

575. *The Mesomerism of Keten and Three of its Derivatives.*

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The following apparent moments have been determined (refractivity method) in benzene: keten, 1.4<sub>3</sub>; dimethylketen, 1.8<sub>7</sub>; diphenylketen, 1.7<sub>6</sub>; mesitylphenylketen, 1.7<sub>4</sub> D. Keten as a gas (temperature method) has—as predicted from  $\mu_{\text{C}_6\text{H}_6}$  by the Barclay-Le Fèvre formulæ—a higher moment than that formerly quoted for it.

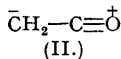
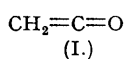
The polarities now found can be understood if the chief mesomeric displacements in ketens and ketones are opposite in character.

THAT a 1 : 2-dienoid system, X=Y=Z, having an unshared valency duplet in atoms X and/or Z, might exist in a mesomeric state, was first forecast by Ingold (*Chem. Reviews*, 1934, 15, 225). The ketens were explicitly included as examples, since among them the terminal oxygens should allow the process,  $\text{R}_2\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowleft}{\text{C}}=\text{O}$ . At that time, the relevant evidence available was mainly of a qualitative kind, *e.g.*, that many (but not all; cf. Wilsmore and Deakin, *J.*, 1910, 97, 1969; Gilman and Heckert, *J. Amer. Chem. Soc.*, 1920, 42, 1010; Farmer and Farooq, *J.*, 1938, 1025) addition reactions proceeded as though the normal "carbonyl" activation, represented in ketones by  $\text{R}_2\overset{\curvearrowright}{\text{C}}=\text{O}$ , were developed less than another which polarised the C=C link (cf. Gilman, "Organic Chemistry," 2nd Edn., 1943, p. 1914).

Earlier physical work had not provided any unexpected information; thus Lardy (*J. Chim. physique*, 1924, 21, 294; 353; cf. Henri, *Compt. rend.*, 1923, 177, 1039) from the visible and ultra-violet spectra of keten and some substituted ketens had recognised only the presence of

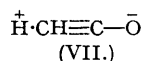
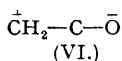
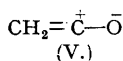
bands usually found for molecules containing ketonic groups or olefinic double bonds, and von Auwers (*Ber.*, 1918, 51, 1124) had observed the molecular refractions of diethyl- and diphenyl-keten to be approximately equal to the figures estimated by means of the usual atomic and group constants—an agreement predicted generally for 1 : 2-dienes by Brühl eleven years previously (*Ber.*, 1907, 40, 1160).

However, in 1938 (*J. Chem. Physics*, 6, 75), Beach and Stevenson published an electron-diffraction study of keten indicating that the distances C to C and C to O were 1.35 and 1.17 Å. respectively, and that the C—C—O arrangement was linear. Since the corresponding dimensions



expected for (I) were 1.34 and 1.24 Å., a 25% contribution from (II) was inferred. Recent spectroscopic data (Herzberg, quoted by Allen and Sutton, *Acta Cryst.*, 1950, 3, 46) suggest a slightly greater variation from the "normal" interatomic separations, particularly for the C—O link, for which 1.102 Å. is quoted. The Beach-Stevenson structure has been found compatible with the infra-red absorptions observed by Drayton and Thompson (*J.*, 1948, 1416), Halverson and Williams (*J. Chem. Physics*, 1947, 15, 552), and Harp and Rasmussen (*ibid.*, p. 778).

Mesomeric polarisations of the type shown in the opening paragraph should be detectable by comparing the dipole moments of ketens and ketones, because for the latter an approximately equal contribution from the forms (III) and (IV) seems to be agreed (Pauling, "The Nature of the Chemical Bond," 2nd Edn., 1944, p. 75). In the two classes therefore the mesomeric moments will act in opposite directions, the effect of (IV) or (V) being to raise, and that of (II) to lower, the observable moment from a basic value which for both (I) and (III) should not be very different from that for formaldehyde, *i.e.*, 2.27 D. (Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1943, 65, 89). The discovery by Hannay and Smyth (*ibid.*, 1946, 68, 1357) that the moment of keten, as a gas, appeared in fact to be much less than 2.27 D. was therefore of obvious significance. These authors, however, noted that if the real state of keten involves a 75% contribution of structures (I plus V) and 25% of (II) the molecular resultant should have its positive pole towards the oxygen atom, *i.e.*, the usual sense of ketonic polarity would be reversed. This conclusion was not pressed, and other contributory structures, such as (VI) and (VII), which tend to keep the oxygen negative, were mentioned.



