Pyridine-4,β-acrylic Acid.—A mixture of 13.5 g. of ethyl pyridine-4,β-hydracrylate with 26 ml. of water and 26 ml. of concd. sulfuric acid was boiled (130°) for forty-five minutes and then diluted with 50 ml. of water. The resulting pyridine-4,β-acrylic acid precipitated (yield, 4 g.) when the strongly acid solution was treated with sodium acetate. The pure substance was easily soluble in warm glacial acetic acid, but it precipitated when such a solution was diluted with water. It became brown at 190° and melted with decomposition at 280–285° (reported[17] 296°, (cor.)).

The **copper salt** was a deep green crystalline powder, insoluble in water; it became brown at 235° and melted with effervescence at 255°.

Anal. Calcd. for $C_{16}H_{12}N_2O_4Cu$: Cu, 17.6. Found: Cu, 17.4.

Four grams of pyridine-4,β-acrylic acid in 100 ml. of *n*-butyl alcohol was reduced with 10 g. of sodium[17]; the product was isolated as the crystalline hydrochloride[18] (0.9 g.) Benzoylation of the reduction product (200 mg.) in excess 10% sodium hydroxide gave 250 mg. of an oil which crystallized completely when it was seeded with 1-benzoylpiperidine-4,β-propionic acid (Part I). The m. p. of the benzoylation product could not be raised above 135–140°, and it was found that traces of unsaturated substances were present. When these were removed (potassium permanganate in cold sodium carbonate solution), the product melted at 145–147° alone or mixed with the acid obtained in Part I.

Analyses for carbon and hydrogen reported in the present paper were performed by Mr. Stanley T. Rolfson, those for hetero elements by the author.

Summary

A series of reactions leading from epichlorohydrin to 1-benzoyl-4-bromomethylpiperidine in an over-all yield of >12% is described. This halide could not be coupled successfully with ethyl quinoline-4,β-ketopropionate, but it was converted into 1-benzoylpiperidine-4,β-propionic acid, an intermediate in Rabe's synthesis of "vinyl-free quinine." The reactions are of importance in that they point a way to the synthesis of certain analogs of quinine.

MINNEAPOLIS, MINNESOTA RECEIVED SEPTEMBER 7, 1943

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[17] Rabe and Kindler, *Ber.*, **52**, 1848 (1919).

[18] *Cf.* Prelog and Cerkovnikov, *Ann.*, **532**, 83 (3197).

NOTES

2-Chloroacetylpyrrole[1]

BY F. F. BLICKE, J. A. FAUST, J. E. GEARIEN AND R. J. WARZYNSKI

The interaction of phenylmagnesium bromide with aceto-, propio-, butyro- or valeronitrile was shown by Shriner and Turner[2] to yield an acyl benzene in 70–90% yield.

When Majima and Hoshino[3] allowed indolylmagnesium bromide to react with chloroacetonitrile, they did not obtain the ketone, 3-chloroacetylindole, but isolated 3-indolylacetonitrile in 50% yield[4]; similarly, β-(3-indolyl)-propionitrile was obtained from β-chloropropionitrile.

In order to determine whether or not pyrrylmagnesium bromide would react in a manner analogous to that of indolylmagnesium bromide, we treated pyrrylmagnesium bromide with chloroacetonitrile. The only product which could be isolated was 2-chloroacetylpyrrole. The latter compound was obtained also from pyrrole, chloroacetonitrile and hydrogen chloride in 20% yield. 2-Chloroacetylpyrrole was converted into 2-iodoacetylpyrrole, and the latter into 2-acetoxyacetylpyrrole.

From pyrrylmagnesium iodide and chloroacetonitrile, we obtained 2-acetylpyrrole in very small amount.[5]

Experimental Part

2-Chloroacetylpyrrole. (a) From Pyrrylmagnesium Bromide and Chloroacetonitrile.—A solution of ethylmagnesium bromide, prepared from 15.3 g. of magnesium, 69.0 g. of ethyl bromide and 125 cc. of ether, was cooled in an ice-bath and 40.2 g. of pyrrole, dissolved in 35 cc. of ether, added. Then 45.0 g. of chloroacetonitrile,[6] dissolved in 30 cc. of ether, was dropped slowly into the mixture. The latter was refluxed for one-half hour, cooled to 0° and kept at this temperature while 46 g. of acetic acid, which had been diluted with 200 cc. of water, was added. The ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were shaken with sodium bicarbonate solution and then submitted to steam distillation in order to remove unchanged pyrrole and acetonitrile. When the solution in the steam distillation flask was cooled, long colorless needles formed. In order to dissolve the latter, benzene was added and the mixture heated on a steam-bath. The hot benzene layer was separated, the solvent removed and the residue distilled under 2 mm. pressure; 20 g. (23%) of crystalline material was obtained. After recrystallization from carbon tetrachloride, the 2-chloroacetylpyrrole (14 g. or 16%) melted at 118–119°.[7]

Anal. Calcd. for C_6H_6ONCl: N, 9.76. Found: N, 9.54.

When this experiment was repeated with the substitution of ethyl iodide for ethyl bromide, we obtained only a small

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[1] This compound was prepared incidentally during an extensive study of pyrrole derivatives which was supported by grants from Parke, Davis and Company, Eli Lilly and Company and the Board of Governors of the Horace H. Rackham School of Graduate Studies.

[2] Shriner and Turner, THIS JOURNAL, **52**, 1267 (1930).

[3] Majima and Hoshino, *Ber.*, **58**, 2042 (1925). See also Hoshino and Kobayashi, *Ann.*, **520**, 20 (1935).

[4] This experiment was confirmed by Jackson (*J. Biol. Chem.*, **88**, 659 (1930)).

[5] In this connection it is of interest to mention that Salway (*J. Chem. Soc.*, **103**, 354 (1913)) found that 2-methylindolylmagnesium bromide reacted with chloroacetyl chloride to yield 2-methyl-3-chloroacetylindole. However, when 2-methylindolylmagnesium iodide was employed, he obtained a mixture of 2-methyl-3-chloroacetyl- and 2-methyl-3-acetylindole.

[6] Steinkopf, *Ber.*, **41**, 2541 (1908).

[7] Prepared by a different procedure, Oddo and Moschini (*Gazz. chim. ital.*, **42**, II, 257 (1912)) found 115°.

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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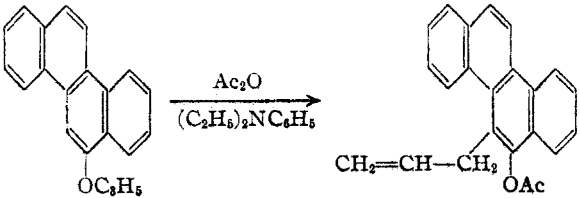
Rearrangement of 6-Allyloxychrysene

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.



I II

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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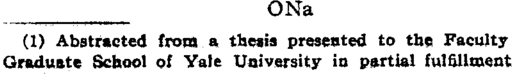
β-Substituted Acryloylacetic Esters

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).