force for catalysis and the mechanism of that catalysis appears to be through entropy loss.

The catalytic constants obtained for micellar oxidation at higher buffer concentrations, k_b', are plotted as the closed circles in Figure 3. These catalytic constants also show a large pK_a dependence with $\beta = 3.7$. This is much larger than the β of 0.1 that is observed for the second-order buffer term in the nonmicelle oxidation, and the magnitude of this value strongly suggests that the catalyzed reaction occurs on the micelle surface. The chemical nature of this step is not altogether clear. The pK_a dependence gives an observed free-energy change of −530 cal/mol per $-CH_2-$, strongly suggesting a binding step. The simplest model that is consistent with the data (Scheme I, pathway C) includes this second binding step as a parallel pathway to K_B. The binding constant, K_b, must be less favorable than K_B by at least 100-fold because no curvature can be detected in the plots of k_{obsd} vs. buffer concentration above 0.01 M. The fact that the rate constants for the second phase are only three fold smaller than the first means that the kinetic expressions differ in a more complex way than simply the magnitude of the binding constant. This is most easily explained by assuming a change in rate-limiting step between the accessible regions of the two pathways, i.e., rate-limiting hydrolysis at low buffer and rate-limiting attack with rapid anhydride formation at high buffer. The physical meaning of two parallel binding constants for the formation of the carboxylate–micelle can be envisioned as rapid binding of carboxylate to the available regions on the SDS micelle (K_B) followed by less favorable binding of carboxylate that results in some deformation of the micelle ultrastructure (K_b).

It is interesting to compare the factor of about 100-fold acceleration that has been observed here with what might be expected if all of the translational entropy were lost due to micelle binding. Following Jencks' arguments,[3] at the cmc of SDS the volume of the micelles comprises about one-thousandth of the volume of the aqueous phase. If all of the reaction was confined to this volume, this would represent a change in entropy of $\Delta S = R \ln (V_1/V_2) = -14$ eu, which is equivalent to a free energy of −4.1 kcal/mol or an observed rate acceleration of about 10^3 at 25 °C.[3] Based on linear extrapolation of Figure 3, this rate acceleration should be achieved at a ΔpK_a of about 0.76 or at approximately octanoate. Unfortunately, the long extrapolations involved and the extremely low buffer concentrations that would be required make it impractical to pursue this entropy-related limit. It is interesting to note that the prediction of a 1000-fold acceleration is general for any bimolecular reaction which occurs *entirely* in the micellar phase. This means that anything less than this factor of 10^3 actually represents an *inhibition* of the bimolecular reaction by the surfactant micelles. Since in the majority of the literature micellar rate accelerations are below this 1000-fold limit, special care should be exercised in interpreting such results in terms of ground state or transition state perturbations.

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Registry No.—Diethyl sulfide, 352-93-2; iodine, 7553-56-2; SDS, 151-21-3.

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Partial Molal Volumes of Organic Compounds in Carbon Tetrachloride. 3. Aromatic Hydrocarbons: Steric Effects[1]

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The partial molal volumes of 31 aromatic and alkylaromatic hydrocarbons in carbon tetrachloride solution at 25 °C may be calculated with reasonable accuracy by addition of group increments (=C<, 3.03; =CH–, 13.22 mL mol^{-1}; established values for methyl, methylene, and methine) to a covolume of 11.61 mL mol^{-1}, and subtraction of fixed amounts for structural features known to involve intramolecular overcrowding.

More than 30 years ago Newman[2] resolved 4,5,8-trimethyl-1-phenanthrylacetic acid and attributed its dissymmetry to the steric interference of the 4- and 5-methyl groups (situation e of Scheme I), which caused one methyl to be displaced above and one below the molecular plane. Even the interference of a 4-methyl group with a 5-hydrogen in phenanthrene (situation d) could give rise to dissymmetry.[3] Later many other cases of intramolecular overcrowding in aromatic compounds (e.g., octamethylnaphthalene,[4] 3,4-benzophenanthrene[5]) which caused them to be distorted from a planar shape were revealed by X-ray crystallography.[6] It should be expected that such overcrowding would show up in reduced molecular volumes,[7] but so far there have been (to our knowledge) no studies to confirm this. In the present paper we investigate the effect of overcrowding on the partial molal volumes $\bar{V}^0$ in carbon tetrachloride at 25 °C of a variety of aromatic compounds and their alkyl derivatives, shown in Table I.

