

flame below T. This arc now sinks to the water surfaces, and operates at 3.5 amperes and 170 volts. As a much larger amount of mercury is displaced on the cathode side, the enlargement E is necessary to accommodate it. As the mercury distils from the hot cathode to the cooler anode,<sup>4</sup> it returns via the bridge B, which has a dam D to break up the trickles into drops and thus avoid momentary short circuits.

When the transparency of the quartz is seriously impaired (after about 500 hours' use in the case of  $\lambda 406\text{ m}\mu$  or  $\lambda 366\text{ m}\mu$ ) the lamp is taken down. The section M to M<sub>1</sub> (only) is treated with hydrofluoric acid and heated in an oxygen-gas flame until softening begins. After several such treatments this section must be replaced, but the original trap can be used repeatedly.

The light intensities obtainable, at the various wave lengths, are comparable to those already reported<sup>5</sup> for a lamp carrying a similar discharge. With a steady source of current, also nearly constant barometric pressure, and ventilation the total variations in light intensity over considerable periods seldom exceed three per cent.

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RECEIVED SEPTEMBER 14, 1931

PUBLISHED DECEMBER 10, 1931

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## ISOMERIC ALPHA-PHENYL-BETA-PARA-TOLYL-DELTA-KETONIC ACIDS

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RECEIVED JUNE 22, 1931

PUBLISHED DECEMBER 10, 1931

### Introduction

In a communication "Isomeric Alpha,Beta-Diphenyl-Delta-Ketonic Acids. I,"<sup>1</sup> it was pointed out that  $\delta$ -ketonic acids of the formula  $\text{CO}(\text{R})\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{COOH}$  show in their inactive forms essentially the same isomerism as glutaric acids of similar configuration. It was anticipated that the inactive forms discussed might, like the glutaric acids, be resolved into optically active isomers. Since this communication was published, the authors of this paper have definitely isolated in pure form the lower melting isomeric  $\alpha,\beta$ -diphenyl- $\gamma$ -trimethylacetylbutyric acid. Further, they have found that none of the acids previously considered can be resolved into optical isomers by the methods used in the glutaric series. After a brief statement of this work in the experimental part, attention will

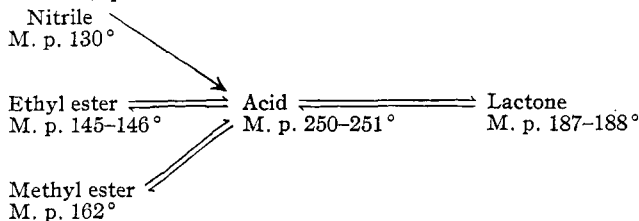
<sup>4</sup> P. A. Leighton and Forbes, *J. Opt. Soc. Am.*, **12**, 58 (1926).

<sup>5</sup> Ref. 3, p. 3550.

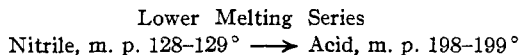
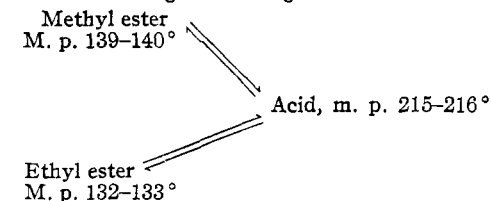
<sup>1</sup> Avery and Jorgensen, *THIS JOURNAL*, **52**, 3628 (1930).

be turned to the  $\alpha$ -phenyl- $\beta$ -*p*-tolyl- $\delta$ -ketonic acids which were synthesized in the hope of obtaining inactive isomers susceptible of optical resolution. The following will be described.