An alternative point of view has been argued by Walsh (*ibid.*, p. 2408) who explained the lowered carbonyl polarity in keten without recourse to resonance. The central C-atom is "acetylenic" or "digonal," forming two hybrid *s-p* bonds at 180°, and two  $\pi$  bonds having their central planes at right angles, thereby precluding conjugation and also reducing the C=O polarisation in keten relatively to that in, *e.g.*, formaldehyde.

*Present Work.*—The dipole moments of keten and its dimethyl, diphenyl, and mesitylphenyl derivatives have been determined in benzene solution. For other reasons (see later) the measurements of Hannay and Smyth on gaseous keten have been extended.

Results (refractivity method) are shown in Table I (top row).

*Discussion.*—The electrical effect of a methyl group on an attached olefinic link is to cause a small permanent polarity disposed in the direction to be expected if Me were "electron repelling." This action is quantitatively much the same in Me·CH=CH<sub>2</sub> ( $\mu = 0.35$  D., McAlpine and Smyth, *ibid.*, 1933, 55, 453; cf. Farmer and Warren, *J.*, 1933, 1297, 1302) as in toluene ( $\mu = 0.37$  D.; McAlpine and Smyth, *loc. cit.*). If therefore the observed moment of keten were caused by reversal of the normal carbonyl polarisation, the result of hydrogen replacement by methyl should be to make  $\mu_{\text{Me}_2\text{C}=\text{CO}}$  less than  $\mu_{\text{CH}_2=\text{CO}}$ . Unfortunately the difficulties of handling dimethylketen in this work proved severe and, of many attempts, we only produced one solution of composition and purity on which we could depend. Its  $\epsilon$  and  $d$  were therefore determined in triplicate, from which comes an estimated moment of 1.8 D. This is greater than 1.4<sub>3</sub>, the figure for keten.

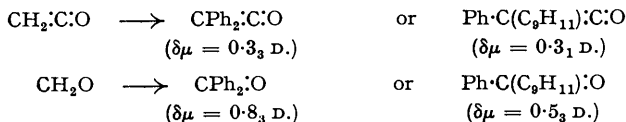
The increase of moment following dimethylation thus is about 0.4 D. for keten compared with *ca.* 0.6 D. for formaldehyde. Further, the moments of the four ketens are all smaller than those of the related ketones by amounts approximately 30—40% of  $\mu_{\text{ketone}}$ ; for the first two pairs these ratios are practically the same at 32% :

TABLE I.

	Parent.	Dimethyl-.	Diphenyl-.	Mesitylphenyl-.
Keten .....	1.4 <sub>3</sub>	1.8 <sub>7</sub>	1.7 <sub>6</sub>	1.7 <sub>4</sub>
Ketone .....	2.1 <sub>3</sub> *	2.7 <sub>4</sub>	2.9 <sub>5</sub>	2.6 <sub>5</sub>
$\delta\mu$ .....	0.6 <sub>9</sub>	0.8 <sub>7</sub>	1.1 <sub>9</sub>	0.9 <sub>1</sub>

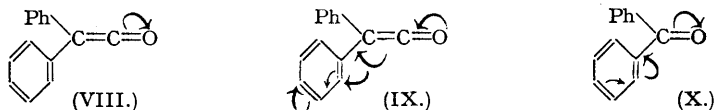
\* The data presented are measurements made in solution. Attempts to examine formaldehyde dissolved in benzene have been unsuccessful. From the molecular dimensions listed by Allen and Sutton (*Acta Cryst.*, 1950, **3**, 46) we find  $A : B : C = 3.80 : 3.61 : 2.90$ , whence by eqn. (2) of *J.*, 1950, 3370, the required  $(\mu_{\text{CH}_2\text{O}})_{\text{C}_6\text{H}_6}$  is calculable as 2.1<sub>3</sub> D. from  $(\mu_{\text{CH}_2\text{O}})_{\text{gas}} = 2.2$ , D. We note that this result shows the polarity changes from formaldehyde to acetone not to be markedly affected by state:  $(\mu_{\text{Me}_2\text{CO}})_{\text{gas}} = 2.8_5 - 3.0_2$ ,  $(\mu_{\text{Me}_2\text{CO}})_{\text{C}_6\text{H}_6} = 2.7_4$ ,  $(\mu_{\text{CH}_2\text{O}})_{\text{gas}} = 2.2_7$ , estimated  $(\mu_{\text{CH}_2\text{O}})_{\text{C}_6\text{H}_6} = 2.1_2$  D.

