

pure products could be separated by fractional crystallization with difficulty. This points to isomeric compounds. From analogy with other δ -ketonic nitriles studied it was anticipated that the nitrile just described would lead to the higher rather than the lower acid. The work on its synthesis and hydrolysis, as reported, was confirmed by both authors working independently.

The yields of the pure isomeric α -phenyl- β -*p*-tolyl- γ -trimethylacetylbutyric acids were too small to permit of attempting optical resolution, and from analogy with other δ -ketonic acids the prospects of accomplishment too remote to make worth while the preparation of the isomers in quantities required for such resolution.

Summary

The lower melting α , β -diphenyl- γ -trimethylacetylbutyric acid has been obtained in pure condition; the inactive isomeric δ -ketonic acids, previously reported, cannot be resolved into optical isomers by the methods used in resolving the corresponding acids in the glutaric series.

α -Phenyl- β -*p*-tolyl- γ -benzoylbutyric acid and its derivatives have been synthesized. No isomeric forms could be detected.

Isomeric α -phenyl- β -*p*-tolyl- γ -trimethylacetylbutyric acids have been synthesized. The small yields of the pure acids have precluded efforts to effect optical resolution.

Benzal ketones condense in the reaction reported, more readily than the corresponding *p*-tolual ketones, forming δ -ketonic derivatives having higher melting points in the higher series and lower melting points in the lower melting series.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

VAPOR PHASE ESTERIFICATION IN PRESENCE OF SILICA GEL

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Some years ago vapor phase esterification in the presence of silica gel was studied by Milligan, Chappell and Reid,¹ who obtained as high as 89.6% of ester at 150° in a mixture of equivalent amounts of acetic acid and alcohol but stated that they had no reason to believe that an equilibrium had been reached.

Later Edgar and Schuyler² measured the equilibrium for this same reaction by a distillation method and obtained 79–84% of the ester at 72–77°. Similar results were obtained at a lower pressure and temperature with varying mixtures, but they calculated that, under the conditions employed by Milligan, Chappell and Reid, the equilibrium should correspond to about 95% esterification.

¹ Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

² Edgar and Schuyler, *THIS JOURNAL*, **46**, 64 (1924).

Recently W. Swietoslowski and S. Poznanski,³ whose work we have seen only in abstract, using a similar method, reported a " K_g " of 59 which corresponds to an esterification of 88.5%, with a possible experimental error of $\pm 10\%$, which they considered to be only two-fifths the experimental error of Edgar and Schuyler. They reported the equilibrium to be independent of temperature. Still later they reported⁴ that unlike the equilibrium constant in the liquid phase, that in the gas phase does not vary with different mixtures.

Since the catalyst adsorbs appreciable amounts of the reactants and products in unknown proportions, the composition of the first portion to go through may not represent the true equilibrium. This difficulty was avoided as far as possible by passing the mixture for a long time at a steady rate until the composition of the product became constant. It is realized that the values so obtained are only approximations but it is believed that they are close to the true equilibrium values. Thus in one run the percentage of esterification was 90.6 at the end of the first day and gradually fell off for six days until it became constant at about 83.5%, where it remained for five days of continuous running as is seen in Table II. At any temperature the rapid passage of the mixture gives relatively low esterification; as the rate is lowered the percentage of ester goes up. It was assumed that the rate was sufficiently slow when doubling the time in the catalyst tube did not increase the esterification. The equilibrium was approached from the other side by the use of a mixture of ethyl acetate and water. The samples for analysis were collected in a flask surrounded by "Dry-Ice" to prevent loss by volatilization and many of the titrations of free acid were checked by saponification of the ester. The averages of the figures obtained are given in Table I and the percentage of esterification is plotted against time in furnace in Fig. 1.

TABLE I
THE ESTERIFICATION EQUILIBRIUM APPROACHED FROM BOTH ENDS

Temperature, °C.	Alc.-acid, %	Ester-water, %	Difference	Average, %	K
150	84.2	85.2	1.0	84.7	30.9
200	82.6	84.0	1.4	83.3	24.9
250	77.7	78.5	0.8	78.1	12.7
300	74.2	75.5	1.3	74.9	8.9

The close approximation of the values obtained from the two directions indicates that the equilibrium is between the two. No satisfactory results were obtained below 150°, since at lower temperatures the esterification rate is too slow.

³ Swietoslowski and Poznanski, *Roczniki Chem.*, **8**, 527 (1928); *C. A.*, **23**, 2093 (1929).

⁴ Swietoslowski and Poznanski, *Roczniki Chem.*, **9**, 354 (1929); *C. A.*, **23**, 4126 (1929).

