be treated as practically irreversible in such a calculation.
(23) The most probable or most easily comprehensible course of RC≡CCl is a Cl–Li exchange followed by elimination of LiF. However, RCF=C-ClLi may or may not be formed at all. Hence the term "Cl–Li exchange" for these reactions is only tentative in the strict sense of the word.
(24) The reactions of halogeno olefins of other types (e.g., RCH=CHCl) with organolithiums to form acetylenic compounds have been described: M. Schlosser and V. Ladenberger, *Chem. Ber.*, **100**, 3901 (1967); G. Köbrich, *Angew. Chem.*, **77**, 75 (1965); G. Köbrich and P. Buck, "Chemistry of Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 2. See also ref 5.
(25) Such considerations lead to the suspicion that the Cl–Li exchange reactivities of the chlorines in **6** would be greater than those of the respective chlorines of the corresponding trichlorovinyl compound. In a competitive experiment α,β,β-trichlorostyrene was converted into chloroethynylbenzene at 2.2 times the rate for **6d**. However, which of the chlorines of α,β,β-trichlorostyrene is preferentially exchanged is not clear.
(26) Previously the stabilization was explained by hyperconjugation by fluorine. However, this mechanism has been criticized: A. Streitwieser, Jr., and D. Holtz, *J. Am. Chem. Soc.*, **89**, 692 (1967); A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1968); D. Holtz, *Chem. Rev.*, **71**, 139 (1971).
(27) A. Vaitiekunas and F. F. Nord, *J. Org. Chem.*, **19**, 902 (1954).
(28) L. Brandsma "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971: (a) p 97; (b) p 117.
(29) R. E. Atkinson, R. F. Curtis, D. M. Jones, and J. A. Taylor, *J. Chem. Soc. C*, 2173 (1969).
(30) T. B. Patrick, J. M. Disher, and W. J. Probst, *J. Org. Chem.*, **37**, 4467 (1972).
(31) D. Bertin, *C. R. Acad. Sci.*, **229**, 660 (1949); *Chem. Abstr.*, **44**, 2969*i* (1950).
(32) P. Cadiot and W. Chodkiewicz, "Chemistry of Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, N.Y., 1969, pp 622–625.
(33) R. Eastmond and D. R. M. Walton, *Tetrahedron*, **28**, 4591 (1972).
(34) The formation of $C_6H_5(C{\equiv}C)_2Cl$ from the reaction between $C_6H_5C{\equiv}CMgBr$ and dichloroacetylene is also reported: H. G. Viehe, *Chem. Ber.*, **92**, 3064 (1959).
(35) The applicability of a one-flask procedure for the present method was tested in the case of the preparation of 2-ethynylthiophene. To a solution of thiophene (0.3 mol) was added successively ethereal butyllithium, **1** (in four portions over 12 min keeping the internal temperature between −40 and 5 °C), and ethereal butyllithium (at −50 °C), refluxing being conducted after the first and the second additions. On distillation of the product mixture obtained after work-up, exothermic decomposition of the pot residue, though not vigorous, occurred after 2-ethynylthiophene (53% yield, bp 35–37° at 10 mm) came out.
(36) C. P. Carpenter, H. F. Smyth, Jr., and U. C. Pozzani, *J. Ind. Hyg. Toxicol.*, **31**, 343 (1949); *Chem. Abstr.*, **44**, 3140*h* (1950).
(37) T. R. Torkelson, C. D Kary, M. B. Chenoweth, and E. R. Larsen, *Toxicol. Appl. Pharmacol.*, **19**, 1 (1971); *Chem. Abstr.*, **75**, 46979c (1971).
(38) W. T. Miller, Jr., E. W. Fager, and P. H. Griswald, *J. Am. Chem. Soc.*, **72**, 705 (1950).
(39) The results of related studies together with discussion of mechanistic implication of the stirring effect will be presented elsewhere.
(40) "Sadtler Standard Infrared Spectra", Sadtler Research Laboratories, Philadelphia, Pa., Midget ed, no. 7604 (sample source: Philadelphia College of Pharmacy and Science).
(41) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1084 (1963).
(42) R. D. McLachlan, *Spectrochim. Acta, Part A*, **26**, 919 (1970).

