were combined with others from the literature to give the second virial coefficient, the heat capacity of the perfect gas, the barrier to internal rotation, and the entropy.

The general picture of the nature and cause of barriers to internal rotation is discussed briefly and applied to nitromethane.

BERKELEY, CALIFORNIA RECEIVED AUGUST 11, 1941

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES]

Macromolecular Properties of Linear Polyesters. The Viscous Flow and Kinetic Interaction in Solution of ω-OH-Undecanoic Self-polyesters

BY W. O. BAKER, C. S. FULLER AND J. H. HEISS, JR.

In a previous paper,[1] fourteen members of a polymer-homologous series of the self-polyesters of ω-OH-undecanoic acid have been characterized by several independent methods of molecular weight determination. Because of their linearity, accurately known molecular structure and known average size distribution, these compounds are excellent subjects for investigation of the viscosity of high polymeric solutions.[2–10] The present work is intended as a critical study over a range of concentration of the viscosity behavior of these well characterized polymers. The results obtained, which agree with published data on analogous compounds,[7,10] supplement and extend previous work. Thus, several properties of linear polymer solutions not heretofore emphasized, which are significant in the application of viscosity measurements to the determination of molecular weight, are treated.

Experimental Methods

The same compounds and techniques described previously[1] were employed. Each concentration was prepared separately by weighing, to avoid dilution errors. The tabulated concentrations are in grams per 100 cc. of solution. Where significant, the densities of the solutions were accounted for in the kinematic relative viscosity. Duplicate measurements were made repeatedly and particular care was taken to obtain precise values at low concentrations. As before,[1] measurements were at 25.00 ± 0.02° in reagent grade chloroform of uniform purity. The polymers were stable during all measurements. All samples contained their "natural" distribution of molecular weights, as encountered in practice. The deviations from linearity at the lowest concentrations in Fig. 1 are within the experimental error, which rises rapidly on dilution because of both low η_r and low c.

Results and Discussion

Table I includes representative values for the concentration dependence of the relative viscosities in chloroform of more than a hundredfold variation in chain length, from the monomer, ω-OH undecanoic acid, upward. The solution viscosity of linear polymers extrapolated to $c = 0$ is related to the average molecular weight by[7–10]

$$\ln \eta_r/c = K_w M_w + B \qquad (1)$$

The data appear in Fig. 1. The function $\ln \eta_r/c$, however, is evidently not concentration independent, even for polyundecanoate U1, of weight average molecular weight[1] $M_w = 5000$. This agrees with the observations of Lovell and Hibbert[11] on three monodisperse polyoxyethylene glycols, and with the majority of other literature data when examined by a similar plot. The slopes in Fig. 1 connote a polymer–polymer or polymer–solvent interaction increasing with chain length unaccounted for in any of the present configurational or hydrodynamic[12–16] solution viscosity theories. Also, from Fig. 1

$$\frac{d(\ln \eta_r)/c}{dc} = M_w + d \qquad (2)$$

which represents the simple relation of the concentration dependence of $\ln \eta_r/c$ to chain length.

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(8) Meyer and van der Wijk, *Helv. Chim. Acta*, **18**, 1067 (1935).

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(12) Kuhn, *Z. physik. Chem.*, **A161**, 1, 247 (1932).

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TABLE I

SOLUTION VISCOSITIES OF POLYUNDECANOATES AT VARIOUS CONCENTRATIONS

c, g./100 cc. solution	η_r	ln η_r/c
	U0, M_w = 202	
0.4020	1.015	0.037
0.6000	1.026	.042
1.0004	1.044	.044
2.0000	1.096	.048
3.0000	1.147	.049
	U1, M_w = 5,000	
0.0400	1.009	0.219
.1004	1.023	.226
.1996	1.047	.229
.3008	1.070	.225
.3984	1.094	.226
.6008	1.147	.228
1.2004	1.318	.230
	U5, M_w = 12,000	
0.0396	1.017	0.423
.1004	1.045	.435
.1992	1.091	.439
.2992	1.139	.435
.4012	1.190	.433
.5996	1.292	.427
1.2004	1.636	.410
	U7, M_w = 17,600	
0.0396	1.025	0.626
.0992	1.064	.621
.2000	1.133	.626
.3000	1.205	.620
.4000	1.276	.610
.8000	1.607	.593
1.1992	1.952	.558
	U10, M_w = 20,800	
0.0404	1.031	0.743
.1000	1.077	.744
.2004	1.156	.725
.3000	1.242	.722
.3984	1.333	.722
.6004	1.511	.687
.8012	1.712	.671
1.1996	2.153	.639
	U14, M_w = 25,200	
0.0400	1.034	0.848
.1020	1.091	.854
.1996	1.188	.860
.3008	1.296	.862
.4004	1.408	.854
.6016	1.654	.836
.8000	1.898	.801
1.0000	2.182	.780
2.305	4.462	.649
2.881	5.858	.613
3.601	8.082	.580