$\alpha$ -PHENYL- $\beta$ -*p*-TOLYL- $\gamma$ -BENZOYLBUTYRIC ACID AND ITS DERIVATIVES



$\alpha$ -PHENYL- $\beta$ -*p*-TOLYL- $\gamma$ -TRIMETHYLACETYL DERIVATIVES  
Higher Melting Series



### Experimental Part

When the impure product obtained by condensing benzyl cyanide with benzalpinacolone is crystallized from ligroin, there remains in solution, after filtering off the nitrile of the higher melting acid, a small amount of oil, which, on saponification in acid solution, yields a mixture of isomeric  $\alpha,\beta$ -diphenyl- $\gamma$ -trimethylacetylbutyric acids in which the lower melting acid predominates. These were separated by fractional crystallization from dilute alcohol. The lower acid thus obtained formed needles melting at 179-180°.

*Titration.* 0.2971 g. required 9.12 cc. of *N*/10 NaOH. Calcd.: 9.16 cc.

Though the proportion of the lower to the higher acid is not more than 1:10, the isomerism of the acid under consideration is now definitely established.

Both isomeric  $\alpha,\beta$ -diphenyl- $\gamma$ -benzoylbutyric acids and the higher melting  $\alpha,\beta$ -diphenyl- $\gamma$ -trimethylacetylbutyric acid (the lower was insufficient in quantity) were treated in water, in dilute alcohol, and in acetone with equal moles of brucine, and strychnine. No crystalline salts were obtained in any case, though the conditions of temperature and concentration were widely varied.

#### $\alpha$ -Phenyl- $\beta$ -*p*-tolyl- $\gamma$ -benzoylbutyric Acid and Derivatives

The methyl ester, ethyl ester and nitrile of  $\alpha$ -phenyl- $\beta$ -*p*-tolyl- $\gamma$ -benzoylbutyric acid were synthesized through the direct condensation of *p*-tolualacetophenone with the methyl ester, ethyl ester and nitrile of phenylacetic acid, respectively. Sodium methoxide in methanol solution was used as the condensing agent in the case of the methyl ester condensation, while sodium ethoxide in ethanol solution was employed as the condensing agent in the ethyl ester and nitrile condensations. The acid was formed

through the hydrolysis of the nitrile and the esters; the lactone, by treatment of the acid with acetyl chloride.

TABLE I  
 $\alpha$ -PHENYL- $\beta$ -*p*-TOLYL- $\gamma$ -BENZYL BUTYRIC ACID AND DERIVATIVES

Derivative	Formula	Solvent	M. p., °C.	Crystal habit	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Acid	$C_{24}H_{22}O_4$	Glac. HAc	250-251	Fine needles	80.41	80.28	6.19	6.22		
Me ester	$C_{24}H_{24}O_3$	MeOH	162	Fine needles	80.60	80.50	6.50	6.50		
Et ester	$C_{26}H_{26}O_3$	EtOH	145-146	Long needles	80.78	80.77	6.79	6.81		
Nitrile	$C_{24}H_{21}ON$	Abs. EtOH	130	Prisms <sup>a</sup>	84.91	84.90	6.24	6.38	4.13	4.09
Lactone	$C_{24}H_{20}O_2$	<i>Tert.</i> -amyl alc. <sup>b</sup>	187-188	Coarse needles	84.67	84.32	5.93	5.98		

<sup>a</sup> Superficially resembling quartz. <sup>b</sup> Containing a small percentage of chloroform.

The five compounds above tabulated under the heading  $\alpha$ -phenyl- $\alpha$ -*p*-tolyl- $\gamma$ -benzoylbutyric acid and derivatives show, in crystalline form, solubilities, and melting points, a close similarity to the members of the higher melting  $\alpha,\beta$ -diphenyl- $\gamma$ -benzoylbutyric series. However, fractional crystallization of the crude synthetic esters, and the nitrile, failed to show any lower melting (more soluble) isomers. The very high yields of the pure products obtained showed that only traces of isomers at most could be present. Hence attention was turned to the possible corresponding  $\gamma$ -trimethylacetyl compound.