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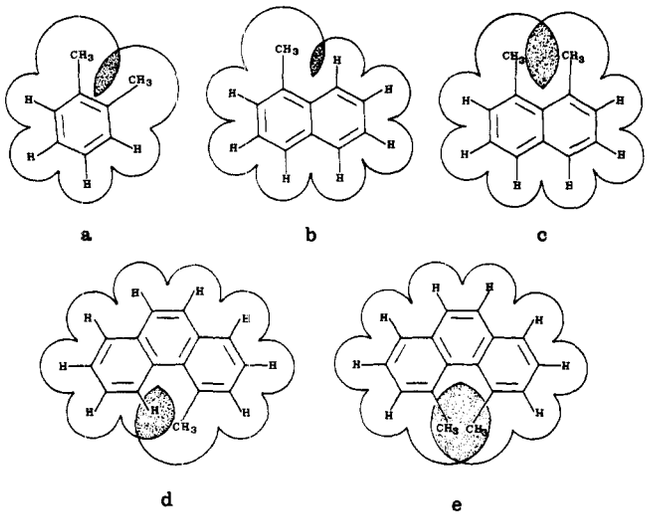
Table I. Partial Molal Volumes ($\overline{V}^0$, in mL mol^{-1}) of Aromatic Hydrocarbons and Their Methyl Derivatives in Carbon Tetrachloride at 25 °C

no.	hydrocarbon	registry no.	structural features[a]	$\overline{V}^0$(calcd)	$\overline{V}^0$(exptl)
1	benzene	71-43-2		90.9	90.5 ± 0.3
2	toluene	108-88-3		107.7	107.2 ± 0.2[b]
3	*p*-xylene	106-42-3		124.3	124.4 ± 0.2
4	*m*-xylene	108-38-3		124.3	124.4 ± 0.2
5	*o*-xylene	95-47-6	1 × a	121.9	121.2 ± 0.1
6	mesitylene	108-67-8		140.9	141.3 ± 0.2[c]
7	durene	95-93-2	2 × a	152.9	153.6 ± 0.2
8	pentamethylbenzene	700-12-9	4 × a	164.8	166.2 ± 0.1
9	hexamethylbenzene	87-85-4	6 × a	176.8	175.4 ± 0.3
10	naphthalene	91-20-3		123.4	122.5 ± 0.3[d]
11	1-methylnaphthalene	90-12-0	1 × b	139.2	139.3 ± 0.2
12	2-methylnaphthalene	91-57-6		140.1	139.3 ± 0.2
13	1,3,5,7-tetramethylnaphthalene[e]	7383-94-0	2 × b	188.4	185.9 ± 0.6
14	1,2,4,5,6-pentamethylnaphthalene[f,g]	68844-46-2	2 × a; 1 × b; 1 × c	193.6	193.5 ± 1.1
15	anthracene	120-12-7		155.9	156.8[h]
16	phenanthrene	85-01-8		155.9	155.8 ± 0.7
17	1,3-dimethylphenanthrene[i]	16664-45-2		189.3	189.6 ± 0.3
18	4,10-dimethylphenanthrene[i]	23189-63-1	1 × b; 1 × d	185.5	187.6 ± 0.3
19	1,2,4-trimethylphenanthrene[i]	23189-64-2	1 × a; 1 × b; 1 × d	199.8	202.8 ± 0.3
20	1,3,6,8-tetramethylphenanthrene[i]	18499-99-5	2 × b	220.9	221.9 ± 0.4
21	2,4,9,10-tetramethylphenanthrene[i]	23189-68-6	1 × a; 2 × b; 1 × d	215.6	214.2 ± 0.3
22	pyrene	129-00-0		162.0	166.5 ± 0.5
23	triphenylene	217-59-4		188.4	187.0 ± 0.7
24	1,3-dimethyltriphenylene[j]	17157-14-1	1 × d	218.8	219.4 ± 0.7
25	2,4,5,7-tetramethyltriphenylene[k]	35058-25-4	1 × e	248.2	245.7 ± 0.9
26	2,4,9,10-tetramethyltriphenylene[j]	68844-47-3	2 × d	249.2	245.6 ± 0.5
27	1,3,5,7,10,12-hexamethyltriphenylene[k]	35058-23-2	1 × d; 1 × e	278.6	281.5 ± 0.8
28	1,3,5,8,10,12-hexamethyltriphenylene[g]		1 × d; 1 × e	278.6	278.2 ± 2.0
29	1,2,3,4-dibenzanthracene	215-58-7		220.9	218.8 ± 2.0

