

From the 1-, 2- and 3-aminophenanthrenes, we have synthesized 1-chlorophenanthrene (m. p. 120–120.5°), 2-chlorophenanthrene (m. p. 85.5–86°), 3-chlorophenanthrene (m. p. 80.5–81.5°), 1-bromophenanthrene (m. p. 109.5–110°), 2-bromophenanthrene (m. p. 95–96°), 3-bromophenanthrene (m. p. 83–84°), 1-iodophenanthrene (m. p. 112.5–113°), 2-iodophenanthrene (m. p. 116–116.5°) and 3-iodophenanthrene (m. p. 83.5–84°). All but one of these compounds have not been described previously. The bromo and iodophenanthrenes are being tested for their ability to form Grignard reagents, for the latter should prove useful in the synthesis of phenanthrene derivatives. The details of these experiments will be published later.

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CONCERNING SCHÖNBERG'S CLAIM TO PRIORITY FOR THE BIRADICAL FORMULA OF RUBENES

Sir:

When, indisputably the first to do so, I assigned the biradical formula to the rubenes. I wrote underneath it the two words, "état intermédiaire," in order that there should be no doubt about its role as intermediary in the closed cycle of reactions: rubene + oxygen \rightleftharpoons dissociable oxide [*Bull. soc. chim.*, **53**, 838 (1933)]. Moreover, I stated explicitly the structural reasons for the existence of this biradical structure, viz., the presence in the rubene molecule of carbons "du type des carbones aryl-méthaniques, réputés justement pour l'affaiblissement de leur quatrième valence et les phénomènes de dissociation qui en résultent, comme la scission en radicaux libres, $Ar_3 \equiv C -$, par exemple" (*ibid.*, p. 837).

Finally, I insisted strongly on the reversibility of the whole process: rubene \rightleftharpoons dissociable oxide (*ibid.*, p. 836), to the extent of including the word "reversible" in the title of several publications [for example see *Compt. Rend.*, **191**, 1321 (1930)].

I cannot, therefore, now understand Schönberg's insistence, against any evidence, on the priority as to the reversibility in the first period of the transformation, namely, rubene \rightleftharpoons biradical form; unless he believes that the process may be reversible in its entirety without being reversible in its parts?

It follows that Schönberg has made no original contribution of any kind to the problem of the rubenes, neither to the idea of reversibility nor to the several theories or constitutions which he has unjustly ascribed to himself [see my claim: *Ber.*, **67**, 1021 (1934)].

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THE SYNTHESIS OF THE ALDOBIONIC ACID OF GUM ACACIA

Sir:

In 1929 Heidelberger and Kendall [*J. Biol. Chem.*, **84**, 639 (1929)] described a crystalline aldobionic acid, a galactose-glucuronide, obtained from the hydrolysis of gum acacia. This substance was later shown by Challinor, Haworth and Hirst [*J. Chem. Soc.*, 258 (1931)] to be galactopyranose-6-glucuronopyranoside. The configuration of the biase linkage, however, was not at that time fully established. The chemical synthesis of the heptacetyl methyl ester of the aldobionic acid, glucose-6- β -glucuronide, has recently been described by the writers [*Science*, **83**, 353 (1936)]. The present communication deals with an account of the synthesis of the naturally occurring aldobionic acid derived from gum acacia.

When 1-2,3-4 diacetone galactose is condensed with acetobromo glucuronic acid methyl ester [Goebel and Babers, *J. Biol. Chem.*, **111**, 347 (1935)] in ether solution in the presence of silver oxide, the compound 1-2,3-4 diacetone galactose-6- β -triacetylglucuronide methyl ester is formed in yields of 35%. This substance crystallizes in fine needles, melting at 112.5–114°, and shows the rotation $[\alpha]^{25D} -68.0^\circ$ in chloroform ($C = 1.9\%$) (Found: C, 51.85; H, 6.45; OCH₃, 5.39; COCH₃, 21.5). Upon deacetylation with barium hydroxide and subsequent removal of the acetone groups by boiling with dilute sulfuric acid, the above compound is converted into the crystalline aldobionic acid. The synthetic acid is identical in properties with the naturally occurring aldobionic acid obtained from gum acacia. The melting point of a mixture of the two substances shows no depression.

For purposes of further identification, the heptacetyl methyl ester of the synthetic aldobionic acid was prepared. The latter substance is identical in crystalline structure, solubility and melt-