1735 and 1785 cm^{-1}; uv 217 nm (log ε 4.47), 258 (4.47), and 345 (3.43).

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.28; H, 5.23; N, 9.05.

***N*-Amino-1,2-naphthalenedicarboximide (3f).**—This compound was prepared from **2f** by the same method used for preparation of **3e**. The yield was 80% for **3f**: mp 196–197°; ir 1720 and 1770 cm^{-1}; uv 218 nm (log ε 4.59), 258 (4.51), and 346 (3.32).

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.98; H, 3.81; N, 13.32.

Compound **3f** was further characterized by its isomerization in refluxing *n*-butyl alcohol to the corresponding cyclic hydrazide, mp 332–335° (lit.[1a] mp 340°).

Registry No.—**2c**, 34387-89-8; **2e**, 34387-90-1; **2f**, 34387-91-2; **3e**, 34387-92-3; **3f**, 34387-93-4.

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Hydrogen Abstraction from Arylmethanes by Bromine Atom

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An excellent correlation of the relative rates of hydrogen abstraction from a series of arylmethanes by the trichloromethyl radical with the change in SCF-π-binding energies between the incipient radicals and the arylmethanes recently has been reported.[2] No such correlation was found for abstraction by *tert*-butoxy radical.[2] Unruh and Gleicher[2] interpret this as evidence that the transition state for hydrogen abstraction by the trichloromethyl radical must strongly resemble the intermediate free radical while that for abstraction by *tert*-butoxy radical probably has a structure between the reactant and the intermediate. We wish to report a similar study in which bromine atom is the abstracting species.

Competitive brominations were carried out at 75.5° using standard techniques.[3] Analysis of the resulting arylmethyl bromides was done by nmr techniques so that ring substitution in arenes by bromine atom was not an analytical problem. The results are reported in Table I. Unfortunately, 2-methylanthracene, 9-methylanthracene, and 1-methylpyrene did not afford benzylic bromination but rather a rapid ring substitution reaction. As a result, the kinetic results have a spread of only about six.

Table I

Relative Rates of Hydrogen Abstraction by Bromine in Benzene at 75°

Arylmethane	No. of expt	k/k_0[a]
Toluene		(1.00)
2-Methylphenanthrene	3	2.03 ± 0.03
2-Methylnaphthalene	3	2.72 ± 0.01
3-Methylphenanthrene	6	3.19 ± 0.32
1-Methylphenanthrene	3	4.00 ± 0.13
1-Methylnaphthalene	3	5.69 ± 0.05

[a] Experimental error represents average deviation of the number of experiments shown.

Table II

Correlations of the Relative Rates of Hydrogen Abstraction from Unsubstituted Arylmethanes by Bromine Atom with Various Molecular Orbital Parameters

Parameter	Correlation coefficient
HMO charge density	0.947
SCF ΔE_π[a]	0.935
SCF charge density	0.934
HMO free valence	0.899
HMO ΔE_π	0.898

[a] Values taken from ref 2.

Correlation of the natural logarithms of the relative rates of hydrogen abstraction with some calculated molecular orbital parameters are shown in Table II. While none of the correlations are as excellent as that obtained by Unruh and Gleicher[2] for trichloromethyl radical with SCF ΔE_π, it is interesting to note that all are good. Charge density calculations[4] were made using an arylmethyl cation as a model and the correlation was made with charge density at the methyl carbon atom. It is not clear what such a correlation represents, especially from the somewhat surprising result that the Hückel method gives better results than does the SCF approach. One is tempted to explain the correlation with charge density on the basis of the suggestion of Russell and Williamson[5] of stabilization of the transition state by a significant contribution of a polar canonical structure I. On the basis of the rather good

$$\mathrm{ArCH_2H\cdot X} \longleftrightarrow \underset{\mathrm{I}}{\mathrm{Ar\overset{+}{C}H_2H\overset{-}{X}}} \longleftrightarrow \mathrm{ArCH_2H\text{-}X}$$

correlation with the SCF ΔE_π parameter and the interpretation given to such a correlation by Unruh and Gleicher,[2] the transition state for the hydrogen abstraction by bromine atom must strongly resemble the radical intermediate.