[a] For coding, see Scheme I. [b] L. G. Longsworth, *J. Colloid Interface Sci.*, **22**, 3 (1966), reports 106.7 mL mol^{-1}. [c] 140.7 mL mol^{-1}. [d] 123.5 mL mol^{-1}. [e] P. Canonne and A. Regnault, *Can. J. Chem.*, **45**, 1267 (1967). [f] P. Canonne, Le Khae Huy, and W. Forst, *ibid.*, **49**, 4073 (1971). [g] A. Regnault, Doctoral Dissertation, Laval University, Quebec, Canada, 1968. [h] From L. G. Longsworth, footnote *b*. [i] A. Regnault and P. Canonne, *Tetrahedron*, **25**, 2349 (1969). [j] M. F. Gangloff-Delepoule, Master's Thesis, Laval University, Quebec, Canada, 1971. [k] R. Saint-Jean and P. Canonne, *Bull. Soc. Chim. Fr.*, 3330 (1971).

Scheme I. Scale Drawings of Some Over-Crowded Aromatic Molecules; van der Waals Radii of 1.2 Å for Hydrogen and 2.0 Å for Methyl Indicated



Results and Discussion

We have already shown[8] that $\overline{V}^0$ of aliphatic hydrocarbons in carbon tetrachloride may be calculated with good accuracy by the equation

$$\overline{V}^0 = V_c + \sum_1^m n_i I_i - 2.5 Z_g \qquad (1)$$

where V_c is a covolume of 11.61 mL mol^{-1}, I are volume increments due to methyl, methylene, or methine groups or quaternary carbon atoms, n are the numbers of such groups in the molecule, and Z_g is the average number of gauche conformations present in the molecule at 25 °C.[8,9] Z_g values were calculated using Pitzer's steric partition function, following a method employed extensively by Mann.[9]

Table II. Parameters I and δ (in mL mol^{-1}) for Calculation of $\overline{V}^0$ Using Equation 2

group	I	I/V_w	structural feature	δ
$-CH_3$	26.85[a]	1.96	a	2.35
$>CH_2$	17.36[a]	1.70	b	0.85
$>CH$	10.35[a]	1.53	c	7.61
$=CH-$	13.22	1.64	d	2.95
$=C<$	3.03	0.55[b], 0.64[c]	e	6.83

[a] From ref 8. [b] Based on V_w of $=C<$ (alkyl), ref 11. [c] Based on V_w of $=C<$ (condensation), ref 11.