Attention may also be drawn to the alterations in moment, consequent on arylation, through the series :



Replacement of phenyl by mesityl affects the ketones more than the ketens.

From what has been said earlier it is evident that in  $\text{CPh}_2:\text{C}:\text{O}$  and  $\text{CPh}_2\cdot\text{O}$  major mesomeric polarisations, of the types exemplified by (VIII), (IX), and (X), may be expected :



The last two will create, in the real structures of such molecules, a tendency for the diarylmethylene portions to become planar. The Ph-C-Ph angle in diphenylmethane or 1:1-diphenylcyclopropane seems to be about 116° (Goldsmith and Wheland, *J. Amer. Chem. Soc.*, 1948, **70**, 2632), but when there is resonance—as in 1:1-diphenylethylene—this angle is increased to 125° (Coates and Sutton, *J.*, 1942, 567), although even so a 30° twist of the phenyl groups out of the common plane is necessary to provide the minimum permissible distance of 2.4 Å. between unbonded hydrogen atoms. Accordingly, when in (IX) and (X), a phenyl is replaced by the bulkier mesityl, the steric inhibition of resonance (cf. Birtles and Hampson, *J.*, 1937, 10; Ingham and Hampson, *J.*, 1939, 981) should be aggravated. Consistently with this, the moment of mesityl phenyl ketone (2.6<sub>5</sub> D.) is smaller than that of benzophenone (2.9<sub>5</sub> D.). The moments of the two arylketens are, however, the same—from which fact we infer that the spatial requirements of the aryl groups influence the mesomeric state less than they do with the ketones. Moreover, polarisations of type (VIII) cannot be transmitted by the usual duplet transfer mechanisms into the phenyl groups. We conclude therefore that forms such as (IX)—namely those conferring a partial double-bond character on the Ar-C links—are evidently not predominant contributors with diphenylketen.

We submit therefore that our measurements can be most readily interpreted if in ketens the mesomerism expressed by  $\text{>C}=\text{O}$  is reduced but not extinguished by competition with other displacements, such as  $\text{CH}_2=\text{C}=\text{O}$ , which are not probable with ordinary aldehydes or ketones.

*Dependence of the Apparent Dipole Moment of Keten on the Solvent.*—In a previous paper (*J.*, 1950, 3370) we have examined three equations whereby the ratio  $\mu_{\text{solution}}/\mu_{\text{gas}}$  may be predicted. One of these requires knowledge of the refractive index of the solute at the temperature of comparison (25°) and is therefore inapplicable in the present case. There remain however (A) and (B) :

$$\mu_s^2/\mu_g^2 = 1 + f(\epsilon)[\text{Exp } x^2 - \text{Exp } (h_2^2 - h_1^2)] \quad \dots \quad (A)$$

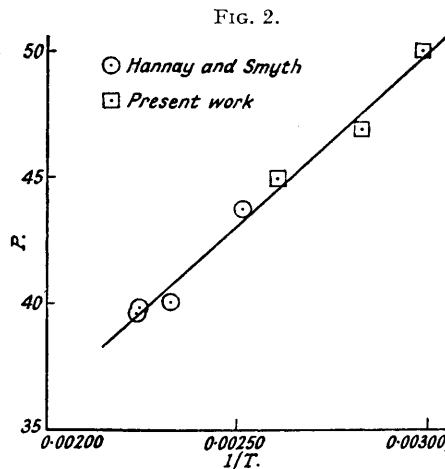
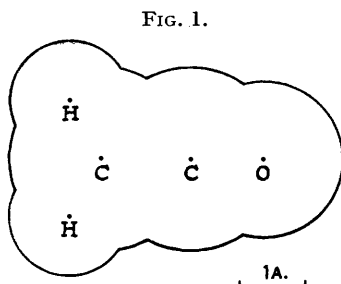
$$\mu_s^2/\mu_g^2 = 1 + f(\epsilon)\{\text{Exp } x^2 - \text{Exp } [(R_1/R_2)(1 - A_1B_1C_1/A_2B_2C_2)]\} \quad \dots \quad (B)$$

The symbols are explained in the reference cited. For brevity we here write  $f(\epsilon)$  for the volume polarisation of the solvent, taking it as 0.2962 for benzene at 30°. In addition,  $h_2^2 = 0.101$ ,  $R_2 = 26.15$  c.c., and  $A_2B_2C_2 = 117.6$  (Holland and Le Fèvre, *J.*, 1950, 2166). From the scale drawing (Fig. 1; cf. Allen and Sutton, *loc. cit.*) the dimensions  $A_1$ ,  $B_1$ , and  $C_1$  are seen to be 5.19, 3.65, and 2.90 respectively.

