pairs of mixed solvents; they are tabulated in Table VI and shown graphically in Fig. 3.[26]

TABLE VI

SOLUBILITY OF LEAD CHLORIDE IN MIXED SOLVENTS

Weight % water in solvent	Moles $PbCl_2 \times 10^{-2}$ per 1000 g. of solvent Dioxane–water	Alcohol–water	Acetone–water	Glycerol–water
100	3.905[a]	3.905	3.905	3.905
90	2.90	2.380	2.65	4.04
80	2.173	1.410	1.74	4.20
70	1.44	0.885	1.08	4.38
60	0.932	.568	0.640	4.57
50	.550	.360	.350	4.79
40	.323	.215	.164	5.04
30	.210	.111	.064	5.33
20	.120	.050	.016	5.66
10	.060	.021	.0091	6.07
0	.0013	.0077	.0038	6.55

[a] Carmody, ref. 2.

The plot of solubility *vs.* mole fraction (Fig. 3) gives an interesting comparison of relative solvation effects in mole for mole of solvent.

It appears that the number and the character of polar groups on the solvent which is used with water is a factor that determines the direction of the solubility effect. Within the particular solvent pair the dielectric constant of the mixture plays an important role, but a minor one compared with the "solvent character" effect. This is in accord with the conclusions of Kraus.[27]

Summary

1. The electromotive force of the cell $Pb(Hg)/PbCl_2/AgCl/Ag$ has been measured at several concentrations in 20, 40, and 60% dioxane–water mixtures.

2. The solubility of lead chloride has been determined in dioxane–water mixtures with added potassium chloride and potassium nitrate. The solubility has also been determined in alcohol–water, glycerol–water and acetone–water mixtures with no added salt present.

3. From these data the activity coefficients of lead chloride are calculated over a wide range of concentrations. The divergence in the slope of $-\log \gamma$ *vs.* $\sqrt{\mu}$ is attributed to association.

4. The solubility product constants are calculated for the 20, 40, and 60% mixtures of dioxane and water and for pure water.

5. The data in the various mixed solvent pairs are discussed.

COLUMBUS, OHIO RECEIVED NOVEMBER 12, 1943

---

[26] The data on the lead chloride–ethylene glycol–water system were published in THIS JOURNAL, **65**, 293 (1943). The data are tabulated here in weight per cent. rather than mole per cent. for the sake of condensing the tables. The data are shown in Fig. 3 as mole fraction which serves as a better basis of comparison of solvation effects.

[27] Kraus, *Science*, **90**, 381 (1939).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

The Dipole Moments of Friedelin, Cerin, Isomers of Friedelinol and Isomers of 3-α-Naphthyl-1-chloro-1-propene[1,2]

BY JOHN J. LANDER AND W. J. SVIRBELY

The presence of specific functional groups in friedelin, cerin and high and low melting friedelinol have been decided upon on the basis of chemical evidence.[3] While dipole moment determinations would not be able to locate the positions of the functional groups in these cases, nevertheless such measurements could be regarded as a check on the accepted structures since their magnitudes should be of about the same order as those usually attributed to those same functional groups. This investigation was undertaken to check the structures of the above compounds. Dipole moments were also determined for two compounds which were suspected of being *cis–trans* isomers of 3-α-naphthyl-1-chloro-1-propene to decide whether such isomerism was possible on the basis of their moments.

Materials

Benzene.—J. T. Baker thiophene-free benzene was refluxed over mercuric acetate, dried with calcium chloride, refluxed over sodium and fractionally distilled over sodium, collecting the middle fraction (b. p. 78.1° uncor.). Subsequent distillations of benzene solutions were made to recover the benzene for reuse. The benzene was stored over sodium wire in a glass bottle and used as required.

Friedelin.—Slightly impure friedelin was recrystallized twice from pyridine (m. p. 254–260°). This may be compared with the melting range of 256–262° for the pure material.

Low-melting Friedelinol.—Slightly impure compound was recrystallized twice from dioxane. The melting point range, 278–282°, was the same as for the pure material.

High-melting Friedelinol.—This compound was prepared by hydrogenating some of the pure friedelin in dioxane solution over a copper–chromium oxide catalyst at 200° and 2000 lb. pressure. The crude material was recrystallized once from dioxane. The melting point range, 299–301°, may be compared to the range 301–304° for the pure material.

