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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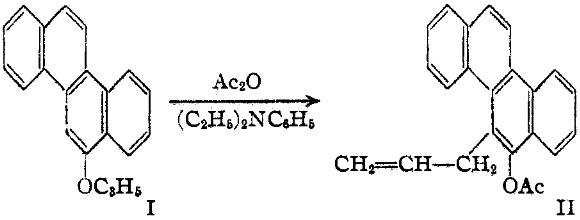
Rearrangement of 6-Allyloxychrysene

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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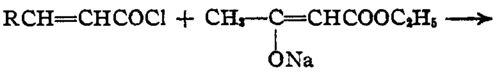
RECEIVED SEPTEMBER 10, 1943

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



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

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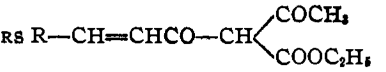
(1) Abstracted from a thesis presented to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1943.

(2) Present address: Ansbacher Siegle Corp., Brooklyn, N. Y.

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

TABLE I

β-SUBSTITUTED ACRYLOYLACETOACETIC ESTERS R—CH=CHCO—CH



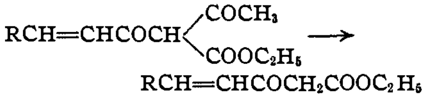
$$R\text{—}CH\text{=}CHCO\text{—}CH\left\langle\begin{matrix}COCH_3\\COOC_2H_5\end{matrix}\right.$$

R	Formula	M. p., °C.	Yield, %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl[5]	.....	46	75	...	...	..	..
α-Furyl[6]	$C_{13}H_{14}O_5$	48	45	62.40	62.31	5.60	5.50
1-Naphthyl	$C_{19}H_{18}O_4$	80	42	73.55	73.56	5.81	6.26
p-Methoxyphenyl	$C_{16}H_{18}O_5$	65	80	66.20	66.10	6.21	6.14
Cyclohexyl	$C_{15}H_{22}O_4$		45	67.67	67.62	8.27	8.25
3,4-Methylenedioxyphenyl[4]	.....	104	55	...	...	..	..

TABLE II

β-SUBSTITUTED ACRYLOYLACETIC ESTERS, R—CH=CHCOCH$_2$COOC$_2$H$_5$

R	Formula	M. p., °C.	Yield, %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl[4]	.....	45–46	82	...	...	..	..
α-Furyl	$C_{11}H_{12}O_4$	60	64	63.46	63.70	5.77	6.05
p-Methoxyphenyl	$C_{14}H_{16}O_4$	44–45	70	67.75	67.55	6.45	6.57
3,4-Methylenedioxyphenyl[4]	$C_{14}H_{14}O_5$	60	64	...	...	..	..



$$RCH\text{=}CHCOCH\left\langle\begin{matrix}COCH_3\\COOC_2H_5\end{matrix}\right. \longrightarrow RCH\text{=}CHCOCH_2COOC_2H_5$$

Although reactions of this type have been carried out by Borsche,[4] repetition of this work revealed a need for further study of the process with a view to developing a practical synthesis.

The procedure as finally adopted was as follows. The appropriate substituted acrylic acid was refluxed with 2-3 moles of thionyl chloride and the acid chloride fractionally distilled under reduced pressure, except in the case of the naphthyl derivative, where phosphorus pentachloride in dry benzene was found more advantageous. Yields of from 82-97% of the β-substituted acryloyl chlorides were obtained with melting points or boiling points in good agreement with the values given in the literature.

The conversion of these chlorides to the corresponding acylated acetoacetic esters was accomplished by adding them in dry xylene solution to a freshly prepared suspension of the theoretical quantity of sodium ethylacetoacetate, also in dry xylene. After stirring at room temperature for twenty-four hours, the solution was centrifuged and the xylene removed in vacuum. The phenyl- and naphthylacryloylacetoacetates were thus obtained as dark oils which crystallized on standing and were purified by recrystallization from petroleum ether and alcohol, respectively. In the remaining cases the crude products were converted, by shaking with saturated aqueous copper acetate, into their crystalline copper salts. These in turn were readily converted, by treatment with cold dilute acids, into the pure β-substituted acryloylacetoacetic esters, which could be distilled at low pressures (below 1 mm.) without noticeable decomposition.

β-Substituted acryloylacetic esters were prepared from the above acetoacetic esters by saturating solution of 0.01 mole of the latter in 10 cc. of 1 normal sodium hydroxide with ammonia at 0°. After standing at room temperature for one hour, the solution was filtered and the filtrate acidified with 3 normal sulfuric acid. An oily precipitate resulted which in the case of the phenylacryloyl ester solidified and was recrystallized from petroleum ether. The others were purified by means of their copper salts. This method failed with the naphthyl and cyclohexyl analogs.

Tests for physiological activity were carried out by the pea test[7] method on all the products prepared. All were found to be either inactive or only very slightly active by this assay.[8]

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(4) Borsche, *Ber.*, **66**, 1792 (1933).

(5) Fischer and Kuzel, *ibid.*, **16**, 167 (1883).

(6) Lampe, *Chem. Listy.*, **26**, 454 (1932); *Chem. Abs.*, **27**, 721 (1932).

(7) Thimann and Went, "Phytohormones," The Macmillan Co., New York, N. Y., 1937.

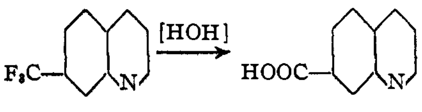
(8) We are indebted to Dr. Paul Burkholder for his helpful cooperation in carrying out the physiological tests.

5- and 7-Trifluoromethylquinolines

BY HENRY GILMAN AND DENNIS BLUME

In connection with a study of fluorine derivatives of polynuclear heterocycles, 5- and 7-trifluoromethylquinolines have been prepared. The Skraup synthesis was used, starting with *m*-trifluoromethylaniline, and the 7-isomer was formed predominantly.

The structures of the two compounds were established by acid hydrolysis to the known quinolinecarboxylic acids



Addition of organolithium compounds occurs normally. For example, *p*-tolyllithium gives a dihydro derivative which on oxidation by nitrobenzene yields 2-*p*-tolyl-7-trifluoromethylquinoline.