Alkylation–Reduction of Carbonyl Systems. VII. Synthesis of α-Cyclopropyl Aromatic Hydrocarbons by Cyclopropylation–Reduction of Aromatic Aldehydes and Ketones. Parameters of Cyclopropyl α, β, and γ Carbon-13 Shieldings in Cyclopropyl Aromatic Hydrocarbons

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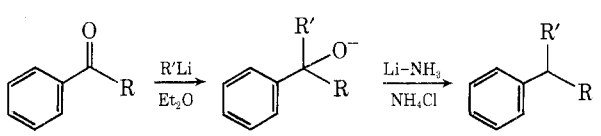
α-Cyclopropyl aromatic hydrocarbons are conveniently prepared, in excellent yields, from aromatic carbonyl compounds by tandem cyclopropylation–reduction. By this procedure cyclopropyl benzyl alkoxides, generated in situ by cyclopropylation, are reduced by lithium–ammonia–ammonium chloride to the corresponding cyclopropyl aromatic hydrocarbons. Examples include cyclopropyl(4-*tert*-butyl)phenylmethane (**8**) from 4-*tert*-butylbenzaldehyde (**1**), 1-cyclopropyl-1-phenylethane (**9**) from acetophenone (**2**), 1-cyclopropylindan (**10**) from indanone (**3**), dicyclopropylphenylmethane (**11**) from cyclopropyl phenyl ketone (**4**), cyclopropyldiphenylmethane (**12**) from benzophenone (**5**), and 1-cyclopropyl-1,3-diphenylpropane (**13**) from benzylideneacetophenone (**6**). Cyclopropylation–reduction of phenyl vinyl ketone (**7**), in contrast, yielded 3-cyclopropyl-1-phenylpropane (**14**) via 1,4 addition. Carbon magnetic resonances were assigned to the cyclopropyl aromatic hydrocarbons. A comparison of the chemical shifts with those of model compounds possessing a hydrogen in place of the cyclopropyl group allowed the estimation of the following cyclopropyl substituent parameters: 17 ± 3.7 ppm (eight values) for α, 6.1 ± 1.3 ppm (five values) for β, and −1.6 ± 0.8 ppm for the γ position (four values). These shielding parameters are smaller but in the same direction as those for a phenyl group. Those compounds possessing a chiral or prochiral center adjacent to the cyclopropyl group exhibit chemical shift nonequivalence of the cyclopropyl methylene carbons.

Synthesis. This laboratory has been exploring the potential applications of tandem alkylation–reduction of aromatic carbonyl systems as a convenient method of preparing aromatic hydrocarbons.[2] The method involves the lithium–ammonia–ammonium chloride reduction of benzyl alkoxides generated in situ by alkylation. Since the entire sequence is performed in the same reaction vessel without the isolation or purification of intermediates, the total synthesis consumes only a few hours and the isolated yield of the product is usually excellent.



The introduction of a cyclopropyl group at the α position in an aromatic hydrocarbon is a very difficult task using classical procedures. After cyclopropylation of the requisite aromatic carbonyl system, for example, the α-cyclopropyl group would not be expected to survive the dehydration[3]–hydrogenation[4] sequence.[5] On the other hand, our tandem alkylation–reduction procedure, using in this case cyclopropyllithium and an aromatic carbonyl compound, offered a potential method of preparing α-cyclopropyl aromatic hydrocarbons.

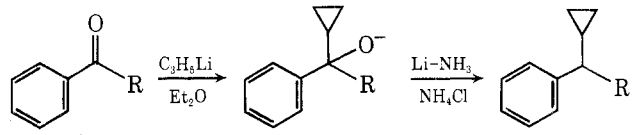


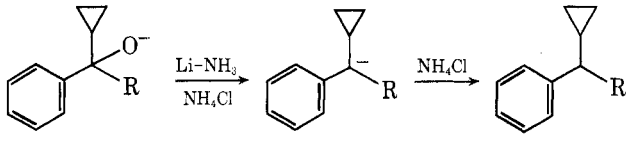
Table I. Cyclopropylation–Reduction of Aromatic Carbonyl Compounds

Carbonyl compd	Cyclopropylation–reduction product	% yield Analytical[a]	% yield Isolated[b]
4-*tert*-Butylbenzaldehyde (**1**)	Cyclopropyl(4-*tert*-butyl)phenylmethane (**8**)	99	98
Acetophenone (**2**)	1-Cyclopropyl-1-phenylethane (**9**)	90	82
Indanone (**3**)	1-Cyclopropylindan (**10**)	85	79
Cyclopropyl phenyl ketone (**4**)[c]	Dicyclopropylphenylmethane (**11**)	99	97
Benzophenone (**5**)	Cyclopropyldiphenylmethane (**12**)	99	98
Benzylideneacetophenone (**6**)	1-Cyclopropyl-1,3-diphenylpropane (**13**)	93	91
Phenyl vinyl ketone (**7**)	3-Cyclopropyl-1-phenylpropane (**14**)	60	51[d]

[a] Analyzed by GLC (% of volatiles). [b] Isolated by filtration column chromatography. [c] Owing to the low solubility of **4** in Et_2O, THF was used as the cosolvent. [d] The yield is low because of the presence of polar and higher molecular weight material (polymerization of phenyl vinyl ketone) that was efficiently removed by filtration chromatography.