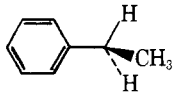
Preliminary calculations showed that $\overline{V}^0$ of about half of the hydrocarbons in Table I could be calculated with reasonable accuracy by an equation containing only the first two terms on the right-hand side of eq 2:

$$\overline{V}^0 = V_c + \sum_1^m n_i I_i - \sum_1^m p_j \delta_j \qquad (2)$$

However, in order to accommodate overcrowded compounds having one or more of the features a–e shown in Scheme I, it was necessary to add to the right-hand side of this equation the third term, where δ_j represents the decrement due to feature j and p_j the number of such features present in the molecule. Accepting the covolume V_c and the increments I

for methyl, methylene, and methine found previously, the parameters I and δ of Table II were obtained by a least-squares fitting of eq 2 to the experimental data of Table I. The decrements δ have roughly the values expected from the degree of overlapping shown in the scale drawings of Scheme I.

The values of $\overline{V}^0$ calculated by eq 2 with these parameters appear in the fourth column of Table I and agree well with experimental values. On the other hand, ethylbenzene and the compounds of Table III all have values of $\overline{V}^0$ less than calculated. These compounds, unlike those of Table I, can have a variety of torsional conformations in which the arrangements of the carbon skeletons differ. In fact ethylbenzene exists predominantly in the conformation shown in **1**, in which the



1

methyl group is gauche to an ortho carbon atom.[10] Evidently this results in a reduction in volume about equal to that resulting from gauche interactions in butane and other alkanes.[8,9] Similar considerations probably apply to most of the other compounds of Table III. (The case of hexaethylbenzene is special and is discussed below.)

The extent to which the ratio I/V_w (V_w being the van der Waals volume[11,12]) exceeds unity gives a measure of the empty volume[13] associated with a group in solution, and hence of the closeness of packing of the approximately spherical carbon tetrachloride molecules about the group. The value of I/V_w of =C< (third column of Table II) indicates that solvent molecules can approach the nucleus of the aromatic carbon atom more closely than indicated by the van der Waals radius r_w (normal to the plane of the aromatic molecules) of 1.77 Å adopted by Bondi.[11] Other lines of evidence point to weak charge-transfer complexation between carbon tetrachloride and aromatic molecules.[14] Such complexation would be expected to take place on the π surfaces of the aromatic molecules, and not at the edges, and hence to reduce I/V_w of =C< much more than I/V_w of =CH–. Thus studies of the structures of complexes of carbon tetrabromide with aromatic molecules show the haloalkane molecules located above the aromatic rings, with typical interplanar spacings in the range 3.0–3.5 Å.[15] The relationships between vertical ionization potentials and electronic spectra of such donor–acceptor complexes imply that similar molecular arrangements exist in solution.[15]

It seems likely that in hexaethylbenzene the crowding of the ethyl groups results in an arrangement having three methyl groups held fairly rigidly above the plane of the aromatic ring and three methyl groups below. Such an arrangement might obstruct the approach of carbon tetrachloride to either of the π surfaces of the molecule, and hence cause the volume $\overline{V}^0$ to be greater than expected on the basis of the overcrowding in this molecule. This is in accord with the much weaker donor–acceptor interactions found for hexaethylbenzene, relative to hexamethylbenzene, with both aromatic acceptors such as *s*-trinitrobenzene and 7,7,8,8-tetracyanoquinodimethane and nonaromatic acceptors such as tetracyanoethylene, iodine, iodine monochloride, etc.[16] Similar unfavorable steric interactions have been proposed to account for the relative complexing abilities of other polyalkylated aromatics and also for the decrease in association constants for complexes with ethylbenzene, isopropylbenzene, and *tert*-butylbenzene, respectively. Accordingly, it seems likely that eq 2 may cope much less well with $\overline{V}^0$ values of alkylaromatic compounds having propyl and higher alkyl groups than it does with the polymethylaromatic compounds of Table I.