Experimental Section

All methylarenes were commercially available. Toluene and benzene were distilled as constant-boiling heart cuts.

Brominations were run at 75.5° in a 50-ml, three-necked flask fitted with a nitrogen bubbling tube, a water condenser, and an addition funnel. Hydrocarbons to be studied were weighed into the flask and benzene was added so that the total initial concentration was about 0.2 *M*. After the flask was placed in the constant-temperature bath the solution was degassed with bubbling nitrogen. A benzene solution of bromine was added slowly with irradiation of the solution with 275-W Sylvania sunlamp. The rate of addition was adjusted so that the reacting solution remained nearly colorless. Evolved hydrogen bromide was entrained by bubbling nitrogen through the solution, which also served to agitate the solution. Upon completion of the reaction, about 15 min, the mixtures were reduced to a volume of approximately 2 ml on a rotary evaporator at room temperature and 80–140 mm pressure. Ethylene dichloride was weighed into the concentrated solution as a standard and the arylmethyl

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[1] (a) National Science Foundation, COSIP participant; (b) National Science Foundation, URP participant.

[2] J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 2008 (1971).

[3] R. D. Gilliom and B. F. Ward, Jr., *ibid.*, **87**, 3944 (1965).

[4] HMO calculations were made utilizing the program of J. R. Howles and R. D. Gilliom, "Huckel," Program 132, Quantum Chemistry Program Exchange, Indiana University. SCF charge density calculations were made using J. E. Bloor and B. R. Gilson, "SCFCIO-Closed-Shell SCF-LCAO-MO," Program 71.2, Quantum Chemistry Program Exchange, Indiana University, rewritten in SPS for calculations on an IBM 1620-40K.

[5] G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.* **86**, 2357 (1964).

bromides were quantitatively analyzed by integration on a Varian HA-60IL nmr spectrometer. Each integration was performed at least ten times. Reactions were run with varying quantities of bromine to ensure consistent results. Relative rate constants were calculated using the standard equation[5]

$$k/k_0 = \ln\,[(A_0 - X)/A_0]/\ln\,[(T_0 - Y)/T_0]$$

where A_0 and T_0 are initial moles of hydrocarbon and toluene and X and Y are the corresponding moles of bromides obtained upon completion of the reaction. No reaction was carried beyond consumption of 30% of the methylarenes.

Registry No.—Hydrogen, 1333-74-0; bromine, 7726-95-6; 2-methylphenanthrene, 2531-84-2; 2-methylnaphthalene, 91-57-6; 3-methylphenanthrene, 832-71-3; 1-methylphenanthrene, 832-69-9; 1-methylnaphthalene, 90-12-0.

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Reductive Conversion of 1-Aryl-3-hydroxymethyl-3,4-dihydro-2-naphthoic Acid Lactones into Substituted Tetrahydro-1*H*-cyclopropa[*a*]naphthalenes[1a]

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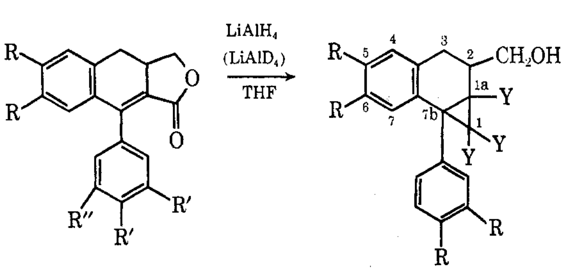
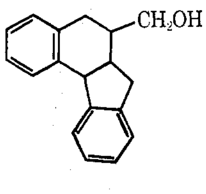
The ease of synthesis of cyclolignan lactones of the 3,4-dihydronaphthalene type **1** by means of the intramolecular Diels–Alder reaction[2,3] prompted us to investigate the formation of reduction products of **1**. Cis and trans addition of hydrogen to the α,β-unsaturated lactone system of γ-apopicropodophyllin (**1c**) by means of catalytic[4] and electrochemical[3] processes, respectively, have been described previously. We now report the chemical reduction of **1a** and **1b** by means of excess lithium aluminum hydride in tetrahydrofuran.

