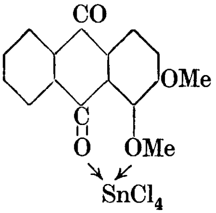
271. *The Basic Character of α-Methoxyanthraquinones.*

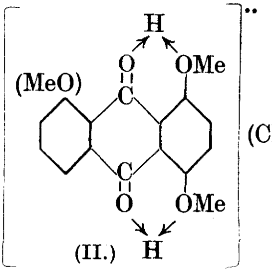
By K. C. ROBERTS.

THE formation of salts by methoxyanthraquinones observed by Fischer (*J. pr. Chem.*, 1911, **84**, 369; 1912, **86**, 297) is now shown to be peculiar to α-methoxyanthraquinones, and is explicable in terms of the views developed (J., 1929, 863, 1322; 1931, 520; this vol., p. 1792) to account for the similar characteristics of xanthones and thioxanthones containing methoxyl in the *o*-position to carbonyl.

The methods of examination are similar to those previously adopted. The mono-α-methoxyanthraquinones are not sufficiently basic to permit the isolation of salts by the methods successful with corresponding xanthone and thioxanthone derivatives. The mean alcohol-titration values (J., 1929, 869) are 19 c.c. for 1-methoxy-, 1 : 2-, and 1 : 3-dimethoxy-anthraquinones, 24 c.c. for 1-methoxyxanthones, and 30 c.c. for 1-methoxythioxanthones, 1 : 2-Dimethoxyanthraquinone forms a red *stannichloride* (I): a 1 : 2-dimethoxyanthraquinone stannichloride having the same composition is described by Pfeiffer (*Annalen*, 1913, **398**, 187) as being non-bathochromic.



(I.)



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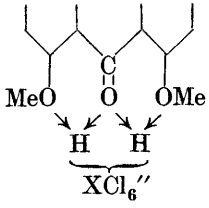

(III.)

The presence of two carbonyl-α-methoxy-groups in the 1 : 4- and 1 : 5-dimethoxy-derivatives enhances the stability of the salts (titration values, 35 c.c. and 32 c.c. respectively). Both substances form red *diperchlorates* (II) and corresponding *chlorostannates*, B,H_2SnCl_6, but the red *stannichlorides* have the same composition as that found for the 1 : 2-derivative.

1 : 8-Dimethoxyanthraquinone is soluble in concentrated hydrochloric acid and, having a titration value of 75 c.c., is the most strongly basic of the derivatives examined. It yields a *chlorostannate* and a *chloroplatinate* derived from a diacid type B,H_2XCl_6, to which is ascribed the dichelate structure (III) assigned (this vol., p. 1793) to the salts of a 1 : 8-dimethoxythioxanthone.

EXPERIMENTAL.

Derivatives of α-Methoxyanthraquinones.—1 : 2-Dimethoxyanthraquinone (from alizarin by the method of Baker and Robinson; J., 1928, 3116) formed with excess of $SnCl_4$ in C_6H_6 a deep red cryst. *stannichloride* (I), volatile at 150° in vac. (Found: Sn, 22·3. $C_{16}H_{12}O_4,SnCl_4$ requires Sn, 22·4%).

1 : 4-Dimethoxyanthraquinone, unlike the 1 : 2-derivative, yielded a red solution in HCl aq. and a red hydrochloride with dry HCl. The *stannichloride* was a brick-red solid, volatile at 150° in vac. (Found: Sn, 22·5%). The anthraquinone in C_6H_6 and 60% $HClO_4$ aq. gave an orange solid, which dried in vac. to a hygroscopic deep-magenta *diperchlorate* (II) (Found: $HClO_4$, 44·0. $C_{16}H_{12}O_4,2HClO_4$ requires $HClO_4$, 42·8%): this also separated in permanganate-coloured needles from the hot reagent. A *chlorostannate* was obtained from $SnCl_4$ and the anthraquinone in C_6H_6 saturated with HCl as a violet-black flocculent material which became orange-coloured on removal of C_6H_6 (Found: Sn, 19·7. $C_{16}H_{12}O_4,H_2SnCl_6$ requires Sn, 19·7%): an orange form was obtained with the aq. reagent. Orange hydrated chloroplatinates were similarly obtained with aq. H_2PtCl_6, the formulæ probably being $C_{16}H_{12}O_4,H_2PtCl_6,nH_2O$. Heated in vac. at 110°, they gave a deep purple material apparently retaining H_2O.

1 : 5-Dimethoxyanthraquinone yielded a red solution in HCl aq. and a

yellow hydrochloride with dry HCl. The *stannichloride* was a brick-red cryst. substance volatile at 150° in vac. (Found : Sn, 22·1. $C_{16}H_{12}O_4,SnCl_4$ requires Sn, 22·4%). The purple-black cubes, with a metallic lustre, of the *diperchlorate* (II) (Found: $HClO_4$, 40·6. $C_{16}H_{12}O_4,2HClO_4$ requires $HClO_4$, 42·8%) deposited from hot aq. 60% $HClO_4$ were extremely hygroscopic and rapidly became yellow in air. The *chlorostannate* was obtained in contact with C_6H_6 as a deep blue flocculent material which when purified for analysis in contact with C_6H_6 vapour became orange-brown (Found: Sn, 15·7. $C_{16}H_{12}O_4,H_2SnCl_6,2C_6H_6$ requires Sn, 15·7%) : the blue material, purified in vac. over paraffin, became red, but retained a small amount of C_6H_6 (Found : Sn, 18·2. $C_{16}H_{12}O_4,H_2SnCl_6$ requires Sn, 19·7%. $2C_{16}H_{12}O_4,H_2SnCl_6$ requires Sn, 13·6%). The hydrated yellow *chloroplatinate* dried at room temperature to a deep brown substance (Found: Pt, 23·6. $C_{16}H_{12}O_4,H_2PtCl_6,8H_2O$ requires Pt, 23·7%).

1 : 8-Dimethoxyanthraquinone yielded an orange solution in HCl aq. but did not absorb dry HCl. It did not form a stannichloride, but in presence of a very large excess of $SnCl_4$ a scarlet *chlorostannate* (as III) resulted (Found : Sn, 19·6. $C_{16}H_{12}O_4,H_2SnCl_6$ requires Sn, 19·7%), which was also obtained by usual methods (Found: Sn, 19·4%). The *chloroplatinate* (as III) was obtained as yellow needles, which yielded a stable reddish-brown form when dried over P_2O_5 in vac. at 110° (Found : Pt, 21·6; H_2O, 24·3.

$$C_{16}H_{12}O_4,H_2PtCl_6,12H_2O$$

requires Pt, 21·8; H_2O, 24·1%): intermediate scarlet and magenta stages were observed during dehydration. An orange *monoperchlorate* crystallised from the hot reagent in needles (Found: $HClO_4$, 27·6. $C_{16}H_{12}O_4,HClO_4$ requires $HClO_4$, 27·2%), which absorbed *ca.* 3 mols. H_2O from the air, giving a stable yellow hydrate.

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