[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Condensations of Ketene

BY JOHN A. SPENCE[1] WITH ED. F. DEGERING

Recent work[2] has shown that ketene can be condensed with certain simple or mixed ketones, in the presence of a trace of an acid catalyst.

The present investigation has shown that ketene can be condensed, in a similar manner, with certain keto esters and diketones. The compounds used were ethyl acetoacetate, ethyl levulinate, biacetyl and acetylacetone. The corresponding acetates of the enolic tautomers were prepared and some of their physical properties established.

Experimental Part

Apparatus.—The ketene was prepared by the pyrolysis of acetone. The apparatus was the one originally used by Gwynn and Degering,[2] with some modifications. The ketene generator is fundamentally the same as proposed by Hurd.[3] The operation of the apparatus was carried out in a manner prescribed by Gwynn and Degering.[2]

Materials Used.—The reagents were freshly distilled before use except for the acetone, from Carbide and Carbon Chemicals Corporation, which was used for the preparation of the ketene. The sulfuric acid was of commercial grade.

Reaction of Ketene with Ethyl Acetoacetate.—The ester was dried for twenty-four hours by means of calcium chloride. The dried ester was decanted into a Claisen flask from which it was distilled (b. p. 79–80° (20 mm.)). The distilled ester (0.5 mole) was added immediately with twelve drops (0.003 mole) of concentrated sulfuric acid, to the reaction flask. A reaction temperature of 70 ± 5° was maintained. While under continual agitation, ketene was added for four hours. The ketene flow was between 0.15 and 0.2 mole per hour.

The dark reaction mixture was rectified by a Podbielniak column. Forty-two ml. of a colorless fraction (b. p. 89° (10 mm.)) was obtained. The other compounds, tabulated in the table, were prepared similarly.

TABLE I

PREPARATION AND PROPERTIES OF SOME ENOL-ACETATES

Original compound	Moles of ketone	Hours of ketene[a]	B. p. of the enol acetate °C.	Mm.	% Conversion	M. p. of deriv.,[b] °C.	Analyses, % Calcd. C	H	Found C	H
Acetylacetone	0.50	4	79	11	35.7	122	59.10	7.07	59.20	7.00
Ethyl levulinate	0.42	4	89–90	5	21.5	101	58.05	7.57	57.10	7.66
Biacetyl	1.00	5	34–45	5	2.7	230	56.25	6.25	56.37	6.06
Ethyl acetoacetate	0.50	4	89	10	52.5	93	55.80	6.98	55.90	7.02

[a] The generator produced 0.15 to 0.23 mole of ketene/hr. [b] The derivatives were the 2,4-dinitrophenylhydrazones. The reaction temperatures were maintained between 70 and 90°. For every mole of ketone used, 0.006 mole of concd. sulfuric acid was used as a catalyst.

The equation for the reaction may be written as: $CH_3COCH_2CO_2Et + CH_2{=}C{=}O \text{ (concd. } H_2SO_4) \longrightarrow CH_3C(OCOCH_3){=}CHCO_2Et$.

The isomeric forms have not been isolated and characterized, but work along this line is in progress.

Summary

Ketene, in the presence of a small amount of concentrated sulfuric acid, had been found to condense with certain keto-esters and diketones. The products are the corresponding acetates of the enolic tautomer. The enol acetates of ethyl acetoacetate, ethyl levulinate, biacetyl and acetylacetone were prepared and some of their physical properties were characterized.

LAFAYETTE, INDIANA

RECEIVED JUNE 12, 1944

---

[1] Abstract of the thesis by J. A. Spence, submitted to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in February, 1944.

[2] B. H. Gwynn and Ed. F. Degering, THIS JOURNAL, **64**, 2216 (1942).

[3] Hurd, *J. Org. Chem.*, **5**, 122 (1940).