as the quenching agent; which resulted in the isolation of the corresponding phenylated compound 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-phenyl-*trans*-1-buten-3-ol (**41**) as the sole product: nmr (60 MHz, CCl_4) δ 7.64–7.10 (5 H, m), 6.14 (1 H, d with fine splitting, J = 16 Hz), 5.69 (1 H, d, J = 16 Hz), 2.77 (1 H, broad peak which disappears when D_2O is added), broad multiplets at 2.15–1.79 (2 H) and 1.79–1.31 (4 H) on which is superimposed a broad singlet at 1.60 (6 H, s, 2 CH_3–), and 0.97 (6 H, s, 2 CH_3–). See also footnote *g* of Table I.

(14) J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973).

(15) See (a) ref 2; (b) ref 3, pp 118–119; (c) H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Nonaqueous Ionizing Solvents," Vol. I, Part 2, Wiley, New York, N.Y., 1963, p 228.

(16) The ir spectra were determined with a Beckman Model IR-10 infrared recording spectrophotometer. The nmr spectra were determined at 60 MHz with a Varian Associates Model A-60 nmr spectrometer, at 100 MHz with a Varian Associates Model XL-100 nmr spectrometer and at 220 MHz with a Varian Associates HR-220 nmr spectrometer. The chemical shift values are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Consolidated Electronics Corp. Model 110-21B mass spectrometer and a Varian Associates Model CA5 mass spectrometer with a Varian Associates Model 620/l computer attachment.

(17) Normally *ca.* 10 min elapsed before proceeding with the quenching step, although the time interval does not seem too critical.

(18) The ammonium chloride was most conveniently introduced by attaching a glass tube filled with the salt to a side arm with Tygon tubing. When the ammonium chloride is to be added, the tube is raised and tapped gently to smoothly introduce the quenching agent. Should this step start to become violent, the addition and the vigorous stirring should be momentarily stopped to avoid an eruption.