Cerin.—Pure cerin was used,[4] m. p. 248–251°.

---

[1] Presented in part at the Washington Section meeting of the A. C. S. held at the University of Maryland, May, 1942. Original version received March 15, 1943.

[2] A portion of this paper is abstracted from the Master's thesis presented by John J. Lander to the Graduate School of the University of Maryland, December, 1942.

[3] Drake and Jacobsen, THIS JOURNAL, **57**, 1570 (1935); Drake and Shrader, *ibid.*, **57**, 1854 (1935); Drake and Campbell, *ibid.*, **58**, 1681 (1936); Drake and Haskins, *ibid.*, **58**, 1684 (1936); Drake and Wolfe, *ibid.*, **62** 3018 (1940); G. K. Holmes, Thesis, University of Maryland 1940; J. Lann, Thesis, University of Maryland, 1941.

[4] Impure friedelin, impure low-melting friedelinol, and pure cerin were supplied us through the courtesy of Dr. N. L. Drake and his collaborators.

TABLE I

SUMMARY OF DATA IN BENZENE

Densities in parentheses have been picked off a density–mole fraction plot. Dielectric constants of pure benzene in parentheses have been obtained by extrapolating a dielectric constant–mole fraction plot.

$N_2 \times 10^4$	d	ϵ	P_2
	Friedelin at 32°, Run no. 1		
0.0000	0.86481	2.2548	$P_\infty = 298$
1.0814	.86494	2.2561	300
3.1674	.86519	2.2588	300
3.7381	(.86526)	2.2596	302
4.3511	.86532	2.2603	303
	Run no. 2		
0.0000	.86450	2.2579	$P_\infty = 292$
1.0850	.86462	2.2592	293
2.1149	.86473	2.2604	290
2.1549	(.86473)	2.2605	294
3.1889	.86484	2.2622	297
3.2184	(.86480)	2.2621	305
4.2163	(.86493)	2.2634	307
4.2563	(.86494)	2.2634	302
	Low-melting friedelinol at 32°, Run no. 1		
0.0000		2.2473	
.0000	.86496	(2.2478)	$P_\infty = 206$
1.0737	.86504	2.2484	211
2.2226	(.86515)	2.2491	207
3.1665	.86523	2.2496	203
4.2384	(.86532)	2.2502	205
6.4113	.86550	2.2513	203
8.4656	(.86568)	2.2526	206
	Run No. 2		
0.0000		2.2432	
.0000	(.86496)	(2.2436)	$P_\infty = 201$
1.5328	(.86509)	2.2444	208
3.1805	(.86523)	2.2451	193
4.4085	(.86533)	2.2459	200
5.9086	(.86546)	2.2467	200
7.3475	(.86558)	2.2473	197
	Run No. 3		
	$P_\infty = 196$		
	Cerin at 50°, Run no. 1		
0.0000	0.84581	2.2098	$P_\infty = 252$
1.5088	.84598	2.2111	250
2.5645	.84609	2.2121	254
	Run no. 2		
0.0000	(.84581)	2.2081	$P_\infty = 243$
1.6184	(.84599)	2.2094	240
2.6152	(.84609)	2.2100	233
3.5246	(.84620)	2.2107	231
	High-melting friedelinol at 50°, Run no. 1		
0.0000		2.2090	
.0000	(.84507)	(2.2085)	$P_\infty = 196$
1.3441	.84519	2.2091	193
2.6271	(.84530)	2.2095	189
3.7044	(.84539)	2.2099	180
5.4875	(.84554)	2.2109	187
	Run no. 2		
0.0000	(.84507)	2.2093	$P_\infty = 203$
2.2205	(.84527)	2.2105	205
3.2496	.84535	2.2110	201
4.0342	.84542	2.2115	203
	Solid $C_{13}H_{11}Cl$ at 32°		
N_2			
0.0000	0.86459	2.2427	$P_\infty = 98.8$
.001138	(.86535)	2.2465	98.4
.003842	.86680	2.2547	98.1
.006319	.86825	2.2626	98.1
.008199	(.86922)	2.2681	97.9
.009679	(.87003)	2.2719	96.8
.01481	.87276	2.2872	96.9
	Liquid $C_{13}H_{11}Cl$ at 32°		
.0000	.86462	2.2502	$P_\infty = 111$
.001481	.86544	2.2560	110.6
.006758	.86833	2.2745	105.9
.01137	(.87077)	2.2933	109
.01253	(.87142)	2.2973	108.5
.02932	.88055	2.3580	107

3-α-Naphthyl-1-chloro-1-propene.—Two compounds, one a liquid and the other a solid, both having the same chemical analysis, were furnished us by Mr. T. H. Harris and Dr. Colin M. Mackall of the George Washington University. Since elaborate purification procedures had already been used[8] in their preparation, the compounds were used as received.