Substitution, etc., gives from (A) :  $\mu_{\text{gas}} = 1.091\mu_{\text{C}_6\text{H}_5}$  and from (B) :  $\mu_{\text{gas}} = 1.134\mu_{\text{C}_6\text{H}_5}$

Since the moment now found in benzene is 1.43 D, our predictions of  $\mu_{\text{gas}}$  [from (A), 1.56; from (B), 1.62 D.] are higher than the figure (1.45 D.) quoted from experiment by Hannay and Smyth (*loc. cit.*). These authors had listed polarisations at four temperatures between 397.8° and 446.3° K. inclusive, and we noticed that—*via* least squares—their data fitted the relation:  $P = 5.62 + 15031/T$ , whence  $\mu = 1.57$  D. The matter was discussed in correspondence with Professor Smyth, who rightly commented that the temperature range covered in his determinations with Hannay was too short to justify the deduction of constants for the Debye equation. Accordingly we undertook additional measurements at three points below 398° K., thus providing the extension illustrated in Fig. 2 (total polarisation plotted against  $1/T$ ).

It is seen that all seven points can be fairly represented by a single line, the (calculated) equation to which is:  $P = 7.97 + 14080/T$ , whence  $\mu = 1.52$  D. Although this is smaller than either of the predicted values of  $\mu_{\text{gas}}$ , it is nearer to that (1.56 D.) required by (A) than to



that required by (B). Such a relative applicability of the two expressions is in accord with our earlier conclusions (*J.*, 1950, 3370).

In previous papers, whenever a distortion polarisation ( ${}_D P$ ) has seemed dependable, we have estimated  $\mu_s^2/\mu_g^2$  directly as a ratio of orientation polarisations, *i.e.*, as  $(\infty P_s - {}_D P)/(P_g - {}_D P)$ . Yet in view of the refractometric evidence from substituted ketens (cf. von Auwers and Brühl, *loc. cit.*) and because the calculated  $(R_L)_D$  for keten is 11.0 c.c., we suspect that 7.97 c.c. is too low for the  ${}_D P$  of this molecule. In general,  ${}_D P$  is difficult to fix accurately from polarisation-temperature measurements, and for a given substance may vary according to the observer without greatly affecting the values for  $\mu_{\text{gas}}$  also produced (cf. *J.*, 1950, 561, for an example), the latter depending only on the slope—not the height—of the  $P$  versus  $1/T$  curve. In the present case therefore we have compared  $\mu_s$ , obtained *via* a  ${}_D P$  of 11.0 c.c., with  $\mu_g$  estimated from the inclination of the best fitting straight line through the seven points shown in Fig. 2.

#### EXPERIMENTAL.

**Keten.**—This was obtained from acetone in a "lamp" of the type described by Williams and Hurd (*J. Org. Chem.*, 1940, 5, 122) and purified by the method of Rice, Greenberg, Waters, and Vollrath (*J. Amer. Chem. Soc.*, 1934, 56, 1760). It was admitted to the dielectric constant apparatus at  $E$  of Fig. 2 of *J.*, 1950, 278, and redistilled into trap  $D$  immediately before measurement.

**Dimethylketen.**—Owing to the rapidity with which this substance reacted with atmospheric moisture, we eventually attempted to make only one solution straight away from each high-vacuum decomposition of dimethylmalonic anhydride (Staudinger, *Helv. Chim. Acta*, 1925, 8, 306, cf. Adams *et al.*, "Organic Reactions," 1946, Vol. III, p. 135). The crude condensates were redistilled under oxygen-free nitrogen and collected (b. p. 34°/760 mm.) in a liquid-air trap, from which absorption into a known weight of benzene was induced as described for sulphur dioxide (*J.*, 1950, 283).