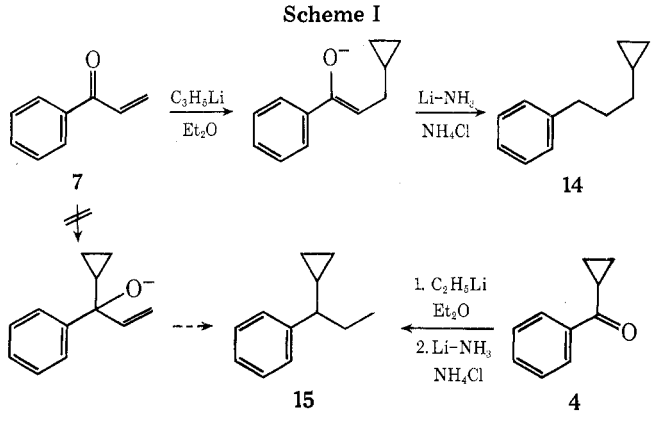
The general procedure adopted for this study was to generate a cyclopropyl benzyl alkoxide in a metal–ammonia reaction vessel[6] by the addition of the aromatic carbonyl compound to cyclopropyllithium, prepared in situ from cyclopropyl bromide and excess lithium, in ether. Ammonia is subsequently distilled into the vessel and then the resulting dark blue mixture is cautiously quenched with ammonium chloride. Table I is a listing of the aromatic carbonyl systems that were subjected to this procedure. Cyclopropylation–reduction of the aromatic aldehyde and ketones **1–5** afforded the corresponding α-cyclopropyl aromatic hydrocarbon in excellent isolated yields.

Since the α-cyclopropyl group does survive these reduction conditions, one significant mechanistic conclusion is possible. During the reduction sequence, from cyclopropyl benzyl alkoxide to product, the intermediate cyclopropyl benzyl anion protonates *exclusively* at the benzylic position.[7]



The cyclopropylation–reduction of the α,β-unsaturated aromatic ketones **6** and **7** requires some additional comments. The saturated product **13** from benzylideneacetophenone (**6**) was expected since benzylidene benzyl alkoxides are reduced to benzyl alkoxides in lithium–ammonia.[2c] The cyclopropylation–reduction of phenyl vinyl ketone (**7**)[8] resulted in exclusive 1,4 addition of the cyclopropyllithium yielding 3-cyclopropyl-1-phenylpropane (**14**) after reduction. Since we were somewhat surprised by this result, the expected product from 1,2 addition and subsequent reduction (1-cyclopropyl-1-phenylpropane, **15**) was prepared by ethylation–reduction of cyclopropyl phenyl ketone (**4**).[9] See Scheme I.

Scheme I



This synthetic study demonstrates that tandem cyclopropylation–reduction of aromatic carbonyl systems is an extremely simple and efficient procedure for the synthesis of α-cyclopropyl aromatic hydrocarbons, compounds that have been heretofore unavailable or difficult to prepare.

Carbon-13 Studies. The structural analysis of organic compounds can be greatly facilitated by carbon magnetic resonance (^{13}C NMR) techniques. Essential to such analysis is the establishment of characteristic substituent chemical shifts. While such shifts for alkyl and phenyl groups (as well as for a number of other functional groups) are well documented,[10] to our knowledge no such values are available for the cyclopropyl substituent in hydrocarbons. The synthesis of cyclopropyl aromatic hydrocarbons in our laboratories made available a unique series of compounds whose ^{13}C NMR spectra we here report. Based on the comparison of the ^{13}C NMR chemical shifts of these compounds with models in which the cyclopropyl group is replaced by hydrogen, one can estimate the α, β, and γ cyclopropyl substituent shielding parameters.

Table II presents the results on the cyclopropyl hydrocarbons and the corresponding model compounds. Distinction between methyl, methylene, and methine carbons was achieved by the off-resonance decoupling technique. Spectra in the gated decoupling plus mode (corresponding to no decoupling but retaining the nuclear Overhauser enhancement) were also collected for compounds **10, 13,** and **14.** The only dubious assignment arose in the β and γ carbons of compound **14** (both complex multiplets). These assignments were made by comparisons with the other cyclopropyl compounds. For clarity, the resonances of the aliphatic, cyclopropyl, and phenyl regions will be discussed separately.

