quantity of 2-acetylpyrrole as the reaction product; b. p. 107° (25 mm.)[8]; m. p. 87–89°[8]; mixed with an authentic sample, m. p. 88–89°.

(b) **From Pyrrole, Chloroacetonitrile and Hydrogen Chloride.**—A mixture of 13.6 g. of pyrrole, 20.8 g. of chloroacetonitrile and 100 cc. of ether was cooled with ice and saturated with hydrogen chloride in such a manner that moisture was excluded. The precipitated imine hydrochloride was filtered, dissolved in 100 cc. of water and heated for two hours on a steam-bath. The black, solid product was powdered and extracted with carbon tetrachloride in a Soxhlet apparatus; yield 5.7 g. (20%); m. p. 117–119°.

2-Iodoacetyl- and 2-Acetoxyacetylpyrrole.—Three and three-tenths grams of 2-chloroacetylpyrrole, dissolved in 30 cc. of acetone, was added to 10 g. of sodium iodide dissolved in 80 cc. of the same solvent. After eight hours the mixture was filtered from sodium chloride, the acetone removed from the filtrate and the residue washed with water. The crude iodo compound weighed 6.6 g. (95%) and melted at 130–131°[9] after recrystallization from benzene.

Anal. Calcd. for C_6H_6ONI: N, 5.98; I, 54.30. Found: N, 5.99; I, 54.00.

Seven grams of the iodo compound, 7 g. of silver acetate and 120 cc. of benzene were refluxed for ten hours, the mixture filtered and the solvent removed from the filtrate. The crude acetoxy compound weighed 4.5 g. (90%); m. p. 70–71° after recrystallization from petroleum ether (60–70°).

Anal. Calcd. for $C_8H_9O_3N$: N, 8.38. Found: N, 8.33.

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[8] Oddo (*Ber.*, **43**, 1012 (1911)) found the boiling point to be 208° and the melting point 90°.

[9] Oddo and Moschini (ref. 7, p. 266) stated that they obtained 2-iodoacetylpyrrole from pyrrylmagnesium bromide and iodoacetyl chloride; they found the melting point to be 81°.

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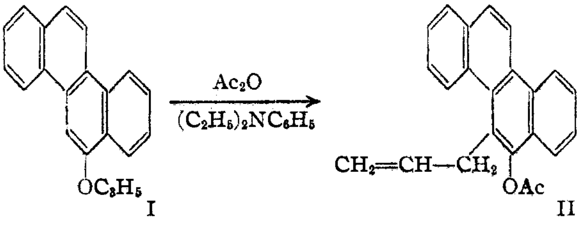
Rearrangement of 6-Allyloxychrysene

By Charles K. Bradsher[1] and S. Thomas Amore

In the course of a study of the preparation of olefins suitable for cyclization by the olefin oxide method,[2] we investigated the rearrangement of 6-allyloxychrysene (I). While the ultimate goal was not attained, we feel that our observations are worthy of record as being the first example of such a rearrangement in the chrysene series.



The ether (I) was prepared from chrysenol[3] in essentially the usual manner and rearrangement was carried out by heating it in a mixture of diethylaniline and acetic anhydride.[4] Under these conditions an 87% yield of a product having the composition of 5-allyl-6-acetoxychrysene (II) was obtained. This compound proved too sensitive to alkali to permit hydrolysis of the ester linkage and rearrangement of the allyl to the propenyl group.

Experimental

6-Chrysenol.—A slight improvement was made in the directions of Newman and Cathcart[3] by using a smaller volume of a more concentrated solution of sulfuric acid. Thus 10 g. of 6-aminochrysene when heated at 225° for six hours with 30 cc. of 20% sulfuric acid gave an 86% yield of chrysenol, m. p. 248–249° (N. and C. 76%; 248–250°).

6-Allyloxychrysene.—Chrysenol (4.5 g.), acetone (90 cc.), allyl bromide (15 cc.) and anhydrous potassium carbonate (7 g.) were refluxed together for six hours and the mixture worked up in the usual manner. The allyloxychrysene was crystallized from ether–petroleum ether and recrystallized from alcohol, m. p. 110–111°; yield 3.2 g. (63%).

Anal.[5] Calcd. for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 89.07; H, 6.02.

5-Allyl-6-acetoxychrysene (II).—The allyl ether (0.5 g.) was heated at 160–180° for two hours with a mixture of acetic anhydride (2 cc.) and diethylaniline (2 cc.). After cooling, the mixture was poured on ice, collected, and recrystallized from methyl alcohol. In this way it was obtained as small light tan needles, m. p. 101–103°; yield 0.5 g. (87%). Recrystallized, it was colorless, melted at 103° alone, and at 80–97° when mixed with allyloxychrysene.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.69; H, 5.62.

No crystalline product could be isolated when the compound was heated with aqueous or alcoholic alkali.

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[1] National Research Fellow (participating basis) 1941–1942.

[2] *E. g.*, Bradsher, This Journal, **61**, 3131 (1939); Bradsher and Amore, *ibid.*, **63**, 493 (1941); **65**, 2016 (1943).

[3] Newman and Cathcart, *J. Org. Chem.*, **5**, 618 (1940).

[4] The technique of acetylative rearrangement was first used by Fieser and Lathrop, This Journal, **58**, 749 (1936). Attempts at rearrangement in the absence of the anhydride were unsuccessful.

[5] Analyses by T. S. Ma.

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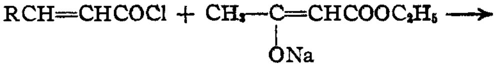
β-Substituted Acryloylacetic Esters

By James English, Jr., and Leon J. Lapides[1,2]

The syntheses reported below were carried out in connection with an investigation having as its objective the preparation of acids containing five carbon atom chains of a structure similar to that proposed by Kögl[3] for the naturally occurring auxins. Such compounds would be expected to be active phytohormones and should be of value in studies of the relationship of structure to physiological activity in the auxin field.

In an approach to compounds of this type, it was found necessary to investigate the condensation of some acid chlorides of substituted acrylic acids with sodium ethylacetoacetate and the hydrolysis of the resulting acetoacetic esters to the corresponding acryloylacetic esters according to the equation



$$RCH{=}CHCOCl + CH_3{-}\underset{\displaystyle ONa}{\underset{|}{C}}{=}CHCOOC_2H_5 \longrightarrow$$

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[1] Abstracted from a thesis presented to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1943.

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[3] Kögl, *Z. physiol. Chem.*, **227**, 51 (1934).