**Diphenylketen.**—This was prepared from benzil monohydrazone and "azibenzil" (Schroeter, *Ber.*, 1909, 42, 2336; Staudinger, *ibid.*, 1911, 44, 1619) by thermal decomposition of the latter, followed by a final distillation immediately before admixture with benzene. All operations were as far as possible conducted in oxygen-free nitrogen. The three solutions (denoted by X, Y, and Z) for which data are tabulated below each contained the total material from a separate preparation, the solute in X having b. p. 85–88 at *ca.* 0.1 mm., those in Y and Z, b. p. 100°/0.2 mm.

At first we obtained poor results for the mercuric oxide oxidation of the hydrazone, but ultimately

it appeared that freshly prepared oxide behaved satisfactorily if used at once. This is in agreement with findings by Ritter and Wiedemann (*J. Amer. Chem. Soc.*, 1929, **51**, 3583) but is in contradiction to those by Taylor *et al.* (*J.*, 1938, 206) who advise that the oxide be given a preliminary exposure for 24 hours to the moist air of the laboratory.

*Mesitylphenylketen.*—The thermal decomposition of mesitylphenylacetyl chloride (from mesitylene and mandelic acid with anhydrous stannic chloride), by the procedure of Fuson, Armstrong, Kneisley, and Shenk (*J. Amer. Chem. Soc.*, 1944, **66**, 1464), gave a yellow liquid, b. p. 182—185°/21 mm., from which a fraction of b. p. 108°/0.2 mm. was selected for the present work.

*Dimeric Ethylcarbethoxyketen.*—For both the preparation of *α*-bromo-*α*-carbethoxybutyryl chloride, and its reaction with zinc filings, the directions of Staudinger and St. Bereza (*Ber.*, 1909, **42**, 4908) were followed, a colourless liquid with a faint ether-like odour, b. p. 89°/0.07 mm., resulting. Staudinger had reported the dimer as boiling at 113—116° under "absolute vacuum;" since our product also had b. p. 100°/0.3 mm., it seemed possible that it was in fact the dimer. Analysis showed a high hydrogen content (Found: C, 59.1; H, 8.2. Calc. for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>: C, 59.1; H, 7.0%). Prolonged heating (5 hours) of this substance at 200—220°/ca. 20 mm. caused only partial decomposition and did not produce any of the monomer.

*Mesityl Phenyl Ketone.*—We are indebted to Mr. D. R. Penman for a specimen of this substance (Louise, *Ann. Chim. Physique*, 1885, **6**, 202; Elbs, *J. prakt. Chem.*, 1887, **35**, 486), b. p. 169—175°/2 mm.

*Measurements.*—The three new determinations of the polarity of keten as a gas have been made with apparatus similar to that described before (*J.*, 1950, 290). The quantities in the third column of Table II are computed relatively to the temperature-invariant total polarisation of carbon dioxide (*viz.*, 7.341 c.c., cf. *Trans. Faraday Soc.*, 1947, **43**, 374) by the expression:  $P_{\text{keten}} = 7.341 (\delta C/p)_{p=0}^{\text{keten}} / (\delta C/p)_{p=0}^{\text{CO}_2}$ . The standardising equation required was found by measurement to be:  $(\delta C/p)_{p=0} = 2307.4/T - 0.054$ .

TABLE II.  
*Polarisations of gaseous keten.*

<i>T</i> (° K.).	$(\delta C/p)_{p=0}$ .	<i>P</i> (c.c.).	<i>P</i> (calc.).	<i>p</i> range (cm. Hg).	No. of observations.
335.5°	46.64	50.17	49.93	20—65	11
355.0	41.26	46.99	47.63	27—68	13
384.0	36.48	44.98	44.63	25—65	11

The following data refer to solutions in sodium-dried benzene; methods, symbols, and calculations are explained in *J.*, 1937, 1805; 1948, 1949; 1949, 333; *Trans. Faraday Soc.*, 1950, **46**, 1. Unfortunately certain of our observations were made at seasons when room temperatures were above 25°. Appropriate values of  $p_2$  and *C* from Table III for use in Table IV are:

Temp. ....	25°	27°	30°
$p_2$ .....	0.3409	0.3410	0.3416
<i>C</i> .....	0.1881	0.1889	0.1904