Aliphatic Carbons. The data in Table II presents the aliphatic carbon positions as 1, 2, and 3 from the phenyl ring. Table III summarizes the effect of cyclopropyl substitution on the chemical shifts. Clearly, the α and β effects are deshielding and the γ effect is weakly shielding. The α effects appear to fall roughly into two groups: 19 ± 1.5 ppm (compounds **9, 10, 11, 14,** and **16**) and 15 ± 1.7 ppm (compounds **11, 12, 13,** and **15**) or overall 17 ± 3.7 ppm. Since the compounds in the latter group have bulky substituents attached to the benzylic carbon (especially compounds **11** and **12**), the lower α effects in this group may reflect the sterically induced polarization of the valence electrons caused by the sterically compressed system. This shielding effect opposes the deshielding electronic effect of the cyclopropyl group. Such shielding has been observed for sterically perturbed carbon atoms in other spatially crowded molecules.[11]

The β effects appear to be more uniform: 6.1 ± 1.3 ppm. In the molecules exhibiting both α and β effects, those that

Table II. Carbon-13 Chemical Shifts of Cyclopropyl Aromatic Hydrocarbons and Model Compounds[a]

Compd	Aromatic				Aliphatic			Cyclopropyl		
	C_i	C_p	C_o[b]	C_m[b]	C_1	C_2	C_3	CH	CH_2	CH_2
Cyclopropylphenylmethane (16)[c]	142.1	125.8	128.3	128.3	40.4			11.9	4.7	4.7
1-Cyclopropyl-1-phenylethane (9)	147.4	125.9	127.0	128.2	47.7	21.6		18.5	4.6	4.3
Dicyclopropylphenylmethane (11)	145.9	125.9	127.7	128.0	53.7			16.6	4.6	2.8
Cyclopropyldiphenylmethane (12)	145.1	126.0	128.1	128.1	55.7			16.7	5.3	5.3
1-Cyclopropylindan (10)	147.4[d]		126.4	124.4	50.1[e]	32.7		15.8	4.1	2.3
	144.2		126.0	123.9	31.5					
1-Cyclopropyl-1,3-diphenylpropane (13)	145.5[f]	126.0	127.6	128.2	50.4[g]	38.2		17.7	5.5	3.6
	142.5[h]	125.6	127.6	128.2	33.7					
3-Cyclopropyl-1-phenylpropane (14)	142.8	125.6	128.2	128.3	35.9	31.5	34.4	10.8	4.4	4.4
1-Cyclopropyl-1-phenylpropane (15)	145.9	125.8	127.6	128.1	52.8	29.6	12.2	17.3	5.6	3.5
Toluene (17)	137.7	125.3	128.2	129.0	21.3					
Ethylbenzene (18)	144.1	125.6	127.8	128.3	29.0	15.6				
n-Propylbenzene (19)	142.6	125.7	128.2	128.5	38.2	24.7	13.9			
Isopropylbenzene (20)	148.8	125.8	126.4	128.3	34.2	24.0				
Diphenylmethane (21)	141.0	126.0	128.4	128.9	41.9					
Indan (22)[i]	143.9		125.9	124.2	32.3	25.3				
1,3-Diphenylpropane (23)	142.2	125.7	128.3	128.3	35.4	32.9				

[a] The chemical shift values are expressed in δ values (parts per million) relative to a Me_4Si internal standard. [b] No attempt was made to discern the ortho and meta carbons. [c] Prepared by the lithium–ammonia–ammonium chloride reduction of cyclopropyl phenyl ketone [S. S. Hall and C.-K. Sha, *Chem. Ind. (London)*, in press]. [d] C_4 = 126.0, C_5 = 123.9, C_6 = 124.4, C_7 = 126.4, C_8 = 147.4, C_9 = 144.2. [e] C_1 = 50.1, C_2 = 32.7, C_3 = 31.5. [f] 1-Phenyl group. [g] C_1 = 50.4, C_2 = 38.2, C_3 = 33.7. [h] 3-Phenyl group. [i] Data taken from L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972, p 342.

Table III. Shielding Effect of the Cyclopropyl Group on Aliphatic Carbons

	δ[a] (cyclopropyl aromatic hydrocarbon)	δ[a] (model aromatic hydrocarbon)	Δ, ppm[b]
α effects	40.4 (16)	21.3 (17)	19.1
	47.7 (9)	29.0 (18)	18.7
	53.7 (11)	40.4 (16)	13.3[c]
		21.3 (17)	19.1[d]
	55.7 (12)	41.9 (21)	13.8
	50.1 (10)	32.3 (22)	17.8
	50.4 (13)	35.4 (23)	15.0
	34.4 (14)	13.9 (19)	20.5
	52.8 (15)	38.2 (19)	14.6
β effects	21.6 (9)	15.6 (18)	6.0
	32.7 (10)	25.3 (22)	7.4
	38.2 (13)	32.9 (23)	5.3
	31.5 (14)	24.7 (19)	6.8
	29.6 (15)	24.7 (19)	4.9
γ effects	31.5 (10)	32.3 (22)	−0.8
	33.7 (13)	35.4 (23)	−1.7
	35.9 (14)	38.2 (19)	−2.3
	12.2 (15)	13.9 (19)	−1.7

[a] The chemical shift values are expressed in δ values (parts per million relative to a Me_4Si internal standard). [b] Positive values indicate deshielding by cyclopropyl; negative values indicate shielding. [c] Represents the α effect of the second cyclopropyl group. [d] Represents the α effect of the first cyclopropyl group.

yield low α parameters (compounds **13** and **15**) also yield low β parameters. The γ effects of the cyclopropyl group are small and, in contrast, shielding: -1.6 ± 0.8 ppm.