As the number and proximity of the long chain molecules increase from extreme dilution, their contribution to the viscosity rises as collisions and entangling introduce the extra flow mechanism of chain articulation. There is a smooth increase with concentration for a range corresponding to the linear portions of the curves on Fig. 1. Then, as interaction gradually approaches the limiting conditions of pure polymer melt viscosity, the solution viscosity rises sharply again, as seen in Fig. 2, and reported generally in the literature. Fig. 2 sharply contrasts the viscosity concentration dependence of equal weights of chains differing in average molecular weight a hundredfold.

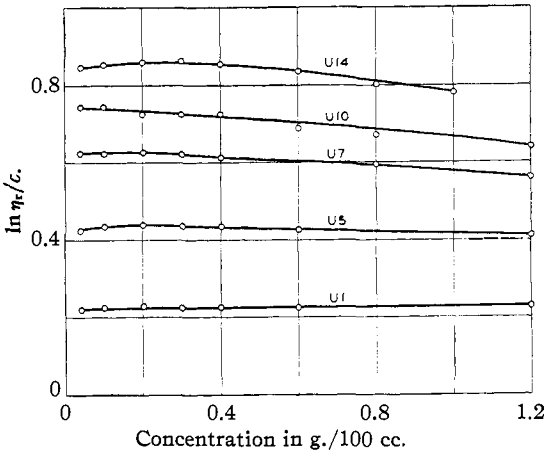


Fig. 1.—Concentration dependence of the reduced viscosity, ln η_r/c, of polyundecanoates.

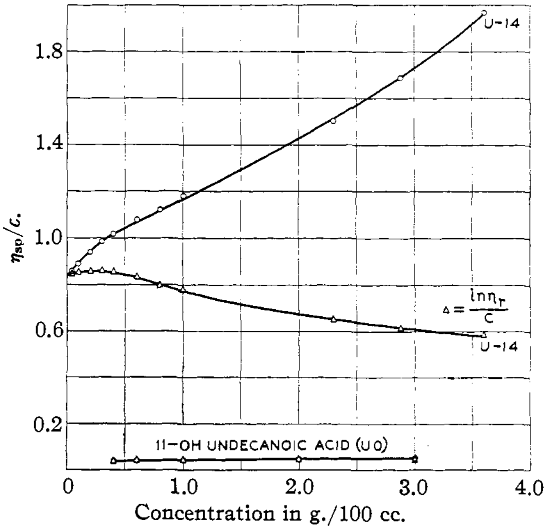
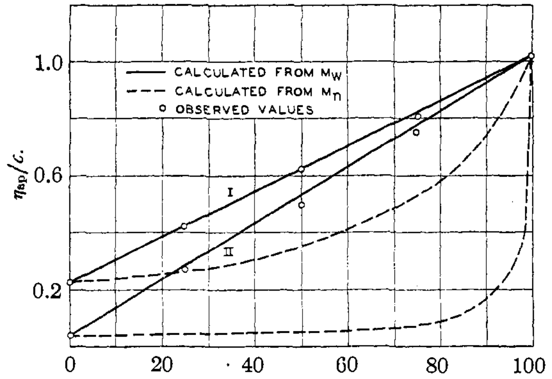


Fig. 2.—Comparison of concentration dependence of the reduced viscosity for long and very short chains.