Table III. Partial Molal Volumes ($\overline{V}^0$, in mL mol^{-1}) of Some Conformationally Mobile Alkylaromatic Hydrocarbons

no.	hydrocarbon	registry no.	structural features	$\overline{V}^0$ (calcd)	$\overline{V}^0$(exptl)	diff
1	ethylbenzene	100-41-4		124.9	122.2 ± 0.2	−2.7
2	*p*-diethylbenzene	105-05-5		159.0	151.9 ± 0.2	−7.1
3	*m*-diethylbenzene	141-93-5		159.0	152.2 ± 0.3	−6.8
4	*o*-diethylbenzene	135-01-3	1 × a	156.6	148.4 ± 0.3	−8.2
5	hexaethylbenzene	604-88-6	6 × a	280.9	268.3 ± 0.5	−12.6
6	diphenylmethane	101-81-5		167.2	165.7[a]	−1.5
7	triphenylmethane	519-73-3		229.3	223.9[a]	−5.4

[a] L. G. Longsworth, *J. Colloid Interface Sci.*, **22**, 3 (1966).

Relation of Equation 2 to Other Additive Schemes. The empirical equation

$$\overline{V}^0 = aV_w + b \qquad (3)$$

of Terasawa et al.[17] has been found to hold very well for the series of polycondensed hydrocarbons benzene, naphthalene, anthracene, phenanthrene, triphenylene, and 1,2,3,4-dibenzanthracene (a = 1.254, b = 30.4 mL mol^{-1}) with a correlation coefficient of 0.9998.[18] Each compound of this series can be considered as being made by the addition of two =C< (I/V_w 0.65) and two =CH– (I/V_w 1.64) to the lower compound of the series; the factor a which takes account of the empty volume associated with these additional six atoms lies between the I/V_w values above, as expected. However, I/V_w for alkyl groups approximates 1.6, and hence eq 3 cannot be expected to apply to the partial molal volumes of compounds containing varying proportions of aliphatic and aromatic carbon atoms. And, of course, it fails to take account of steric encumbrance which can cause isomeric molecules to have different volumes. Similar considerations apply to other equations (e.g., ref 19) which attempt to relate $\overline{V}^0$ to V_w without taking account of steric, conformational, or solvent-complexing effects.

Conclusions. While the usefulness of eq 2 with regard to alkylaromatic compounds generally remains to be established, its usefulness for polymethyl aromatics is manifest. In view of the ease with which partial molal volumes in carbon tetrachloride solution can be determined,[8] it probably affords the most convenient method available for distinguishing some isomeric structures from others.

Experimental Section

The compounds of Tables I and III are commercial products, except for those footnoted, whose preparation has been described elsewhere. All were purified by standard methods of crystallization, sublimation, or distillation to purities >99%, as established by mp or VPC. The purification of the solvent and the method of measuring $\overline{V}^0$ have been described previously.[8]

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Stereospecific Syntheses of the Diastereomeric (±)-α-Bisabolols. A Caveat on the Assignment of Stereochemistry to Natural α-Bisabolol

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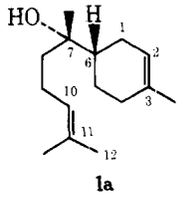
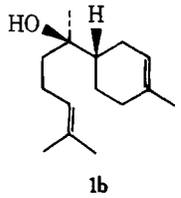
The diastereomeric racemic (6*S*,7*S*–6*R*,7*R*)-α-bisabolol and (6*S*,7*R*–6*R*,7*S*)-α-bisabolol were stereospecifically synthesized from (6*Z*)- and (6*E*)-farnesal, respectively, using intramolecular 1,3-dipolar cycloaddition of the corresponding *N*-methylnitrones as the key ring- and stereochemistry-forming step. A subsequent reductive deamination of a quaternary ammonium salt afforded a mixture of the respective bisabolol and its Δ^1 double-bond isomer in each case. NMR and gas chromatographic comparison of (−)-α-bisabolol isolated from chamomile oil with the two synthetic diastereomers showed the natural material to possess the 6*S*,7*S* stereochemistry, in contrast to a previously reported assignment of 6*S*,7*R* stereochemistry. In initial exploratory work, application of the synthetic sequence to citral smoothly yielded α-terpineol.