It is instructive to compare the effects of phenyl,[12] cyclopropyl, and alkyl groups:[13] 23, 17, and 9 ppm for α; 9.5, 6.1, and 9.4 ppm for β; and −2.0, −1.6, and −2.5 ppm for γ parameters, respectively. All three functional groups shield the 3-carbon position and deshield the 1- and 2-carbon positions. As can be seen, the substituent effect of the cyclopropyl group is consistently smaller than that of the phenyl group.

Successive replacement of cyclopropyl groups for hydrogens, in this study, indicates an α effect of 19.1 ppm (toluene, **17**, to cyclopropylphenylmethane, **16**) for the first and an α effect of 13.3 ppm (cyclopropylphenylmethane, **16**, to dicyclopropylphenylmethane, **11**) for the second. Similar trends and magnitudes have been previously observed in alcohols.[14] Successive replacement of hydrogens by cyclopropyl groups indicated an α effect of 17.9 ppm (methanol to cyclopropylcarbinol) for the first and an α effect of 14.7 ppm (cyclopropylcarbinol to dicyclopropylcarbinol) for the second with neat liquids. These comparisons are probably excellent examples of the effect of steric compression shielding discussed previously. The differences between the first and the second α effect in the two comparisons reflect the shielding caused by the sterically induced polarization of the valence electrons[11] when introducing the second cyclopropyl group. Since the α carbon is more sterically perturbed in dicyclopropylphenylmethane (**11**) than in dicyclopropylcarbinol, this shielding is larger.

Cyclopropyl Carbons. The most interesting features of the cyclopropyl resonances are that usually they are the most highly shielded and that in all cases in which the benzylic carbon is chiral two distinct methylene resonances are observed. The differences between these anisochronous methylene carbons range from ca. 0.3 to 2.1 ppm. This phenomenon, common in proton magnetic resonance, was first documented in ^{13}C NMR in chiral isopropylalkylcarbinols and chiral alkanes containing an isopropyl group.[15] Chemical shift nonequivalence of the cyclopropyl methylene carbons is also evident in dicyclopropylphenylmethane (**11**). This nonequivalence is presumably due to the presence of the prochiral benzylic center.[16] The methine carbon in the

cyclopropyl group is quite susceptible to substituent effects. As can be seen in Table II, its position ranges from 10.8 to 18.5 ppm.

Phenyl Carbons. The ipso phenyl carbon (C_i) and the para carbon (C_p) resonances could be rather unequivocally assigned. The ipso carbon resonance is invariably deshielded by the cyclopropyl group (a β effect at C_i) by ca. 3.8 ± 0.6 ppm (seven cases available). No attempt was made in this study to discern the ortho (C_o) and meta (C_m) carbon resonances. In many cases they coincided.

Experimental Section[17]

General Comments. The entire reaction sequence was performed under a static argon (prepurified) atmosphere, which is connected by a T tube to the assembly and to a soda lime drying trap that is connected in series to an oil bubbler, and is operated at a moderate flow rate throughout the synthesis. All glassware was oven dried and cooled to room temperature in a large box desiccator, and then quickly assembled. Anhydrous ether was used directly from freshly opened containers. Tetrahydrofuran (THF) was freshly distilled under nitrogen from $LiAlH_4$. Lithium wire (0.32 cm, high purity, Foote Mineral Co.) was wiped free of oil, cut into small pieces, and rinsed in petroleum ether just prior to use. Cyclopropyl bromide (99%, Aldrich Chemical Co.) was used without further purification. Anhydrous ammonia was distilled, through a tower of potassium hydroxide pellets, directly into the reaction vessel. Gas chromatography (GLC) analyses were performed on 100 × 0.4 cm (i.d.) glass columns, packed either with 4% silicone gum rubber UCC-W-982 (methylvinyl) supported on 80–100 mesh HP Chromosorb W (AW, DMCS) or with 3% silicone gum rubber OV-17 (methylphenyl) supported on 80–100 mesh HP Chromosorb W, using a 40 ml/min carrier gas flow rate, with a Hewlett-Packard Model 7610A (flame detector) chromatograph. Purification of the product by column chromatography was accomplished on chromatographic grade activated alumina (80–325 mesh, Matheson Coleman and Bell) by elution with petroleum ether. Evaporative distillations, sometimes necessary for microanalyses, were performed in a Kügelrohr oven. The assigned structure of each product is consistent with the spectral data. Satisfactory composition analyses on all products were submitted to the Editor. The cyclopropylation–reduction of 4-*tert*-butylbenzaldehyde (1) is described, in detail, to illustrate the general procedure.