The limits reached are decidedly different at different temperatures.

Since our work was completed two years ago an article has appeared by Frolich, Carpenter and Knox,⁵ who studied this reaction in the presence of a zirconium oxide catalyst and obtained a limit of about 87.5% esterification at 280.° and a slightly higher limit at 300.° The lower value was closely checked by hydrolysis of the ester. They concluded that the limit changes only slightly with the temperature and that the maximum conversion to ester obtainable in that temperature range is about 88–90%. They give no data to show that a steady state had been reached.

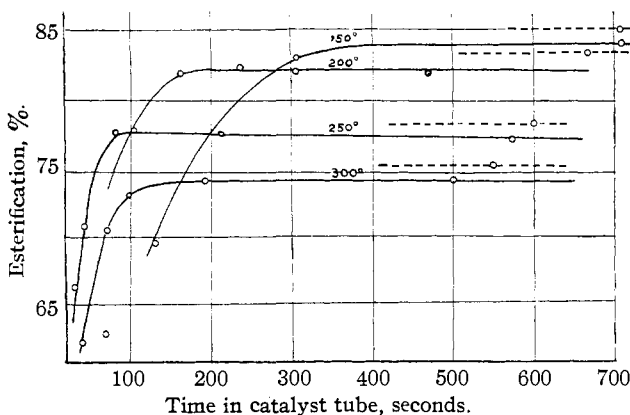


Fig. 1.—Percentage esterified with time in catalyst tube: — — — ester-water limits; — alcohol-acid rates—limits.

In the liquid phase the heat change involved in esterification is small and the limit is known to be practically constant over the temperature range of 20 to 200.° The sum of the heats of vaporization of the acid and alcohol is considerably different from that of the ester and water; the energy change in vapor phase esterification is considerable. Hence a change in the equilibrium with temperature is not unreasonable. Unfortunately the available thermal data are insufficient for reliable calculations.

Experimental

With a few modifications the apparatus was the same as was used in the former work by Milligan, Chappell and Reid; hence a brief description should be sufficient. At the bottom of a 100-cc. reservoir, in which the level was kept approximately constant, was the needle valve dropping device which permitted regulation of the flow of the mixture into the vaporizing chamber. The electrically heated forward end of the catalyst tube served very efficiently in volatilizing the mixture for passage over the catalyst. The catalyst consisted of 66 g. of pure silica gel, prepared from

⁵ Frolich, Carpenter and Knox, *THIS JOURNAL*, 52, 1565 (1930).

silicon tetrachloride according to methods given by Dearing and Reid.⁶ This occupied 285 mm. of the farther end of the catalyst tube of which the portion in the furnace was 560 mm. The catalyst tube, 22 mm. in diameter, was jointed inside the furnace to a small outlet tube which led out through a downwardly inclined 76 mm. water condenser. The apparatus consisted of Pyrex glass with sealed joints throughout. The furnace employed was the same one used in the former work. It was automatically controlled and kept the desired temperature within $\pm 1^\circ$, for the time required. After some preliminary runs the furnace was not turned off during the rest of the work.

The mixture of exactly equivalent amounts of pure acetic acid and absolute ethyl alcohol or the ethyl acetate-water mixture (in the ratio of nearly six moles of the ester to one of the water) was admitted through the needle valve dropping device, which could be regulated to admit the mixture at so many drops per minute. The rate was determined by counting the number of drops per minute after an average drop weight had been found by weighing a large number of drops. These rates were converted to cubic centimeters of mixed vapors at the temperature of the furnace. The rate could be kept fairly constant at from 0.7 to 20 drops per minute or from 7 to 250 cc. of vapors per minute. Since the free space in the catalyst chamber was 86 cc., the time of passage of the vapors through this space could be calculated.

TABLE II
FURNACE TEMPERATURE 150°

No.	Time of run, days	Rate, cc. per min.	Time in furnace, sec.	Esterification, %
1	1	17	304	90.6
2	2	17	304	89.1
3	2	17	304	88.2
4	2	17	304	87.6
5	3	17	304	86.6
6	3	17	304	85.8
7	4	17	304	84.9
8	4	17	304	84.2
9	5	17	304	83.7
10	6	17	304	83.2
11	7	17	304	83.5
12	12	7	737	84.9
13	13	7	737	84.3
14	14	7	737	84.4

The following tabulations give the amount of esterification at the stated temperatures of both the acid-alcohol and acetate-water mixtures. Since water is only moderately soluble in ethyl acetate, the mixture used contained 1 mole of water to 6 of the ester. The percentage of esterification

⁶ Dearing and Reid, *THIS JOURNAL*, 50, 3058 (1928).

for equivalent mixtures was calculated by the formula used in previous studies.⁷

$$\text{Percentage esterification} = \frac{100}{1 + \sqrt{K}}$$

The varying amounts of esterification obtained as checks upon equilibrium established at the conditions specified may be summarized as follows.