The sesquiterpene α-bisabolol (**1**) has been isolated from the essential oils of a wide variety of plants, shrubs, and trees.[1] The (−) enantiomer is the most widespread,[1c-g] but the (+) form has also been reported.[1i,j] Although the assignment of gross structure to synthetic (±)-α-bisabolol was made even prior to isolation of the natural material,[2] the problem of assignment of relative stereochemistry at the two asymmetric centers has been less tractable. None of the various synthetic routes[2,3] to racemic α-bisabolol have been capable of stereospecificity; hence mixtures of (±)-**1a** and (±)-**1b** have always resulted. In only one case was an analysis of the diastereomeric mixture carried out, using capillary column gas chromatography of the corresponding trimethylsilyl ethers.[3b] A tentative assignment of relative stereochemistries was made on the basis of mechanistic considerations, but neither isolation of the diastereomers nor gas chromatographic comparison of the mixture with natural material was reported.[3b]

In more recent work, the 6*S* absolute configuration was assigned to (−)-α-bisabolol by virtue of the levo rotation of a mixture of (6*S*,7*RS*)-α-bisabolols derived by synthesis from (−)-limonene,[4a] but a determination of whether the 6*S*,7*S* (**1a**)



1a

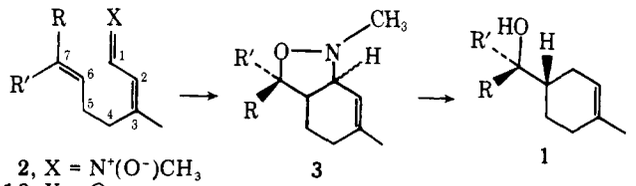


1b

or 6*S*,7*R* (**1b**) stereochemistry represented the natural material was not made. Finally, in a very recent report[4b] of the synthesis of (+)- and (−)-α-bisabolol from (+)- and (−)-limonene, respectively, in which absolute configurations were assigned to intermediate diastereomeric epoxylimonenes, the 6*S*,7*R* stereochemistry (**1b**) was designated for (−)-α-bisabolol.[4c]

As part of a continuing investigation into biogenetically patterned syntheses of terpenes via novel cyclization methods,[5] we sought to develop a stereospecific, cyclization-based synthetic approach to (±)-**1a** and (±)-**1b** that would allow unambiguous assignment of stereochemistry to these compounds. Since the direct biogenetic-type cationic cyclization of farnesol derivatives does not proceed with the required stereospecificity,[3a,b] an alternative approach was sought.

Scheme I



2, X = $N^+(O^-)CH_3$
13, X = O

3

1

a, R = CH_3, R′ = $CH_2CH_2CH{=}C(CH_3)_2$; b, R = CH_2CH_2-$CH{=}C(CH_3)_2$, R′ = CH_3

The work of LeBel et al. on intramolecular 1,3-dipolar cycloadditions of olefinic nitrones[6] suggested a potential solution to this problem (Scheme I). Thus, the nitrone **2** derived from farnesal would be expected to undergo thermal cyclization to give the isoxazolidine **3** as a mixture of isomers at the ring fusion,[6a,7] but with complete retention of the relative configuration of the 6,7 double bond.[7,8] The (6*Z*)-farnesal nitrone **2a** would therefore ultimately yield racemic (*SS*,*RR*)-α-bisabolol (**1a**), and the (6*E*)-farnesal nitrone **2b** would give racemic (*SR*,*RS*)-α-bisabolol (**1b**). Since all four possible 2,3–6,7 double bond isomers of the corresponding farnesols have been prepared and characterized,[9] unambiguous syntheses of (±)-**1a** and (±)-**1b** would be in hand.

Initial studies were carried out in the citral (**4**) series in order to confirm LeBel's assertion[10] that both the (2*Z*)- and (2*E*)-nitrone isomers would ultimately cyclize (the latter by isomerization to the former under the reaction conditions), and to develop a reductive deamination procedure for the conversion

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