TABLE III.  
*Dielectric constants and densities of solutions.*

<i>Keten.</i>					<i>Dimethylketen.</i>				
$10^6 w_1$ .	$\epsilon^{30}$ .	$a\epsilon_2$ .	$d_4^{30}$ .	$\beta d_2$ .	$10^6 w_1$ .	$\epsilon^{27}$ .	$a\epsilon_2$ .	$d_4^{27}$ .	$\beta d_2$ .
0	2.2628	—	0.86718	—	0	2.2687	—	0.87168	—
4,085	2.2821	4.72	0.86689	−0.071	9,249	2.3159	5.10	0.87174	0.006
5,902	2.2876	4.20	0.86853	−0.110					
6,943	2.2932	4.39	0.86656	−0.089					
9,530	—	—	0.86598	−0.126					
12,840	2.3218	4.60	0.86585	−0.103					
13,510	2.3230	4.46	0.86605	−0.084					
13,940	—	—	0.86586	−0.095					
19,050	2.3548	4.83	0.86493	−0.118					
19,540	2.3567	4.81	0.86496	−0.114					
28,160	—	—	0.86430	−0.102					
whence mean $a\epsilon_2 = 4.57$ , mean $\beta d_2 = -0.101$ .					<i>Diphenylketen.</i> $10^6 w_1$ , $\epsilon^{25}$ , $a\epsilon_2$ , $d_4^{25}$ , $\beta d_2$ , $n_D^{25}$ . 0 2.2725 — 0.87378 — 1.4982 (X) 9,099 2.2930 2.25 0.87551 0.190 — (Y) 14,963 2.3086 2.41 0.87679 0.201 1.4998 (Z) 16,284 2.3133 2.51 0.87734 0.219 — whence $(a\epsilon_2)_{w_1} = 1.94 + 33 w_1$ ; $(\beta d_2)_{w_1} = 0.158 + 3.4 w_1$ .				

<i>Mesitylphenylketen.</i>					<i>Mesityl phenyl ketone.</i>					
$10^6 w_1$ .	$\epsilon^{25}$ .	$a\epsilon_2$ .	$d_4^{25}$ .	$\beta d_2$ .	$n_D^{25}$ .	$10^6 w_1$ .	$\epsilon^{25}$ .	$a\epsilon_2$ .	$d_4^{25}$ .	$\beta d_2$ .
0	2.2725	—	0.87378	—	1.5001	0	2.2725	0	0.87378	—
8,484	—	—	0.87522	0.170	1.5007	12,809	2.3184	3.58	0.87602	0.175
0	2.2628	—	0.86718	—		18,908	2.3400	3.57	0.87676	0.153
10,705	2.2788	1.49 <sub>5</sub>	0.86880	0.151	Temp. = 30°	25,492	2.3637	3.58	0.87789	0.161
17,791	2.2890	1.47	0.86987	0.151		31,221	2.3847	3.59	0.87877	0.160
24,797	2.3001	1.50	0.87091	0.150		whence mean $a\epsilon_2 = 3.58$ ; mean $\beta d_2 = 0.162$ .				
37,684	2.3217	1.56	0.87290	0.152						

<i>Dimeric carbethoxyethylketen.</i>				
$10^6 w_1$ .	$\epsilon^{25}$ .	$a\epsilon_2$ .	$d_4^{25}$ .	$\beta d_2$ .
0	2.2725	—	0.87378	—
16,399.5	2.3594	5.30	0.87618	0.146

TABLE IV.  
Calculation of results.

Solute.	Mol. wt.	$\alpha\epsilon_2$ .	$\beta$ .	$\infty P_1$ (c.c.).	$T$ .	$(R_L)_D$ (c.c.).	$\mu$ (D.).
Keten .....	42.0	4.57	-0.116	52.6	30°	11.0 *	1.4 <sub>3</sub>
Dimethylketen .....	70.1	5.10	0.007	91.3	27°	20.2 *	1.8 <sub>7</sub>
Diphenylketen .....	194.2	1.94	0.181	125.1	25°	62.0	1.7 <sub>6</sub>
Mesitylphenylketen .....	236.3	1.51	0.174	134.6	30°	73.5	1.7 <sub>4</sub>
Mesityl phenyl ketone .....	224.3	3.58	0.185	213.4	25°	69.1	2.6 <sub>5</sub>
Supposed dimeric ethylcarb- ethoxyketen .....	284.3	5.30	0.167	364.1	25°	68	3.8 <sub>0</sub>

\* Calc. from constants given in Landolt-Börnstein, "Tabellen," 4th Edn., p. 1039.

A preliminary statement (Hukins and Le Fèvre, *Nature*, 1949, **164**, 1050) on the present work gave certain figures which should now be replaced by these in Table IV.

The authors are grateful to the Commonwealth Science Fund for financial assistance.

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[Received, March 20th, 1951.]