Experimental Procedure

The heterodyne beat apparatus and the dielectric cell used in this work have been referred to in an earlier publication.[5] The solutions were made up in the following manner. One hundred ml. of benzene was pipetted into a series of glass-stoppered flasks. Three of the flasks were weighed empty and reweighed with the benzene. The average weight of the benzene was used throughout the series. The pipet was capable of delivering 100 ml. of benzene to within ±0.01 g. Samples of the solute were weighed and transferred into the flasks containing the benzene. Since time was required for the material to go into solution, the flasks were usually allowed to stand on a warm surface (approx. 40°) overnight. The solubilities of the first four compounds were very slight (low-melting friedelinol, the most soluble one, was soluble to the extent of 0.404 g. per 100 ml. of benzene). The dielectric constants of these solutions as well as that of the benzene used in their preparation were obtained.

Densities were measured using a modified Ostwald–Sprengel pycnometer having a volume of about 24 ml. Duplicate density measurements were made on benzene and on three or four of the solutions scattered over the concentration range. Duplicate checks were obtained to ±0.005%. The densities of the solutions which were not measured were read from the linear plot of density *vs.* N_2 for the particular series of solutions being studied.

Experimental Results

Part of our experimental results are given in Table I, which lists the mole fractions of the

---

(5) Davis, Bridge and Svirbely, THIS JOURNAL, **65**, 857 (1943).

solute, N_2, the densities of the solutions, d, the dielectric constants of the solutions, ϵ, the molar polarizations, P_2, and the extrapolated value of P_∞ obtained separately for each run from the extrapolation of the polarization data. The values of P_2 were calculated in the usual method using, however, the extrapolated value of ϵ_0 in case it appears in Table I. In all other cases the experimental value of ϵ_0 was used in all calculations.

The molar refractions $MR\text{D}$ were calculated in all cases from the atomic and the molar refractions given in Landolt–Börnstein. The values of $P_\text{E} + P_\text{A}$ given in the third column of Table II were taken equal to 1.05 $MR\text{D}$. The value of $MR\text{D}$ for the last compound in Table II was also calculated from the density and the refractive index of the pure liquid and was in very good agreement with the value obtained from the atomic refractions. The fourth column of Table II gives the polarizations P_∞ obtained by averaging the results of the P_∞ values obtained for each run given in Table I. The fifth column of Table II gives the dipole moments calculated in the usual manner along with the probable errors in the values listed.

TABLE II

Compound	Formula	$P_\text{E} + P_\text{A}$	P_∞	$\mu \times 10^{18}$
Friedelin	$C_{30}H_{50}O$	136.2	295 (32°)	2.80 ± 0.03
L. M. Friedelinol	$C_{30}H_{52}O$	137.2	201 (32°)	1.78 ± .07
H. M. Friedelinol	$C_{30}H_{52}O$	137.2	200 (50°)	1.81 ± .05
Cerin	$C_{30}H_{50}O_2$	137.9	248 (50°)	2.39 ± .05
Solid	$C_{13}H_{11}Cl$	65.7	98.8 (32°)	1.27 ± .02
Liquid	$C_{13}H_{11}Cl$	65.7	111 (32°)	1.47 ± .02

Discussion of Results

The effect on the polarization of the solute (P_2) of errors in measurement of N_2, ϵ, d and P_1 has already been treated in a quantitative manner[5] and indicates that errors of 0.1% in all of these quantities except N_1 would result in the possibility of large errors in P_2 for solutions where these values are measured at concentrations below about 0.005 N_2. Since the measurements on solutions of friedelin and its related compounds reported here were made at concentrations of 0.0008 N_2 or smaller and since the change in dielectric constant in going from the pure solvent to the most concentrated solution was so small, it may well be questioned whether our results have any physical significance whatsoever.