TABLE III
SUMMARY OF ESTERIFICATION DATA

Esterification at 300°		Alcohol-acid mixture			
Rate, cc./min.	Time in furnace, sec.	Esterified, several runs under same conditions, %			
27	191	74.5	73.6	74.6	
67	77	69.6	70.9	70.3	
120	43	61.5	61.0		
53	97	73.8 ^a	72.8	73.1	
Esterification at 250°		Alcohol-acid mixture			
9	573	76.5	76.2	75.9	76.3 76.2
49	105	78.5	77.9	77.7	
61	85	76.9	77.1	79.0	77.8
110	47	71.6	70.1	70.8	
183	28	65.5	67.3		
24	215	78.7 ^a	77.8	76.3	77.7
Esterification at 200°		Alcohol-acid mixture			
11	469	81.9	82.3		
22	235	83.1	82.3	82.5	
33	157	82.6	83.1	82.3	
66	78	62.9	61.4	63.7	63.9
17	304	81.9 ^a	82.3		
Esterification at 150°		Alcohol-acid mixture			
7	737	85.0	84.4	83.4	83.6
7	737	84.9	84.4	84.3	
17	304	83.2	82.8	83.5	83.9 82.9
39	132	68.9	68.3	69.9	
7	737 ^a	84.7	83.6	84.3	

^a On return to this temperature and rate.

TABLE IV
HYDROLYSIS OF THE ACETATE-WATER MIXTURE

Temp., °C.	Rate, cc./min.	Time in furnace, sec.	Ester. several runs under same conditions, %			
300	9	573	75.4	75.7		
250	9	573	78.2	79.1	78.3	
200	8	645	83.8	84.5	84.0	83.7
150	7	737	86.0	85.2	84.9	85.0

⁷ Freas and Reid, *THIS JOURNAL*, **40**, 569 (1918); Reid, *Am. Chem. J.*, **43**, 499 (1910); Faber and Reid, *THIS JOURNAL*, **39**, 1930 (1917).

Summary

1. The vapor phase esterification of ethyl alcohol and acetic acid in the presence of silica gel has been studied over the temperature range of 150 to 300°.

2. The limits obtained with the equimolar mixture of the alcohol-acid have been approached from the other side by the hydrolysis of an acetate-water mixture.

3. Close checks by the two methods gave average conversions of from about 85% at 150° to 75% at 300° as limits in the presence of silica gel. These data would indicate that there is some variation of the equilibrium constant with the temperature, with the highest conversion at the lower temperatures.

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[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

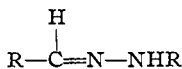
THE OPTICAL ROTATION OF RHAMNOSE AND MANNOSE PHENYLHYDRAZONES

BY C. L. BUTLER AND LEONARD H. CRETCHER

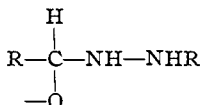
RECEIVED JULY 18, 1931

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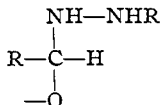
Very little is known of the structure of the sugar hydrazones. Although Behrend and collaborators¹ found evidence of structural isomerism among certain members of this group of substances, it has usually been assumed that the reaction between sugars and hydrazines results in the formation of true hydrazones. Since the sugars are complex substances capable of reacting in several different forms, no assumptions regarding the structure of the hydrazones or the course of reaction would seem to be justified. The only recent work done in this field is that of Wolfrom,² who reported results favoring a true hydrazone structure for several hydrazones of galactose. Formulas I (true hydrazone), II and III (hydrazide, or substituted hydrazine, corresponding to the α - and β -glucosides) were proposed by Behrend¹ and they appear to the present authors to be the most probable ones for the sugar hydrazones although others are possible. These structures are



I



II



III

¹ Behrend and others, *Ann.*, **353**, 106 (1907); **362**, 78 (1908); **366**, 277 (1909); **377**, 189 (1910); see also Lobry de Bruyn, *Ber.*, **28**, 3084 (1895); Simon and Benard, *Compt. rend.*, **132**, 564 (1901); Frèrejacque, *ibid.*, **180**, 1210 (1925).

² Wolfrom and Christman, *THIS JOURNAL*, **53**, 3413 (1931).