We examine second, the molecular weight function to be used in equation (1) for polymer solution viscosities. The original, approximate Staudinger equation was said to require chain molecules of a single species,[6] but the satisfactory form (1) operates well for a broad, natural distribution of condensation polymers,[10,1] as well as for homogeneous chain lengths.[9] This is because of the form of the statistical distribution function obtaining for linear condensation polymers.[17,18] Further, Kraemer and Lansing[19] showed that M_w, the weight average molecular weight, should be used for solution viscosities. This may be submitted to experimental test by solution viscosity measurements on mixtures of polymers of known M_n and M_w, and comparison of the results with the viscosities calculated through use of number and weight averages, respectively. Various weights of the highest and lowest undecanoates, and of the highest undecanoate and the monomer ω-hydroxyundecanoic acid, were made into solutions of constant total weight concentration, 0.4 g. per 100 cc. The circles on Fig. 3 represent the η_{sp}/c^1 values obtained. If the number average molecular weight is used, the mixtures will have average molecular weights calculated by



Weight percentage of U14 in solution, with U1 (curve I); U0 in U14 (curve II).

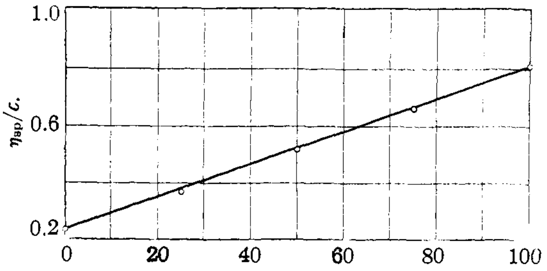
Fig. 3.—Observed η_{sp}/c values for synthetic mixtures of polyundecanoates U1 and U14 (curve I) and U0 and U14 (curve II) compared with calculated values for M_n and M_w.

$$\overline{M}_n = \frac{1}{f_1/M_{n,1} + f_2/M_{n,2}} \tag{3}$$

$\overline{M}_n$ is the number average molecular weight of the mixture, f_1 and f_2 are the respective weight fractions of compounds 1 and 2, and $f_1 + f_2 = 1$. The same additive averaging should apply to the viscosities themselves,[18] and simple additive η_{sp} values for mixtures of single solutes have been found.[11] Thus, the dashed lines on Fig. 3 were computed and show that $\overline{M}_n$ is indeed an unsuitable average. Kraemer and Lansing's proposed weight average requires the form

$$\overline{M}_w = f_1M_{w,1} + f_2M_{w,2} \tag{4}$$

where the meanings of (3) are retained. This yields the solid lines of Fig. 3, which agree precisely with observation except for the small deviations in the mixtures with the monomer, in which its single species is added to the polymolecular distribution. Figure 3 emphasizes how sensitive any quantity or property dependent on the number average molecular weight is to the presence of a small proportion of very low species. Only 10% of material of 13 chain atoms added to one of over 800 number average chain atoms gives the material still a number average little greater than 13. This may be reflected especially in certain mechanical properties. Figure 4 shows the normal additive behavior (weight averaged) of the quite dissimilar polyethylene succinate and polyundecanoate chains in various proportions at a constant weight concentration of 0.4 g. per 100 cc. of solution.



Weight percentage of polyethylene succinate in solution with polyundecanoate U1.

Fig. 4.—Solution viscosities of mixtures of polyundecanoate U1 with polyethylene succinate.

The constancy of the proportionality factor K relating molecular weight to solution viscosity may next be regarded. Figure 5 shows that the K of the Staudinger equation $\eta_{sp}/c = KM$ is strongly average molecular weight dependent, as found by Fordyce and Hibbert for a single species.[9] However, K_w of equation (1) shows satisfactory constancy down to the shortest chain length, the monomer. There, if a constant B is taken in equation (1), K_w is negative, after the fashion of the dashed line of Fig. 5. Actually, apparently B itself decreases markedly for very short chains, and K_w probably changes much less than shown.

We consider finally the additive constant B; it is not a simple proportionality constant yet is not obviously related to structure or mechanism.

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[17] Flory, THIS JOURNAL, **58**, 1877 (1936).

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It varies somewhat with solvent and temperature[7,9,10,20] but is in the range 0.05–0.1 for various conditions with polyundecanoates,[1] polydecanoates,[7] polydecamethylene adipates,[10] and polyoxyethylene glycols.[9]

A possible qualitative conception of B is the following. The term $\ln \eta_r/c$ has the units of volume divided by weight, V/g. B should have these units likewise. It is thus proportional to a specific volume. This may mean that each gram of kinked chain molecules occludes or otherwise immobilizes an amount of solvent such that the specific volume of the solution of the polymer is apparently about 7% higher than that actually reflecting the chain length dependent process of flow. The polymer in solution behaves, in effect, as though it were less surrounded by mobile solvent molecules than expected from the total number of solvent molecules present, and to maintain simple proportionality of solution viscosity, $\ln \eta_r/c$, with chain length, this useless volume per gram must be subtracted. Of course, the total volume occupied by a kinked chain enormously exceeds that of an extended form[13]: a hundredfold for a chain of 10,000 atoms, but the volume of immobilized solvent is probably much less.

