resulted unexpectedly in one case when the acid IV was treated with phosphorus pentachloride. It resulted in small yields when any of the acids (IIIa, IIIb or IV) was heated with concentrated sulfuric acid and glacial acetic acid, and in better yields when any of the acids was treated with thionyl chloride followed by anhydrous aluminum chloride.

Summary

1. Relationships are established between the stereoisomeric α,β-diphenyl-β-benzoylpropionic acids and their saturated reduction products.

2. Relationships are established between the three stereoisomeric α,β,γ-triphenylbutyric acids and the corresponding two methyl esters, one ethyl ester, three amides and two nitriles.

3. Five new compounds are reported.

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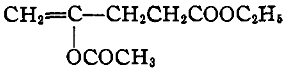
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

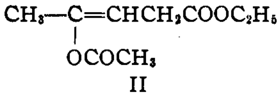
Reaction of Ketene with Keto Esters and Diketones

BY CHARLES D. HURD, OLIVER E. EDWARDS[1] AND J. R. ROACH[2]

Gwynn and Degering[3] have shown that methylvinyl acetate, $\underset{OCOCH_3}{CH_3C{=}CH_2}$ may be prepared from acetone by interaction with ketene in the presence of sulfuric acid. If ethyl levulinate and ketene reacted comparably two possible compounds (I, II) might be formed.


$CH_2{=}\underset{OCOCH_3}{C}{-}CH_2CH_2COOC_2H_5$

I


$CH_3{-}\underset{OCOCH_3}{C}{=}CHCH_2COOC_2H_5$

II

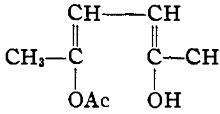
In studying this reaction we found that a 50% yield of product was obtained by maintaining a reaction temperature of 115°. It readily absorbed one mole of bromine. Ozonolysis gave evidence for both I and II in about equal amounts because one mole of the enol acetate yielded 0.42 mole of succinic acid and 1.16 moles of acetic acid. The succinic acid obviously came from 0.42 mole of I, whereas the acetic acid points to 0.37 mole of II (*i. e.*, one-half of 1.16–0.42).

The terminal double bond of ethyl 4-acetoxy-4-pentenoate (I) suggests a polymerizable structure but the substance did not polymerize in four days at 90° in the presence of benzoyl peroxide.

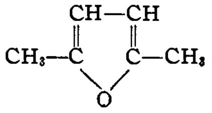
Ethyl acetoacetate, when treated similarly with ketene, yielded the enol acetate, presumably ethyl 3-acetoxycrotonate.

Acetylacetone reacted exothermically with ketene and sulfuric acid catalyst. 1-Methyl-2-acetylvinyl acetate, $CH_3COOC(CH_3){=}CHCOCH_3$, was formed in good yields. That the product was not triacetylmethane seems certain because of its boiling point (92° at 18 mm.) which is twelve degrees lower than that recorded[4] for triacetylmethane (104° at 19 mm.) and because it resisted extraction from ether solution by aqueous sodium carbonate. The 1-methyl-2-acetylvinyl acetate displayed no tendency to polymerize during forty-eight hours at 70° in the presence of 2% of benzoyl peroxide, nor in another forty-eight-hour period with an additional 2% of benzoyl peroxide.

Acetonylacetone, $CH_3COCH_2CH_2COCH_3$, also reacted vigorously with ketene and sulfuric acid but the product isolated in 65% yield was not an enol acetate (III) but was 2,5-dimethylfuran (IV). It is reasonable, however, to believe that the enol acetate was present in an intermediate step. Acetic anhydride was the other product of this reaction.



III



IV

This reactivity of ketene toward the carbonyl group in β- and γ-keto esters and in β- and γ-diketones was not found in ketones which possessed an oxygen or nitrogen atom alpha to the carbonyl group. Thus, when acetonyl acetate, $CH_3COOCH_2COCH_3$, was treated with ketene in the presence of a little sulfuric acid, there was no reaction either at 20° or 75°. (This experiment was performed by Arthur Berger.) Recovery of the acetonyl acetate was practically quantitative. Much the same was true for biacetyl and pyruvonitrile, CH_3COCN, but a slight amount of higher boiling reaction products were observed in these trials.

Recently the claim has been made[5] for preparation of the enol acetate of pyruvonitrile by reaction of ketene with hydrogen cyanide at 35°. In the present work we tried unsuccessfully to prepare pyruvonitrile by addition of hydrogen cyanide to ketene but the only product which was definitely established was diketene. In one of the several experiments undertaken, one mole of ketene (42 g.) was dissolved in one mole of hydrogen cyanide at −78°. This was brought to room temperature during a period of forty hours. Distillation of the products under diminished pres-

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[1] Holder of Weyerhaeuser Timber Company Fellowship, 1941–1943.

[2] Holder of Pittsburgh Plate Glass Company Fellowship, 1941–1943.

[3] Gwynn and Degering, THIS JOURNAL, **64**, 2216 (1942).

[4] Birckenbach, *Ber.*, **65**, 1071 (1932).

[5] Vollmann, Schloffer and Ostrowski, German Patent 736,504, May 13, 1943; *C. A.*, **38**, 2970 (1944).