Cyclopropylation–Reduction of 4-*tert*-Butylbenzaldehyde (1). Cyclopropyl(4-*tert*-butyl)phenylmethane (8). Into a metal–ammonia reaction vessel containing a stirred mixture of 280 mg of lithium (40 mg-atoms, ca. 25 pieces) in 2 ml of anhydrous ether that was cooled by an ice bath was slowly added a solution of 605 mg (5 mmol) of cyclopropyl bromide in 3 ml of ether. The reaction mixture slowly turned black. After the mixture was stirred at 0–5 °C for 1.5 h, it was cooled to ca. −70 °C (dry ice–acetone bath) and then a solution of 405 mg (2.5 mmol) of 4-*tert*-butylbenzaldehyde (1) in 5 ml of ether was slowly added. The mixture was stirred for 1 h at −70 °C and then diluted with 10 ml of ether. Ammonia (ca. 40 ml) was carefully, to prevent excessive splattering, distilled into the mixture and the cooling bath removed. After 20 min ca. 4 g of ammonium chloride was cautiously added[18] (ca. 15 min) to discharge the blue color and then the ammonia was allowed to evaporate. After the residue had been partitioned between brine and ether, the organic phase was dried ($MgSO_4$), filtered, concentrated at water aspirator pressure at 30–40 °C, and then analyzed (GLC). Following column chromatography 461 mg (98%) of cyclopropyl(4-*tert*-butyl)phenylmethane (8) was obtained as a colorless oil: ir (film) 3090, 3020, 2980, 2930, 1465, 1370, 1275, 1020, 820 cm^{-1}; NMR (60 MHz, CCl_4) δ 7.26 (2 H, d, J = 9 Hz), 7.10 (2 H, d, J = 9 Hz), 2.48 (2 H, d, J = 7 Hz), 1.29 (9 H, s), 1.12–0.61 (1 H, m), 0.61–0.30 (2 H, m), 0.30–0.04 (2 H, m); mass spectrum m/e (rel intensity) 188 (M^+, 14), 173 (100), 147 (46), 145 (26), 132 (26), 131 (34), 117 (26), 115 (17), 91 (31), 55 (66), 41 (31).

1-Cyclopropyl-1-phenylethane (9): NMR (60 MHz, CCl_4) δ 7.10 (5 H, apparent s), 2.17–1.73 (1 H, m), 1.30 (3 H, d, J = 6 Hz), 1.18–0.60 (1 H, m), 0.60–0.33 (2 H, m), 0.33–0.04 (2 H, m); mass spectrum m/e (rel intensity) 146 (M^+, 11), 131 (63), 118 (61), 117 (75), 105 (100), 104 (32), 91 (72), 79 (24), 77 (28).

1-Cyclopropylindan (10): NMR (100 MHz, $CDCl_3$) δ 7.60–7.32 (1 H, m), 7.32–7.03 (3 H, m), 3.10–2.59 (2 H, m), 2.59–2.24 (1 H, m), 2.24–1.88 (1 H, m), 1.84–1.53 (1 H, m), 1.10–0.65 (1 H, m), 0.65–0.06 (4 H, m); mass spectrum m/e (rel intensity) 158 (M^+, 25), 130 (100), 129 (44), 117 (96), 115 (54), 91 (19), 51 (17), 39 (29).

Dicyclopropylphenylmethane (11): NMR (100 MHz, $CDCl_3$) δ 7.23 (5 H, s), 1.41 (1 H, t, J = 8.5 Hz), 1.20–0.90 (2 H, m), 0.61–0.03 (8 H, complex m); mass spectrum m/e (rel intensity) 172 (M^+, 1), 143 (59), 129 (100), 115 (28), 104 (99), 91 (52), 77 (29), 51 (41), 39 (69).

Cyclopropyldiphenylmethane (12): NMR (60 MHz, CCl_4) δ 7.16 (10 H, apparent s), 3.20 (1 H, d, J = 9.3 Hz), 1.62–0.90 (1 H, m), 0.82–0.43 (2 H, m), 0.43–0.07 (2 H, m); mass spectrum m/e (rel intensity) 208 (M^+, 3), 180 (73), 179 (36), 165 (33), 152 (12), 115 (17), 104 (100), 91 (24), 77 (17), 51 (24), 39 (25).

1-Cyclopropyl-1,3-diphenylpropane (13): NMR (60 MHz, CCl_4) δ 7.18 (5 H, apparent s), 7.11 (5 H, apparent s), 2.70–2.30 (2 H, m), 2.30–1.45 (3 H, m), 1.14–0.68 (1 H, m), 0.68–0.06 (4 H, complex m); mass spectrum m/e (rel intensity) 236 (M^+, 12), 208 (2), 207 (3), 195 (1), 193 (2), 145 (6), 132 (35), 131 (56), 117 (56), 104 (19), 91 (100).