It appears that shorter chain molecules are insufficiently convolved (into Kuhn's bone-shaped ellipsoids[13]) to occlude enough solvent to decrease the true available volume of the solvent per gram of polymer abnormally; hence the decrease in B observed for the lower molecular weights and the short chain paraffins of Meyer and von der Wijk[8]; hence, also, the lower values of B observed at higher temperatures,[9] for here the increased thermal oscillations of both solvent and solute diminish occlusion and immobilization of the former.

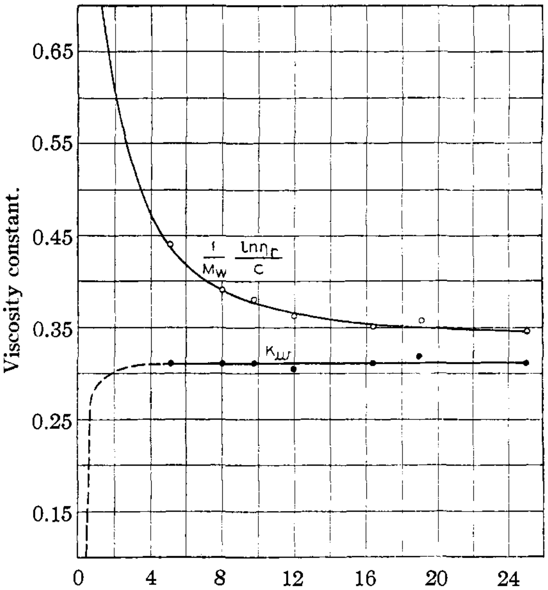

Fig. 5.—Variation of the Staudinger viscosity constant (upper curve) and K_w, with molecular weight.

Orientation by flow has usually been neglected in the study of solution viscosities, especially of well-characterized, linear polymers. However, Kraemer and van Natta[7] noted a 3% decrease in viscosity of 8% solutions of polydecanoates for a five fold increase in pressure in a Bingham viscometer. Mark[21] computed that there should be sufficient shearing force in an ordinary capillary viscometer to unkink a hydrocarbon chain. We have varied the shearing stress, τ, by using capillaries of different radii, r, but with the same length, l, and exposed to the same pressure head, Δp. This is a mild and easily controlled method of producing orientation. Then, the *average* shearing stress

$$\tau = \Delta pr/4l \qquad (5)$$

By this means, no evidence of orientation in viscometers of practical dimensions was found at low concentrations, *i. e.*, <1 g./100 cc., which is the range suitable for molecular weight determinations. However, Table II and Fig. 6 show marked orientation at higher concentrations, where both the reduced viscosity and η_r are lower for the larger capillary size. The capillary sizes are in the ratio 1.51. The values of Table II include, of course, density corrections. The points on Fig. 6 below 2 g. per 100 cc. were from small bore viscometers giving no evidence of orientation; those for U14, for instance, are a composite from several capillary sizes.

TABLE II

EFFECT OF SHEAR RATE ON SOLUTION VISCOSITIES AT HIGH CONCENTRATIONS

Polyundecanoate	c, g./100 cc.	$\frac{\eta_{r2}}{\eta_{r,3}}$	Viscometer 2, r = 0.31 mm. $\eta_{r,2}$	$\frac{\ln \eta_{r,2}}{c}$	Viscometer 3, r = 0.46 mm. $\eta_{r,3}$	$\frac{\ln \eta_{r,3}}{c}$
U4	3.6000	1.226	3.298	0.331	2.691	0.275
M_w = 11,600	10.0000	1.225	13.599	.261	11.106	.241
	20.0020	1.260	72.398	.214	57.468	.203
U11	3.6040	1.221	6.424	.516	5.263	.461
M_w = 21,900	10.0060	1.224	49.364	.390	40.328	.370
	20.0000	1.431	544.16	.315	380.35	.297

The effect of average chain length on the apparent relative viscosity as a function of capillary

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(20) Unpublished results.

