COMMUNICATIONS TO THE EDITOR

DIMENSIONS OF SOAP MOLECULES AS SUPPOSEDLY DEDUCED FROM SURFACE TENSION MEASUREMENTS

Sir:

The surface tension measurements of Du Noüy [*Phil. Mag.*, [6] **48**, 664 (1924)] as carried out with the ring method were recently reproduced by Washburn and Berry [THIS JOURNAL, **57**, 975 (1935)] using the capillary rise method for sodium palmitate solutions. The equilibrium surface tension–concentration curve shows three minima and the same number of maxima.

According to the Gibbs theorem for these concentrations no adsorption at all takes place. Instead, the interpretation of Du Noüy as now repeated by Washburn and Berry introduces the hypothesis that the minima are due to condensed films on the water surface, but differing in orientation corresponding to the three dimensions of the adsorbed molecule. No other confirmation for the validity of this view has been available.

However, the assumptions on which the theory of Du Noüy is based—besides contradicting the thermodynamics of Gibbs—are also objectionable. First, the acceptance of the supposition that the adsorbed quantities are proportional to the concentrations is quite untenable. Second, in calculating the surface tensions the possible influence of the angle of contact was completely disregarded, because it was tacitly taken for granted that perfect wetting always occurred.

This point, alone, seems to lead to a very plausible explanation of the experiments, if they are compared with the wonderful results of Miss Blodgett [THIS JOURNAL, **57**, 1007 (1935)], who proved the existence of polymolecular soap films of alternating orientation as adsorbed on glass and other solids, when in contact with the solutions. The same phenomenon, unfortunately, is to be expected at the platinum ring of Du Noüy as well as at the walls of the glass tubes.

As Miss Blodgett showed, the first layer of molecules is always fixed with the active groups toward the adsorbent, whereas the paraffin groups are directed toward the solution. Therefore, with increasing concentration the glass or platinum is covered at first with a film of paraffin character which, as is well known, repels water. But the second layer may be orientated in the opposite direction, causing a decrease of the angle of contact. Consequently the apparent surface tension rises, unless a new paraffin surface is deposited.

The author in collaboration with E. J. Better applied the bubble pressure method, as being independent of the angle of contact, for the measurement of oleate solutions. Only one minimum was found, and that at a higher concentration than any of the minima of Du Noüy.

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RECEIVED AUGUST 21, 1935

THE RELATIONSHIP OF ERGOTOCIN TO ERGOMETRINE

Sir:

Dudley and Moir [*Brit. Med. J.*, i, 520 (1935)] recently described the isolation from ergot of an alkaloid, chemically and pharmacologically different from any of the then known alkaloids of ergot, which they named ergometrine.

Although there were strong grounds for believing that ergotocin [Kharasch and Legault, THIS JOURNAL, **57**, 956 (1935)] was identical with ergometrine, Kharasch and Legault have not adopted this view, but have suggested that the two substances may be different [*e. g.*, *Lancet*, i, 1243 (1935)]. They have now published a formula, $C_{21}H_{27}O_3N_3$, for ergotocin [THIS JOURNAL, **57**, 1140 (1935)], while analyses of ergometrine and its salts now very accessible [Dudley, *Pharm. J.*, iv, **80**, 709 (1935)] indicate the formula $C_{19}H_{23}O_2N_3$, which is still being critically examined. [Further work on this substance since this "Communication" was dispatched (July 11, 1935) affords convincing evidence that this formula is correct.]

Ergometrine: *Anal.* Calcd. for $C_{19}H_{23}O_2N_3$: C, 70.15; H, 7.08; N, 12.92. Found: C, 70.0; H, 6.96; N, 12.91.

Ergometrine Hydrobromide. *Anal.* Calcd. for $C_{19}H_{23}O_2N_3 \cdot HBr$: C, 56.15; H, 5.91; N, 10.35; Br, 19.71. Found: C, 56.24; H, 6.19; N, 10.71; Br, 19.76.

Ergometrine Hydrochloride. *Anal.* Calcd. for $C_{19}H_{23}O_2N_3 \cdot HCl$: C, 63.08; H, 6.64; N, 11.62; Cl, 9.82. Found: C, 63.1; H, 6.81; N, 11.29; Cl, 9.54.

Ergometrine Oxalate: *Anal.* Calcd. for $C_{19}H_{23}O_2N_3 \cdot$

$H_2C_2O_4$: C, 60.73; H, 6.02; N, 10.12. Found: C, 60.58; H, 5.98; N, 10.18.

Taken by themselves these formulas would seem to support Kharasch and Legault's contention, but all other available evidence points to the identity of the substances. It is therefore probable that the apparent difference in elementary composition is not real, and that further analyses of ergotocin and its salts may yet lead to the establishment of its complete identity with ergometrine.