3-Cyclopropyl-1-phenylpropane (14): NMR (100 MHz, $CDCl_3$) δ 7.38–6.98 (5 H, m), 2.62 (2 H, t, J = 7.5 Hz), 1.72 (2 H, apparent quintet, J = 7.5 and 7.1 Hz), 1.23 (2 H, quartet, J = 7.1 Hz), 0.86–0.50 (1 H, m), 0.50–0.29 (2 H, m), 0.29 to −0.06 (2 H, m); mass spectrum m/e (rel intensity) 160 (M^+, 23), 131 (30), 117 (30), 104 (40), 91 (100), 77 (10), 65 (16), 51 (13), 41 (30), 39 (23).

1-Cyclopropyl-1-phenylpropane (15):[9] NMR (100 MHz, $CDCl_3$) δ 7.50–6.95 (5 H, m), 2.05–1.40 (3 H, m), 0.82 (3 H, t, J = 7 Hz) superimposed on 1.1–0.67 (1 H, m), 0.67–0.04 (4 H, complex m); mass spectrum m/e (rel intensity) 160 (M^+, 10), 131 (100), 119 (12), 117 (38), 104 (28), 91 (78), 77 (12), 51 (12), 41 (12), 39 (12).

Carbon-13 Studies. All spectra were recorded on a JEOL Model JNM-PS-FT-100 fast Fourier transform NMR spectrometer at 25.2 MHz in the pulse Fourier transform mode. Sample tubes (10 mm) contained about 1.5 ml of $CDCl_3$ solution of ca. 1 M hydrocarbon. A 45° pulse was used for an average of 500 scans per sample to achieve satisfactory signal-to-noise ratios. Chemical shifts were recorded by the Texas Instrument JEC-100 computer system against both internal tetramethylsilane (1% Me_4Si) and the center peak of the $CDCl_3$ triplet. The chemical shifts quoted are thought to be accurate to better than ±0.1 ppm. Eight thousand data points were employed with a spectral width of 250 ppm. Exponential window with a −5 setting was employed to improve the signal-to-noise ratio along with a Systematic Noise Reduction device supplied by the JEOL Co., Cranford, N.J. A noise (broad band proton) decoupled spectrum was first collected for all compounds. Next off-resonance decoupling was employed on selected compounds to assure unequivocal assignments. On three compounds spectra were also run without decoupling (in the Gated Decoupling plus mode to retain the nuclear Overhauser enhancement) to allow observation of long-range coupling patterns.

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Registry No.—**1**, 939-97-9; **2**, 98-86-2; **3**, 83-33-0; **4**, 3481-02-5; **5**, 119-61-9; **6**, 4452-11-3; **7**, 768-03-6; **8**, 58249-45-9; **9**, 16510-30-8; **10**, 58249-46-0; **11**, 5689-20-3; **12**, 5746-99-6; **13**, 58280-91-4; **14**, 58249-47-1; **15**, 58249-48-2; **16**, 1667-00-1.

References and Notes

(1) Taken in part from the Master of Science Thesis of C.-K.S. submitted to the Graduate School, Rutgers University, Oct 1975.
(2) (a) Part VI: S. S. Hall, F. J. McEnroe, and Ho-Jane Shue, *J. Org. Chem.*, **40**, 3306 (1975); (b) S. S. Hall and F. J. McEnroe, *ibid.*, **40**, 271 (1975); (c) S. S. Hall, *ibid.*, **38**, 1738 (1973); (d) S. S. Hall and S. D. Lipsky, *ibid.*, **38**, 1735 (1973).
(3) (a) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 4327 (1971); (b) H. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962).
(4) (a) P. N. Rylanders, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, N.Y., 1967, pp 468–472; (b) S. Sarel and E. Breuer, *J. Am. Chem. Soc.*, **81**, 6522 (1959).
(5) Alternatively, one might consider the Simmons–Smith reaction that then introduces the problem of preparing the required β,γ-unsaturated aromatic hydrocarbon.
(6) 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.
(7) For a discussion of the proposed mechanism of the reduction of a benzyl alkoxide to an aromatic hydrocarbon 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). The intermediate cyclopropyl benzyl anion, as well as the corresponding radical intermediate, might be expected to cleave the cyclopropyl ring.
(8) Prepared by the phenylation of acrolein; followed by Jones oxidation of

the benzyl alcohol. Since the ketone rapidly polymerizes, the alcohol should be oxidized and the product ketone **7** distilled and used immediately.

(9) The general ethylation–reduction procedure used was the same as is described in the Experimental Section for compound **8**, except that ethyllithium was generated in situ, from freshly distilled ethyl bromide and excess lithium, in ether. Yield of **15**: 98% (isolated).