On examining the quantities ϵ, P_1 and d in order for the effect of errors in them on the μ value in the light of the experimental data obtained, it appeared that errors in extremely dilute solutions were not as great as those assumed for calculation previously[5] and consequently these results have significance, although the precision of the moments calculated is necessarily not as good as that for moments calculated from measurements in more concentrated solutions.

The dielectric constants of the different samples of pure benzene given in Table I varied at the most ±0.009 from an average value of 2.2489. In any particular run, however, all solutions were made up from the same sample of benzene and the utmost precautions were taken to keep the circuit characteristics as constant as possible. Plots of dielectric constant against N_2 for a series of solutions indicated that the data were consistent to better than 0.1%. The question as to whether these day by day variations in the dielectric constant of the solvent affected the value of μ is easily answered. In Table III the measured values of ϵ_0 and ϵ obtained from a run on friedelin are given in column two. A value of ϵ_0 is assumed in column four. The deviation between the assumed ϵ_0 and the measured ϵ_0 is about 0.4%. The difference between the measured ϵ_0 and assumed ϵ_0 is added to each in column two to obtain the ϵ values in column four. Reference to the polarization values in columns three and five of Table III shows quite definitely that the absolute values of ϵ_0 have little or no effect on the calculated polarization values provided that the slope of the resulting ϵ *vs.* N_2 curve is not affected. One concludes that in a given solvent the P_2 and ultimately the μ values of the solute depend on the change in ϵ with concentration and if the change in ϵ will be the same for the measured ϵ as it is for the true value of ϵ then the P_2 values will be the same and consequently μ will be the same. Evidently if we are dealing with the same solvent, then the day to day values of ϵ_0 will not materially affect the μ value of a solute dissolved in it, providing the ϵ values of the solutions vary correspondingly.

TABLE III

$N_2 \times 10^4$	ϵ (Meas.)	P_2	ϵ (Assumed)	P_2 (Based on assumed ϵ's)
0.00000	2.2502	P_1 = 26.560	2.2581	P_1 = 26.679
1.2117	2.2516	299	2.2595	299
2.1728	2.2528	302	2.2607	303
3.1011	2.2539	301	2.2617	301
4.0923	2.2553	304	2.2632	304

On plotting the values of ϵ against N_2 a linear relationship was obtained in every run for all of the compounds studied. The extrapolation of the resulting straight lines to $N_2 = 0$ gave in some cases values of ϵ_0 which agreed with the experimental values while in other cases they were either higher or lower than the experimental ϵ_0's. If it is assumed that there is a correct value for ϵ_0 relative to the best straight line which can be drawn for the ϵ *vs.* N_2 data and that this correct value is actually the extrapolated value at $N_2 = 0$, then the following conclusions may be drawn. First, if the measured value of ϵ_0 is smaller than the extrapolated value, the P_2 *vs.* N_2 curve will exhibit an upward trend as the dilution progresses. Second, if it is the same as the extrapolated value, then a positive and negative scattering of points due to experimental error will result. Third, if it is larger than the extrapolated value, then a definite downward trend will exist in the curve. This follows from the equation used for the calculation of P_2, namely, $P_2 = [P_{12} - P_1(1 - N_2)]/N_2$ where it can be seen that P_2 results from a subtraction of P_1 from P_{12} and consequently if P_1 is smaller than it should be, then P_2 will be greater and *vice versa*. As dilution progresses, however, the error in P_2 is magnified due to a division of difference which decreases rather slowly by a rapidly decreasing N_2. In Table IV we illustrate the above argument using the data of run no. 1 on low-melting friedelinol which showed an upward trend and using the data of run no. 1 on high-melting friedelinol which showed a downward trend when the experimental data were used in both cases to calculate P_1. If the extrapolated ϵ_0 value is used to calculate P_1, then the corresponding P_2 values change. These are given for the above cases in column four of Table IV. It becomes quite evident that on using[6] the extrapolated ϵ_0 value, the marked curvatures are eliminated and the spottiness of points occurs which has been shown to be due to *non-systematic experimental errors*.[5] The variations in ϵ_0 (exp.) and ϵ_0 (extrapolated) need not be very large in such dilute solutions to cause abrupt changes in curvature in the polarization curves. The values given in Table IV represent deviations of less than 0.03%.