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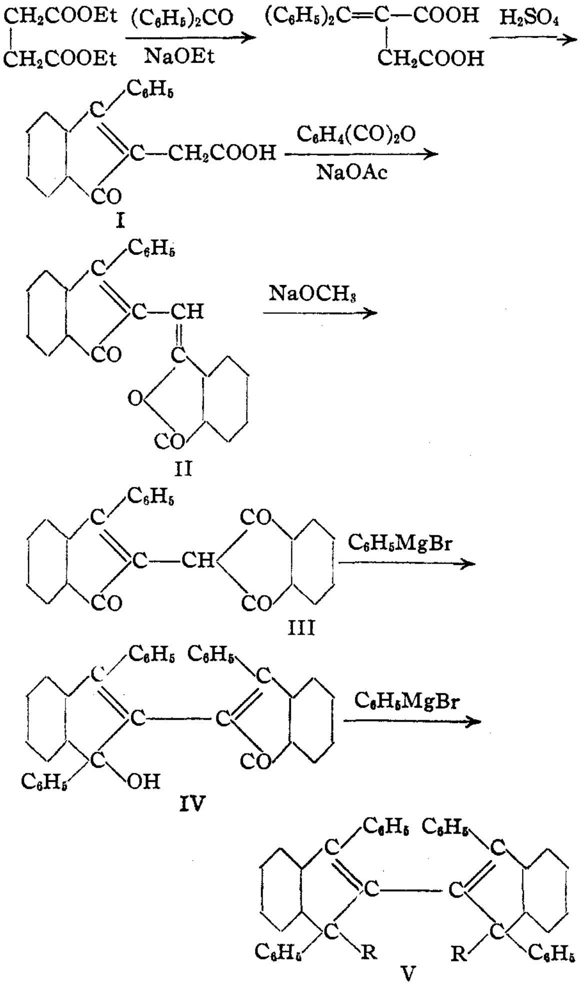
RECEIVED JULY 22, 1935

THE SYNTHESIS OF BIS-2,2′-(1,3-DIPHENYLINDENOL-3)

Sir:

In connection with attempts to synthesize rubrene we have prepared bis-2,2′-(1,3-diphenylindenol-3) by the following series of reactions



$$\begin{matrix}CH_2COOEt\\ |\\ CH_2COOEt\end{matrix} \xrightarrow[NaOEt]{(C_6H_5)_2CO} \begin{matrix}(C_6H_5)_2C{=}C{-}COOH\\ |\\ CH_2COOH\end{matrix} \xrightarrow{H_2SO_4}$$

The product is identical with the one obtained by a different method by Eck and Marvel [THIS JOURNAL **57**, 1898 (1935)].

TABLE I

PROPERTIES OF COMPOUNDS INVOLVED

Compound	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
I	166–167	$C_{17}H_{12}O_3$	[a]			
II	173.5–174	$C_{24}H_{14}O_3$	82.2	4.0	81.9	4.3
III	190.5–191.5	$C_{24}H_{14}O_3$	82.2	4.0	82.0	3.9
IV	244–245	$C_{38}H_{24}O_2$	88.5	4.9	88.0	4.8
V, R = OH	292	$C_{42}H_{30}O_2$	89.0	5.3	89.0	5.5
V, R = Cl	237–242	$C_{42}H_{28}Cl_2$	83.6	4.6	83.6	4.6

[a] Stobbe and Vieweg, *Ber.*, **35**, 1728 (1902).

TABLE II

PROPERTIES OF BIS-2,2′-(1,3-DIPHENYLINDENE) DERIVATIVES

Compound	Source	M. p., °C.[c]	Mixed m. p., °C.[d]
V, R = OH	[a]	293	
			291
	[b]	292	
V, R = Cl	[a]	240–245	
			237–242
	[b]	237–242	

[a] Eck and Marvel. [b] Koelsch and Richter. [c] Melting involves decomposition, and the temperature at which it occurs depends to some extent on the stage of subdivision of the compound and on the rate of heating. [d] We are indebted to Professor Marvel for the melting points reported here.

Like these authors we have found the derived dichloride to be unreactive toward metals (zinc or mercury). The dichloride, however, appears to give an alkali derivative with 40% sodium amalgam and we hope to make use of this reaction in converting it into the di-radical.

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RECEIVED SEPTEMBER 18, 1935

FORMATION OF PORPHYRINS FROM PYRROLE AND ALDEHYDES

Sir:

Porphyrin formation was observed under the following conditions: pyrrole, C. P., was dissolved in a solution of gaseous acetaldehyde (I) or formaldehyde (II) in methanol (saturated in the cold), and the reaction mixture was either (a) kept at room temperature for several weeks, or (b) heated under reflux for fifteen to twenty-five hours, or (c) heated in a sealed tube to 85–90° for ten to twenty hours in a water-bath.