(10) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 55–127.
(11) (a) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966); (b) D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315 (1967).
(12) Reference 10, p 98.
(13) Reference 10, p 58.
(14) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 5348 (1974).
(15) J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 5928 (1969).
(16) W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).

(17) The ir spectra were determined with a Beckman Model IR-10 infrared recording spectrophotometer. The ^1H NMR spectra were determined at 60 MHz with a Varian Associates Model T-60 NMR spectrometer or with a Hitachi Perkin-Elmer Model R-24A NMR spectrometer, and at 100 MHz with a JEOL Model JNM-PS-FT-100 fast Fourier transform NMR spectrometer. The chemical shift values are expressed in δ values (parts per million) relative to a Me_4Si internal standard. ^1H NMR samples were run with and without Me_4Si. The mass spectra were determined with an AEI Model MS-30 mass spectrometer (70 eV) to which was interfaced a Pye Unicam Model 104 gas chromatograph.

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

The Electronic Effect of Substituted Methyl Groups. A Carbon-13 Nuclear Magnetic Resonance Study

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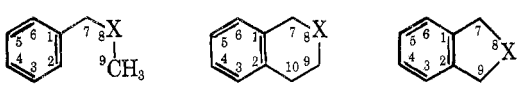
The ^{13}C NMR spectra of a large number of stereochemically well-defined model compounds possessing heteroatoms have been obtained and assigned. An analysis of the data provided the following conclusions: (1) hyperconjugative π-polarization is an important component of the net electronic effect of $-CH_2X$ groups in the neutral ground state; (2) polar field effects play an important role in determining aryl ^{13}C chemical shifts; and (3) the γ shielding effect of second-row heteroatoms is a very general phenomenon.

In order to assess the relative importance of the possible modes of action of substituents in unsaturated systems (polar and π-electron effects) it is necessary to study a series of stereochemically well-defined model systems in which the capacity for the transmission of the electronic effects may be varied systematically. Recently, ^{19}F NMR studies[2,3] have shown that model systems **1**, **2**, and **3** are of value in this regard



1 **2** **3**

since here the CX σ bond is constrained to a varying degree to the nodal plane of the adjacent π system, thus allowing the possible assessment of the relative importance of polar (field-inductive and σ-inductive), π-inductive (inductomesomeric), and mesomeric or resonance (hyperconjugation) effects of substituted methyl groups (vide infra).

In an earlier paper[4] we described a ^{13}C chemical shift study of systems **1**, **2**, and **3** [where X = $Si(CH_3)_2$] which helped to confirm our previous conclusions[2] regarding the importance of metallohyperconjugation in the neutral ground state. Here we report an extension of our ^{13}C NMR studies of these systems to situations where X is an electronegative element or group (NH, NCH_3, CO, O, CF_2, S, and SO_2). The basic objectives in this investigation were threefold. Firstly, we wanted to substantiate our recent proposals[3] regarding the electronic behavior of $-CH_2X$ substituents where X is electronegative: namely, that hyperconjugative electron withdrawal involving the CX σ bond is an important mode of interaction of these groups in the neutral ground state. Secondly, we wanted to examine the effect of pure polar contributions (field-inductive or electrostatic-field effects) on aryl ^{13}C chemical shifts. Previously, this has been prevented because of the difficulty of separating polar and π-electron effects in unsaturated systems where the substituent (X) is directly attached to the substrate, as well as a lack of suitable model compounds with well-defined stereochemistry.

Finally, we wished to assess further the generality of a phenomenon recently reported by Eliel and co-workers.[5] Their ^{13}C NMR studies of a series of model alicyclic systems indicate that a carbon atom located anti or gauche to a second-row heteroatom in the γ position generally resonates at a significantly higher field than an analogous nucleus anti or gauche to a methyl or methylene group, or to a third-row heteroatom. Furthermore, it was also observed that the incremental upfield shift for the anti carbon was generally greater than that for the gauche carbon. A ^{13}C NMR study of systems 2 and 3 should indicate whether this effect can also be transmitted to aromatic carbon centers which are γ disposed to an externally located heteroatom.

Experimental Section

^{13}C Spectra. A Bruker Scientific, Inc. WH-90 Fourier transform spectrometer operating at 22.625 MHz was used to record the spectra. All samples were prepared in deuteriochloroform (0.5–1.0 M) with Me_4Si as an internal reference.

Chemicals. Most of the compounds were known and thus were synthesized by well-established literature procedures: 1-phenylpropan-2-one,[6] benzyldimethylamine,[7] benzyl methyl sulfide,[8] benzyl methyl sulfone,[8] 2-indanone,[9] 1,3-dihydroisobenzofuran,[10] 1,3-dihydroisoindole,[11] *N*-methyl-1,3-dihydroisoindole,[11] 1,3-dihydrobenzo[*c*]thiophene,[12] 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide,[12]