TABLE IV

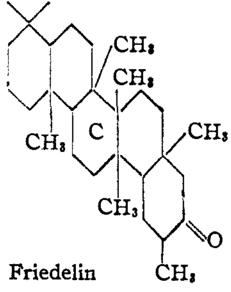
EFFECT OF CORRECTED DIELECTRIC CONSTANT OF THE PURE SOLVENT ON POLARIZATION VALUES

ϵ (meas.)	P_2	ϵ_0 (extrap.)	P_2
Low-Melting Friedelinol, Run no. 1			
ϵ_0 = 2.2473	P_1 = 26.518	2.2478	P_1 = 26.526
2.2484	281		211
2.2491	241		207
2.2496	227		203
2.2502	223		205
2.2513	215		203
2.2526	215		206
High-Melting Friedelinol, Run no. 1			
ϵ_0 = 2.2090	P_1 = 26.548	2.2085	P_1 = 26.541
2.2091	137		193
2.2095	142		189
2.2099	159		180
2.2109	174		187

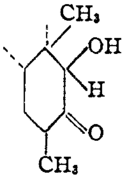
All the polarization data given in Table I were calculated using ϵ_0 (extrapolated) if the ϵ_0 (extrapolated) and ϵ_0 (experimental) values differed.

Errors in the measurement of density because of the subtraction involved in the calculation will be relative to one another just as were those of ϵ and thus any variation of the density curve between separate runs will show up as a change in μ. Here again the absolute value obtained for the density is not important if the same assumption is made as was made previously for ϵ, *i. e.*, that the change in the density as measured would be the same as that for the absolute value. The slope in the density curve would not be expected to vary much even if widely varying values for d_0 were obtained for the same solvent.

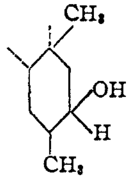
The structures of friedelin, the friedelinols and cerin are believed[3] to be either the following



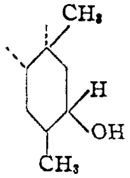
Friedelin



Cerin



L. M. friedelinol



H. M. friedelinol

or some modification of these structures where the functional groups are, however, located near the end of the molecule, definitely not in ring C. The moment found for friedelin, $\mu = 2.8\ D$, may be compared to that of cyclohexanone which is given variously in the literature[7] as 2.75, 2.8, 2.90 and 3.00 *D*. The moments found for the isomers of friedelinol, $\mu = 1.8\ D$ may be compared to that of cyclohexanol which is given[7] as 1.69, 1.82 and 1.9 *D*. The moment found for cerin, $\mu = 2.39\ D$, could not be compared with a compound having similar functional groups since apparently none have been measured.

Thus we conclude that the moments of the compounds given above offer independent evidence for the structures which have been assigned to them. Furthermore, the residues of the structures (besides the functional groups) involved in each case affect slightly if at all the characteristic moments of the functional groups.

The solid and liquid forms of $C_{13}H_{11}Cl$ were thought to be *cis–trans* isomers.[8] While the

---

(6) There appeared recently a paper by Halverstadt and Kumler, THIS JOURNAL, **64**, 2988 (1942), in which they discuss errors which would lead to marked rises in the polarization curves. They also develop methods of treating the data which would eliminate such rises. In this paper and in an earlier one, ref. 5, it was found necessary to explain apparent decreases as well as increases in the polarization curves at high dilutions. The method used by us in getting an extrapolated ϵ_0, while developed independently, is essentially the same as the one proposed by H. and K. However our conclusions differ inasmuch as we believe that both the apparent rise and the apparent fall in the polarization curves are due to experimental error in getting the true dielectric constant of the solvent. The value of ϵ_0 obtained by extrapolation of the ϵ *versus* N_2 curve may be either higher, lower or equal to the measured value of ϵ_0. When the experimental and extrapolated values of ϵ_0 were the same, then in the cases we investigated, the polarization curves behaved linearly; in case they differed then abnormal behavior occurred.

(7) (a) "Dipole Moments," *Trans. Faraday Soc.* (1934); (b) Halverstadt and Kumler, THIS JOURNAL, **64**, 1982 (1942).

(8) T. H. Harris, M.S. Thesis, George Washington University, 1943.

chemical evidence was inconclusive, nevertheless it appeared as though the solid form might be the *trans*-isomer and the liquid form the *cis*-isomer. The moments found for the two compounds, namely, 1.27 *D* for the solid and 1.47 *D* for the liquid, support the assumption of *cis-trans* isomerism.

Acknowledgment.—We wish to acknowledge the assistance of Dr. Peter Oesper in the experimental work on the $C_{13}H_{11}Cl$ compounds.