(21) Mark, *J. Appl. Phys.*, **12**, 41 (1941).

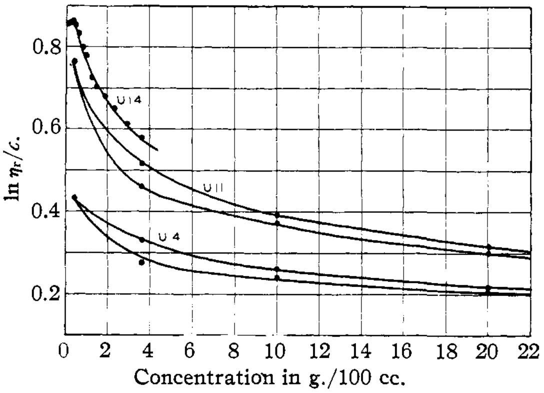

Fig. 6.—Reduced viscosity of polyundecanoates over wide concentration range: for polymers U4 and U11, upper curves are for capillary r = 0.31 mm., lower curves, capillary r = 0.46 mm.

size does not appear until the highest concentration of Table II. In the third column the ratios of the relative viscosity in the small to that in the large capillary for a given concentration show an interesting constancy up to 20 g. per 100 cc. of solution. This ratio would be 1 in the absence of anomalies. Then, the value for the polymer of M_w = 11,600 rises to 1.260, whereas the ratio for U11 of M_w = 21,900 is 1.431. At lower concentrations, the orientation may be a stepwise segment alignment in which the motion of the segments is free enough from polymer–polymer interaction not to reflect a large articulation factor. Hence would result no noticeable dependence on chain length. At higher concentrations, however, this same sort of orientation would increase by chain interaction to the extent of permitting the coöperation of oriented segments to orient other segments in the same chain. Also, the velocity gradient during flow is, of course, much decreased at high concentrations, and the time available to orient may approximate the relaxation time of the chain sections, thus permitting more complete alignment. The data of Table II suggest that both concentration and average particle length can be effective in producing flow orientation of molecularly dispersed mixtures in ordinary capillaries. A 50% increase in shearing stress has caused a 22 to 43% decrease in apparent relative viscosity.

Since the mechanism of polymer flow in solution seems generally to involve interchain action as judged by the concentration studies, it resembles flow in the melt, and highly concentrated solutions should show a transformation to melt behavior. Study of the melt viscosities[1] indicates that the ratio of the term (ln η + 3.47) for one polymer to that for another, at the same temperature, equals a constant determined by their relative molecular weights. η is the melt viscosity in poise. We shall, however, use η_r instead, since an approximation to the viscosity contributed by the polymer molecules and not by the solvent molecules is desired. Figure 7 shows the change of the above ratio with concentration for the polyundecanoates U4 and U11. The point for 100 g. is from the melt viscosity at 90°; the solution viscosities, of course, are at 25°. Points on Fig. 7 include values from both capillaries. Apparently the flow mechanism causes the viscosity to rise toward the melt value at relatively low concentrations, which again emphasizes the mutual interaction of the dissolved polymer chains. Since chloroform, for instance, is miscible with the polyundecanoates in all proportions, insight into solvent plasticizer action may be gained by such studies.

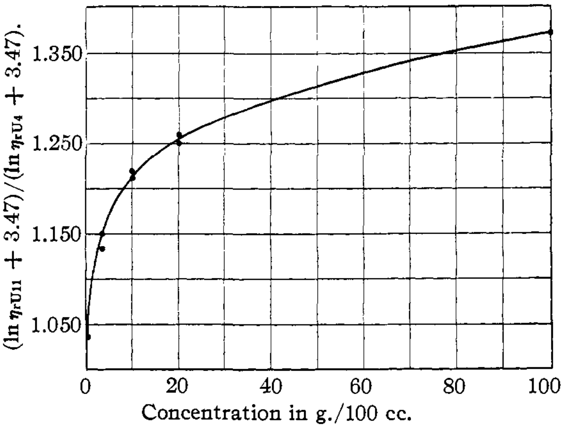

Fig. 7.—Curve showing approach of ratio of solution viscosities containing the melt viscosity constant to the same ratio for melt viscosity, for polyundecanoates U11 and U4.

