The value, $-406.50 \pm 0.33$ kcal·mole$^{-1}$, for the heat of combustion of liquid 1,3-dioxolane is in close agreement with the value, $-406.4 \pm 0.9$ kcal·mole$^{-1}$, reported by Fletcher et al.$^3$ Skuratov et al.$^3$ have reported the value $-407.6$ kcal·mole$^{-1}$.

Kankaanperä measured the free energy difference between the liquid 2,4-dimethyl-1,3-dioxolanes$^8$ and assuming that $\Delta S = 0$ for these isomers, we can estimate that $\Delta H^\circ = -0.36$ kcal·mole$^{-1}$, the cis form being the more stable. Now it is possible to evaluate the heats of formation of both liquid isomers since the experimental result can be expressed as follows:

$$-100.58 = 0.671 \Delta H^\circ_t(l, cis) + 0.329 [\Delta H^\circ_t(l, cis) + 0.36]$$

Thus $-\Delta H^\circ_t(l, cis) = 100.70$ and $-\Delta H^\circ_t(l, trans) = 100.34$ kcal·mole$^{-1}$.

Using a previously proposed bond-bond interaction scheme for aliphatic oxygen compounds,$^8$ we can write:

1,3-Dioxolane: $\Delta H^\circ_t(g) = 3 \Delta H^\circ_\alpha(C, g) + 6 \Delta H^\circ_\alpha(H, g) + 2 \Delta H^\circ_\alpha(O, g) - \Sigma E_b - 2 \Gamma_{COC} - \Delta_{OCO} + [S]$  
2-Me-1,3-d.: $\Delta H^\circ_t(g) = 4 \Delta H^\circ_\alpha(C, g) + 8 \Delta H^\circ_\alpha(H, g) + 2 \Delta H^\circ_\alpha(O, g) - \Sigma E_b - 4 \Gamma_{COC} - 2 \Gamma_{COC} - \Gamma_{COC} - \Delta_{OCO} + [S]$  
cis-2,4-diMe: $\Delta H^\circ_t(g) = 5 \Delta H^\circ_\alpha(C, g) + 10 \Delta H^\circ_\alpha(H, g) + 2 \Delta H^\circ_\alpha(O, g) - \Sigma E_b - 5 \Gamma_{COC} - \Gamma_{COC} - \Delta_{OCO} - \Delta_{COC} - S_{\text{int}} + [S]$  

By substituting the experimental heats of formation and the heats of atomization of the elements, the bond energies ($E_b$) and the values of the group increments given in Ref. 9 in the above equations, the values 6.67, 5.46 and 6.72 kcal·mole$^{-1}$ are obtained for the apparent strain $[S]$ of the 1,3-dioxolane ring in these compounds, respectively. On average $[S] = 6.3$ kcal·mole$^{-1}$.

These and other data for "oxanes" will be discussed in detail in a paper which deals with bond-bond interactions of "oxanes".$^3$

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Mesomorphic Phases in Systems of Water-Nionic Emulsifier-Hydrocarbon

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Our work on the influence of mesomorphic phases on the stability of emulsions showed the existence of a large region with a mesomorphic phase possessing a lamellar structure in the system water—nonylphenol nona-ethylene glycol ether—p-xylene and gave also convincing evidence of the stabilizing action on the emulsion by the presence of this phase.$^1$ Since these results appeared to make a contribution to the understanding of hitherto unexplained behaviour of emulsions, we found further investigations along these lines to be of general value. The results of these investigations have confirmed the hypothesis of stabilizing influence of the mesomorphic phases.$^3$

The investigations have included phase equilibria in three component systems: water—nonylphenol nona-ethylene glycol ether—p-xylene (Fig. 1 A), water—nonyl-
phenol di-ethylene glycol ether—p-xylene (Fig. 1 B) and water—nonylphenol nona-ethylene glycol ether—hexadecane (Fig. 1 C). The emulsifiers were commercial and contain consequently each a distribution of the number of ethylene glycol ether groups, but contain less than 0.01% of foreign substances, when carefully purified from polyglycols.

As shown by the figures the systems contain several mesomorphic phases in addition to the solution. The regions for the different phases were determined by means of visual observation of the phase changes at the addition of one component and by means of centrifugal separation followed by determination of the composition of the phases. Different mesomorphic phases were identified and characterized by their texture under the microscope with crossed nicols and by means of their X-ray diffraction pattern.\textsuperscript{2,4}

X-Ray investigations showed that the mesomorphic phase in region E (Figs. 1 A and C) has a two-dimensional hexagonal structure with long hexagonally disposed rod-shaped aggregates, consisting of amphiphile molecules oriented with the hydrophilic groups outwards.\textsuperscript{5,6} The mesophase in region F (Fig. 1 B) has also a two-dimensional hexagonal structure and is built up of long rod-shaped aggregates consisting of an aqueous core surrounded by amphiphile molecules oriented with the hydrocarbon chains facing outwards.\textsuperscript{4} The mesomorphic phase D and B has a lamellar structure with alternating water and amphiphile layers.\textsuperscript{4,6} The phases in regions I\textsubscript{1} and I\textsubscript{2} are optically isotropic and X-ray diffraction data indicate cubic structures similar to those previously reported.\textsuperscript{7}

A comparison of Figs. 1 A and 1 B shows the changes of phase equilibria when the hydrophilic character of the emulsifier molecule is reduced, when the mean number of the ethylene glycol ether groups of the molecule is being reduced from nine to two. The concentration of the onset of the solubilizing of water in the L\textsubscript{2} region is increased, the size of the D-phase area is reduced to a high degree, the B-phase, the micellar solution L\textsubscript{1} and the hexagonal phase E have disappeared. All these changes can easily be referred to the reduced hydrophilic properties due to shortened ethylene glycol ether chain.

The differences of the phase behaviour when the polarizable p-xylene is being

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replaced by hexadecane (Figs. 1 A and 1 C) is even more pronounced. The L₂ area is
even more pronounced. The L₂ area is reduced to a small region, where the
emulsifier dissolves the hydrocarbon, and
the area of the D-phase is also reduced to a
high degree. The E-phase is able to
solubilize considerably more hexadecane
than p-xylene. The continuous L₁ region
in Fig. 1 A is transformed into three
isotropic phases; one liquid and two vis-
cous isotropic ones (L₁ and L₃) in Fig. 1 C.

The reason for this markedly changed
phase behavior is partly to find in the
difference of the polarizability of the
hydrocarbon which has an influence on the
site of the molecules in the micelles as shown
by NMR investigations.

This would explain the change in L₁ area when p-xylene
is replaced by hexadecane, but could scarcely explain the excess solubility of the
hexadecane in the E-phase. This behavior
is considered to have a close connection
with the packing of the xylene molecules
and the benzene part of the emulsifier, a
fact that may favor a lamellar structure.

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Bacterial Carotenoids XXVIII*

C₅₀-Carotenoids

4. Stereochemistry of the Terminal
Double Bonds of Dehydrogenans-P439

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A year ago we reported on the structure
determination of dehydrogenans-P439
(I). The configuration around the terminal
double bond was not established and was
arbitrarily chosen as trans between the two
largest substituents. Support for the trans-
configuration is now obtained from the

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aldehyde signal in the PMR-spectrum of
P439-dialdehyde (2), compared with data
recently reported for related cis and trans
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