Isolated from the chemical reduction of **1a** was a crystalline product A, molecular formula $C_{18}H_{18}O$, in 70% yield. The infrared spectrum of A indicated the presence of an alcoholic OH group. The mass spectrum showed prominent peaks at *m/e* values of 250 $(M)\cdot^+$, 232 $(M - H_2O)\cdot^+$, and 219 $(M - CH_2OH)^+$. A was readily converted into a crystalline monoacetate and a crystalline monotosylate. The absence of an alkenic double bond in A was apparent from chemical tests on the acetate, the failure of A to absorb hydrogen in the presence of Pd/C at room temperature and pressure, and the relatively low extinction coefficient of the acetate (ϵ_{244} 1540, ϵ_{282} 160) compared to that of styrene ($\epsilon_{244}^{\max}$ 12,000, $\epsilon_{282}^{\max}$ 450)[5] in the wavelength range of 240–285 nm. A Kuhn–Roth determination on A showed no *C*-methyl group. Two structures, **2a** and **3**, seemed plausible on the basis of these data, though the former was preferred because of precedent for reduction of cinnamate esters to phenylcyclopropane[6] under conditions similar to those used on **1a**.

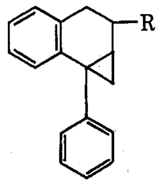


1a, R = R′ = R″ = H
b, R = R′ = CH₃O; R″ = H
c, R = OCH₂O; R′ = R″ = CH₃O

2a, R = H; Y = H
b, R = H; Y = D
c, R = CH₃O; Y = H



3



4a, R = H
b, R = CH₂OAc
c, R = CH₂OTs
d, R = CH₃

Careful integration of the pmr spectrum of A showed the presence of equal numbers of aromatic and aliphatic protons—a situation consistent with structure **2a** but not with **3**. However, the signal at highest field consisted of a multiplet for three protons at δ 1.1–1.7 (Figure 1), considerably downfield from the value of *ca.* 0.2 expected for protons in a cyclopropane ring magnetically unperturbed by the molecular environment.[7] The pmr spectra of A acetate and A tosylate also exhibited similar multiplets. Reduction of **1a** with lithium aluminum deuteride gave trideuterated A, a compound which showed almost exactly the same pmr spectrum as A itself, except for the absence of the high-field multiplet. Construction of a Stuart–Briegleb molecular model of **2a** indicated that protons at C-1 and C-1a should lie in the deshielding zone of the aromatic rings, and hence might be subject to the observed downfield shift.[8] On this basis the structures of A, its acetate, its tosylate, and its trideuterio derivative were assigned as **2a**, **4b**, **4c** and **2b**, respectively (where the stereochemical relationship between substituents at C-1a and C-2 remains undetermined).

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(1) (a) This investigation was supported by Research Grants No. CY-3097 from the National Cancer Institute and No. GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service. (b) Research Assistant, 1962–1964. (c) Research Associate, 1966–1967. (d) Research Associate, 1969–1970. (e) On leave from the Department of Chemistry, Weizmann Institute of Science, Rehovoth, Israel, 1964–1969. (f) Research Assistant, 1970–1971.

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(8) *Cf.* the pmr spectrum of 1-methyl-2,2-diphenylcyclopropane [H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964); J. N. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1962 (1968)] which shows a complexity of signals for three cyclopropane protons at δ 1.00–1.83 in CCl_4.