Summary

The relations of η_r to each quantity in the generally used expression for the solution viscosity of linear macromolecules have been considered as follows.

The concentration dependence of the concentration reduced solution viscosity, ln η_r/c, of self-polyesters of ω-hydroxyundecanoic acid of accurately known average chain lengths was determined. Segment behavior contributing an entropy-like term from articulation of the chain sections during the flow process seems to appear in the mechanism.

Viscosity determinations on artificial mixtures of polymolecular undecanoates demonstrate that

the weight average molecular weight must be used in viscosity studies on inhomogeneous polymers (like those used technically) as prescribed by Kraemer and Lansing.

The Staudinger viscosity constant K is strongly molecular weight dependent, especially at low molecular weights while K_w from the equation (1) containing an additive constant B is satisfactorily independent at least down to $M_w = 5000$. Hence K_w for large molecules appears to contain no factors dependent on chain length.

The additive constant B has similar values for several linear polymer series containing flexible chains, providing the chain length exceeds some minimum. It possibly reflects a statistical property of chain kinking needed to relate the volume of the convolved chain and its occluded solvent molecules during flow to the space occupied by the true chain matter.

Flow orientation has been produced in concentrated solutions of polyundecanoates by varying the shearing stress τ. An average chain length dependence of this anomalous viscosity has been demonstrated, which provides another way of exploring the kinetic interaction of dissolved macromolecules. The solution viscosities of the polyundecanoates appear to exhibit a melt-like mechanism over a wide concentration range.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Position of Two Alicyclic Hydrocarbons in the Acidity Series[1]

BY R. D. KLEENE[2] AND G. W. WHELAND

The method of Conant and Wheland[3] and of McEwen[4] for the determination of the relative acid strengths of hydrocarbons has been extended to include phenylcyclohexane and phenylcyclopentane. The order of decreasing acid strength was found to be diphenylmethane > phenylcyclopentane > isopropylbenzene > phenylcyclohexane. No explanation is offered for the differences between the substances with only one phenyl group per molecule. The position of diphenylmethane is as expected in view of the greater possibilities for resonance in the ion.[5] An attempt to compare 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane[6] with triphenylmethane failed, as neither hydrocarbon would react at a detectable speed with the potassium derivative of the other. The trixylyl compound was shown to be a stronger acid than isopropylbenzene, however.

Experimental

Preparation of Materials.—Isopropylbenzene (cumene) was made by the method of Radziewanowski,[7] and phenylcyclohexane by the method of Kursanoff.[8] Phenylcyclopentane was prepared in 47% yield by a procedure based upon that described by Corson and Ipatieff[9] for the preparation of phenylcyclohexane; the product boiled at 68–72° at 2 mm. pressure and had an index of refraction of n^{20}_D 1.5284, in satisfactory agreement with the values in the literature.[10] Diphenylmethane was prepared by the method of Friedel and Balsohn,[11] and the 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane was the material prepared by Wheland and Danish.[6] The triphenylmethane used was the Eastman Kodak Co. product recrystallized three times from benzene.

The methyl ether of phenyldimethylcarbinol was made by the method of Ziegler, *et. al.*[12] This procedure, however, proved unsatisfactory for the methyl ethers of 1-phenylcyclohexanol and of 1-phenylcyclopentanol. These substances were made, therefore, by the method of Beaufour and of Sontag.[13]

Methyl Ether of 1-Phenylcyclohexanol.—From 50 g. of 1-phenylcyclohexanol,[14] 17 g. of sodamide, and 80 g. of methyl iodide in 150 cc. of dioxane was obtained 30 g. of the methyl ether. The product was a fragrant, colorless oil which did not solidify at −30° and did not immediately decolorize bromine in carbon tetrachloride. The physical constants were: boiling point 93–95° at 3 mm.; d^{20}_4 1.008; n^{20}_D 1.5290.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.10; H, 9.47; OCH_3, 16.3. Found: C, 81.86; H, 9.36; OCH_3, 15.8.

Methyl Ether of 1-Phenylcyclopentanol.—From 20 g. of 1-phenylcyclopentanol,[15] 5 g. of sodamide, and 30 g. of

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(1) Abstract of part of a thesis submitted by R. D. Kleene in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry, December, 1940.

(2) Present address: Chemical Warfare Service, Edgewood Arsenal, Maryland.

(3) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

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