TABLE I

KETENE AND COMPOUNDS CONTAINING CARBONYL GROUPS

Substance	G.	Mole	H_2SO_4, g.	Ketene, mole	Hours	Temp., °C.	B. p. of product, °C. (mm.)	Yield, %
Ethyl levulinate	50	0.35	0.24	0.53	1.5	60–70	100–102 (12)	8
	50	.35	.24	.53	1.5	110–120	100–102 (12)	20
	50	.35	.24	.70	2.0	97	100–102 (12)	27
	50	.35	.24	1.23	3.5	100	100–102 (12)	40
	50	.35	.24	0.88	2.5	110–115	100–102 (12)	50
Ethyl acetoacetate	50	.38	.26	0.5	1.5	60–65	83–87 (11)	13
Acetylacetone	25	.25	.20	1.0	3	50–96	95–96 (20)	59
Acetonylacetone	57	.5	.34	1–1.2	4	50–75	92–94 (750)	65
Pyruvonitrile	34.5	.5	.34	0.9	3	70	....	..

sure yielded 15.3 g. of diketene which, with aniline, produced acetoacetanilide. In the presence of a trace of sulfuric acid similar results were obtained except that less diketene and more of a tacky residue was formed.

Experimental Part

Ethyl Levulinate.[1]—Ketene was passed into ethyl levulinate under conditions listed in Table I. The mixture soon became dark red in color. At the end of the reaction the liquid was shaken with sodium carbonate, filtered, and distilled *in vacuo*. Benzene as diluent lowered the yield markedly. Properties of the enol acetate: b. p. 102° (12 mm.); $n^{20}D$ 1.436; pleasant odor, insoluble in water. It gave acetic acid readily on acid hydrolysis. In alcohol-water solution it absorbed only one equivalent of bromine to yield ethyl acetate and a lachrymatory liquid which was reactive toward dinitrophenylhydrazine (keto group).

Anal. Calcd. for $C_9H_{14}O_4$: mol. wt., 186; sapon. equiv., 93. Found: mol. wt. (cryoscopic in benzene), 181; sapon. equiv., 92.

Ozonolysis.—A 3-g. sample of the enol acetate was ozonized following the usual procedure.[6] A 42% yield (0.8 g.) of succinic acid was obtained: m. p. 183–185°, neut. equiv., 59.5 (calcd. 59.0). The last crop of crystals pointed to some malonic acid (m. p. 110–115° with gas evolution) but the neutral equivalent of 58 was still close to succinic acid.

In another ozonolysis (2.77 g., 0.0149 mole), there was produced 0.0172 mole of acetic acid. Formic acid seemed absent since it was unaffected by alkaline permanganate.

Ethyl Acetoacetate.[1]—The product reported in Table I possessed a refractive index ($n^{20}D$) of 1.448. Determination of its molecular weight gave a value of 167 (calcd., 172).

Acetonylacetone.[2]—For this experiment ketene was collected in ether at −78°, the advantage being to do away with the flow of gases (CH_4, CO, etc.) which would tend to sweep away the acetonylacetone if the ketene was introduced without previous condensation. It was then distilled into the mixture of pure acetonylacetone and sulfuric acid. The color turned brownish-black and the temperature rose to 70–75° within fifteen minutes. On working up the products, fractions were taken at 60–91, 91–97, 97–110 and 110–140°. The last represented acetic anhydride and most of it was collected at 135–139°. The first and third fractions were dissolved in ether, washed with sodium bicarbonate solution, dried and distilled. That portion of the distillate which was collected at 91–97° was put with fraction 2 which was then redistilled with these results (°C., g.): 85–91°, 1.4; 91–92°, 0.9; 92–94°, 27.2, $n^{20}D$ 1.4390; 94–97°, 3. The 31.1 g. in the last three fractions represents a 64.6% yield of 2,5-dimethylfuran.

Acetylacetone.[2]—Ketene was distilled from an ether solution into 25 cc. of acetylacetone, 5 cc. of absolute ether, and the sulfuric acid. Color darkening and temperature rise to 96° were noted. (In a 10-g. run, the temperature reached 75°.) After purification the **1-methyl-2-acetylvinyl acetate** had these constants: b. p. 92° (18 mm.), 95–96° (20 mm.), 100.5° (25 mm.); $n^{25}D$ 1.4507; d^{25}_4 1.0483.

Pyruvonitrile.[2]—This compound was prepared in 77% yield by heating three moles each of acetyl bromide and cuprous cyanide[7] on the steam-bath for two hours. The nitrile boiled at 92–93°. In contrast, no pyruvonitrile was obtainable with these methods: (1) acetyl chloride and cuprous cyanide, refluxed for eight hours; (2) acetyl chloride and potassium cyanide,[8] refluxed for twenty-four hours; (3) acetyl chloride and potassium cyanide heated for twenty-four hours in a sealed tube at 65–130°.

Six runs with pyruvonitrile and ketene were performed. In the run cited in Table I, 3 cc. of absolute ether was used as solvent for the sulfuric acid. Of the 34.5 g. of nitrile taken, 30.2 g. was recovered (b. p. 85–105°). Then there was a 1.7-g. fraction at 105–130°, and a 4.3-g. cut at 130–140°. The last cut was dissolved in ether and was washed with sodium bicarbonate solution until carbon dioxide was no longer evolved. Both diketene and acetic anhydride were tested for solubility in this reagent and although diketene dissolved slowly it did dissolve. After this extraction nothing was left in the ether boiling above 100°, hence no enol acetate was present.

Summary

In the presence of a trace of sulfuric acid ketene reacts readily with β- and γ-keto esters and with β-diketones to form enol acetates. The γ-diketone acetonylacetone also reacts smoothly but the reaction product is 2,5-dimethylfuran. Ketones which possess an oxygen or nitrogen atom alpha to the carbonyl group, as in acetonyl acetate, biacetyl, or pyruvonitrile, do not react smoothly with ketene.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 5, 1944

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[6] Hurd and Pollack, THIS JOURNAL, **60**, 1911 (1938).

[7] Tschelinzeff and Schmidt, *Ber.*, **62**, 2210 (1929).

[8] Karrer (translated by Mee), "Organic Chemistry," Nordeman Publishing Co., New York, N. Y., 1938, p. 240.