To synthesize the trimethylacetyl derivatives, *p*-tolualpinacolone (not found in the literature) was required. This was prepared from *p*-tolualdehyde and pinacolone, according to the methods used in the preparation of benzalpinacolone;<sup>2</sup> yields of pure *p*-tolualpinacolone, 25% of the theoretical; fine, colorless prisms from 95% alcohol; m. p. 83.4°.

*Anal.* Calcd. for  $C_{14}H_{18}O$ : C, 83.12; H, 8.96. Found: C, 83.03; H, 8.88.

#### $\alpha$ -Phenyl- $\beta$ -*p*-tolyl- $\gamma$ -trimethylacetylbutyric Acids and Derivatives

The condensation of *p*-tolualpinacolone with the methyl and ethyl esters of phenylacetic acid led to the formation of derivatives of the higher melting series; the corresponding condensation with benzyl cyanide resulted in the formation of the nitrile of the lower melting series.

TABLE II									
$\alpha$ -PHENYL- $\beta$ -TOLYL- $\gamma$ -TRIMETHYLACETYL BUTYRIC ACIDS AND DERIVATIVES									
De- rivative	Formula	Solvent	M. p., °C.	Crystal habit	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Nitrogen, % Calcd. Found		
Higher Melting Series									
Acid	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>	EtOH	215-216	Fine needles	a				
Me ester	C <sub>22</sub> H <sub>24</sub> O <sub>3</sub>	MeOH	139-140	Fine needles	78.38	78.40	8.01	7.95	
Et ester	C <sub>24</sub> H <sub>26</sub> O <sub>3</sub>	EtOH	132-133	Coarse needles	78.63	78.56	8.26	8.12	

Lower Melting Series										
Acid	$C_{22}H_{22}O_3$	EtOH	198-199	Long prisms	78.06	77.97	7.75	7.83		
Nitrile	$C_{22}H_{21}ON$	Ligroin	128-129	Long prisms	82.70	82.67	7.89	7.79	4.39	4.31

<sup>a</sup> Acid converted into methyl and ethyl esters which were found to be identical with synthetic esters, the analysis of which follows. *Titration.* 0.3098 g. required 9.18 cc. of *N*/10 NaOH. Calcd., 9.17 cc.

The  $\alpha$ -phenyl- $\beta$ -*p*-tolyl- $\gamma$ -trimethylacetylbutyric compounds formed by the action of *p*-tolualpinacolone on the ester or nitrile of phenylacetic acid were mixtures from which

<sup>2</sup> "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 15.

pure products could be separated by fractional crystallization with difficulty. This points to isomeric compounds. From analogy with other  $\delta$ -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  $\alpha$ -phenyl- $\beta$ -*p*-tolyl- $\gamma$ -trimethylacetylbutyric acids were too small to permit of attempting optical resolution, and from analogy with other  $\delta$ -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  $\alpha$ , $\beta$ -diphenyl- $\gamma$ -trimethylacetylbutyric acid has been obtained in pure condition; the inactive isomeric  $\delta$ -ketonic acids, previously reported, cannot be resolved into optical isomers by the methods used in resolving the corresponding acids in the glutaric series.

$\alpha$ -Phenyl- $\beta$ -*p*-tolyl- $\gamma$ -benzoylbutyric acid and its derivatives have been synthesized. No isomeric forms could be detected.

Isomeric  $\alpha$ -phenyl- $\beta$ -*p*-tolyl- $\gamma$ -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  $\delta$ -ketonic derivatives having higher melting points in the higher series and lower melting points in the lower melting series.

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## VAPOR PHASE ESTERIFICATION IN PRESENCE OF SILICA GEL

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RECEIVED JUNE 29, 1931

PUBLISHED DECEMBER 10, 1931

Some years ago vapor phase esterification in the presence of silica gel was studied by Milligan, Chappell and Reid,<sup>1</sup> 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 Schuyler<sup>2</sup> 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.

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

<sup>2</sup> Edgar and Schuyler, *THIS JOURNAL*, **46**, 64 (1924).