Summary

1. The precision of the calculated P_2 values and consequently of the dipole moment of a solute in a given solvent does not materially depend on the absolute values of the dielectric constants and densities.

2. Marked upswings and downswings in the polarization curves at high dilution are shown to be due to experimental error in measuring ϵ_0. It is suggested that an extrapolated ϵ_0 value obtained from an ϵ *vs.* N_2 plot be accepted as the dielectric constant of the pure solvent.

3. The dipole moments of friedelin, low and high-melting friedelinol, cerin and the solid and liquid forms of 3-α-naphthyl-1-chloro-1-propene have been determined.

4. The observed dipole moments of these compounds are compatible with their postulated structures.

COLLEGE PARK, MARYLAND RECEIVED OCTOBER 25, 1943

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA]

The Kinetics of the Antioxygenic Synergism of Quinones with Ascorbic Acid in Fat Systems[1]

BY VINCENT P. CALKINS[2] AND H. A. MATTILL

In a study of the well-recognized capacity of ascorbic acid, under certain conditions, to act as an inhibitor of fat oxidation, Golumbic and Mattill[3] demonstrated that by itself it was a relatively ineffective antioxidant, but that in fats and oils containing tocopherols, it greatly enhanced the stabilizing action of these naturally occurring inhibitors. This reinforcing action of ascorbic acid was shown to extend to other fat stabilizers of phenolic character, including quinols and hydroxy chromans, and appeared to be accomplished by a delaying of the quinol $\rightleftarrows$ quinone oxidation that is fundamentally responsible for their stabilizing capacity. Isler[4] had earlier demonstrated that ascorbic acid markedly protected tocopherol from oxidation.

The oxidation potentials of the antioxygenic quinols[5] are appreciably higher than that of ascorbic acid. Since fat peroxides oxidize quinols, their oxidation potentials are still higher, but despite this considerable difference in potential between ascorbic acid and the fat peroxides, ascorbic acid added to fats is neither appreciably oxidized during their induction period nor does it sensibly prolong this period unless quinones, hydroquinones or other phenolic inhibitors are present.

This investigation is a kinetic study of the role of these intermediary agents in the antioxygenic action of ascorbic acid.

The systems used comprised the ethyl esters of lard fatty acids with and without ascorbic acid, with and without quinone; since quinone is antioxygenic because it is reduced to hydroquinone, the hydroquinone-lard ethyl esters system was also studied.

The ethyl esters of lard fatty acids were prepared according to the method of Olcott and Mattill[6] and were stored in the icebox under nitrogen. The induction period of each system was measured by the oxygen absorption method in oxygen at 75°; from time to time during its progress, determinations were made of hydroquinone, ascorbic acid, dehydroascorbic acid and glycolic acid, and these results were plotted against time.

Hydroquinone was determined by the α,α'-dipyridyl color reaction[7]; a calibration curve (Klett-Summerson photoelectric colorimeter, Filter 52) showed that the logarithmic reading was a linear function of the amount of hydroquinone present and obeyed Beer's law. Peroxides, except in a very low concentration, interfere with this determination.

Ascorbic acid and dehydroascorbic acid were determined by the method of Bessey,[8] slightly modified to fit the existing conditions. A calibration curve prepared from readings made on solutions of known concentration was linear and obeyed Beer's law. In the assay of dehydroascorbic acid, particular care was taken to remove

---

[1] The experimental data in this paper are taken from a dissertation submitted by Vincent P. Calkins to the Faculty of the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy, April, 1943. A preliminary report of some of the results has appeared (*Fed. Proc.*, **1**, 104 (1942)).

[2] A part-time grant to V. P. C. from Merck and Co., Inc., is gratefully acknowledged.

[3] Calvin Golumbic and H. A. Mattill, THIS JOURNAL, **63**, 1279 (1941).

[4] O. Isler, *Helv. Chim. Acta*, **21**, 1756 (1938).

[5] J. B. Conant and L. F. Fieser, THIS JOURNAL, **46**, 1868 (1924).

[6] H. S. Olcott and H. A. Mattill, *ibid.*, **58**, 2204 (1936).

[7] A. Emmerie and C. Engel, *Rec. trav. chim.*, **57**, 1351 (1938).

[8] O. A. Bessey, *J. Biol. Chem.*, **126**, 771 (1938).