

benzoquinone (4.56 g., 0.03 mole) in acetic acid (75 cc.) with this peroxide solution furnished a red oil, which was washed in ether with three portions of saturated sodium bicarbonate to remove unreacted 2-hydroxy-3,6-dimethylbenzoquinone as the deep-violet sodium salt. The ether residue crystallized from petroleum ether (b.p. 20–40°) at Dry Ice temperature to give 3.57 g. (43.0% yield) of orange quinone. Recrystallization from low-boiling petroleum ether afforded rosettes of light-orange needles, m.p. 79–80.5°; yield 2.62 g. (31.6%). Recrystallization of a sample once more from petroleum ether and once from dilute ethanol furnished yellow needles of m.p. 80.0–80.7°. The sparingly soluble, deep-violet sodium salt was formed on treatment of the quinone with sodium hydroxide.

*Anal.* Calcd. for  $C_{17}H_{14}O_3$ : C, 73.88; H, 8.75. Found: C, 74.02; H, 8.92.

**2-Hydroxy-3,6-dimethyl-5-undecylbenzoquinone (XXI).**—An acetic acid solution of 2-hydroxy-3,6-dimethylbenzoquinone (3.04 g., 0.02 mole) was heated for 1 hour on a steam-bath with 8.89 g. (0.022 mole) of commercial lauroyl peroxide.<sup>16</sup> Removal of acetic acid under reduced pressure left a partially crystalline residue. Unalkylated quinone was removed by extraction with bicarbonate and the residue crystallized from ligroin to give 2.68 g. (43.8% yield) of crude product. Recrystallization from ligroin and finally from dilute acetic acid gave cottony clusters of light-orange needles, m.p. 102.0–102.3°. The quinone was sparingly soluble in dilute sodium hydroxide as the deep violet salt.

*Anal.* Calcd. for  $C_{19}H_{20}O_3$ : C, 74.47; H, 9.87. Found: C, 74.33; H, 9.96.

CAMBRIDGE, MASS.

RECEIVED AUGUST 31, 1950

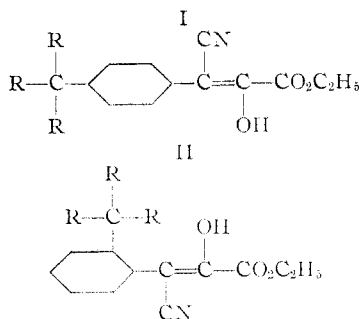
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

## Alkyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates and Pyrrolidinetriones<sup>1</sup>

BY GLENN S. SKINNER, JULES A. GLADNER AND RICHARD F. HEITMILLER

The synthesis and separation of additional isomeric alkyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates has been accomplished. Infrared absorption studies reveal that in the solid state these esters exist in the enol form. As more methyl groups are substituted for the hydrogen of an *o*-methyl group cyclization to a 4-alkylpyrrolidinetrione still takes place but the entry of bromine into the ring is hindered and there is alternation in the melting point. There is little or no evidence of alternation in the para series and bromine in no case enters the ring of the cyclized product.

In a previous report<sup>1a</sup> it was shown that the blocking of the para position of ethyl  $\beta$ -cyano- $\alpha$ -hydroxycinnamate with a methyl group did not prevent cyclization by bromine and water to an arylpyrrolidinetrione, but that it did prevent the entry of bromine into the aromatic nucleus. The further introduction of the methyl group into all ortho and para positions caused the formation of an uncyclized product containing bromine in the side chain. It therefore seemed desirable to investigate the effect of methyl groups outside the nucleus as in (I) or (II) where the number of methyl groups (R-) is varied from zero to three.



Customarily, compounds of this type have been called pyruvates. However, they yield ethers of the enol form which are therefore named as derivatives of  $\beta$ -cyano- $\alpha$ -hydroxycinnamic acid. The infrared spectrograms (Fig. 1) of the ethyl *o*-(A) and *p*-methyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates (B) both show absorption for the ethylenic double bond ( $6.2\mu$ ) and one carbonyl group ( $5.8\mu$ ), in harmony with ethyl  $\beta$ -cyano- $\alpha$ -ethoxycinnamate. The ether (C) gives a very definite absorption for the nitrile group ( $4.6\mu$ ) which it is almost entirely absent for the cyanohydroxycinnamates. In the

latter there is also indication of a bonded OH at  $3.0\mu$ . This behavior suggests that the enols may have the structure (III).

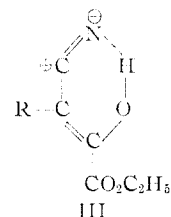


TABLE I

ALKYL  $\beta$ -CYANO- $\alpha$ -HYDROXYCINNAMATES

Alkyl	<i>m</i>	<i>n</i>	M.p., °C.	Nitrogen, %	
				Calcd.	Found
<i>o</i> -Methyl <sup>1a</sup>	0	3	115–117		
<i>o</i> -Ethyl	1	2	66–67	5.71	5.78
<i>o</i> -Isopropyl	2	1	115.5–116.5	5.41	5.36
<i>p</i> -Methyl <sup>1a</sup>	0	3	88–89		
<i>p</i> -Ethyl	1	2	82–83	5.71	5.81
<i>p</i> -Isopropyl	2	1	78–79	5.41	5.46
<i>p</i> - <i>t</i> -Butyl	3	0	74–75	5.13	5.06

The esters (Table I) decomposed to the pure nitriles (Table II) in fair yields when heated with an excess of dilute alkali to a temperature of 70–80°. The nitriles were identified by hydrolysis to the alkylacetic acids (Table IV).

TABLE II

NITRILES  $R-C_6H_4-CH_2CN$

R	B.p., °C. (5 mm.)	Yield, %	$d^{25}_4$	Nitrogen, %	
				Calcd.	Found
<i>o</i> -C <sub>2</sub> H <sub>5</sub> -	95–97 <sup>a</sup>	69		9.66	9.59
<i>p</i> -C <sub>2</sub> H <sub>5</sub> -	100–101	95	0.9775	9.66	9.72
<i>p</i> - <i>iso</i> -C <sub>3</sub> H <sub>7</sub> -	106–108	77	.9631	8.80	8.88
<i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub> -	119–121	79	.9581	8.09	8.14

<sup>a</sup> B.p. at 2 mm.

(1) Previous reports in this series: THIS JOURNAL, (a) **55**, 2036 (1933); (b) **62**, 2882 (1940); (c) **64**, 2600 (1942); (d) **66**, 496 (1944); (e) **70**, 4011 (1948); (f) **72**, 5369 (1950).

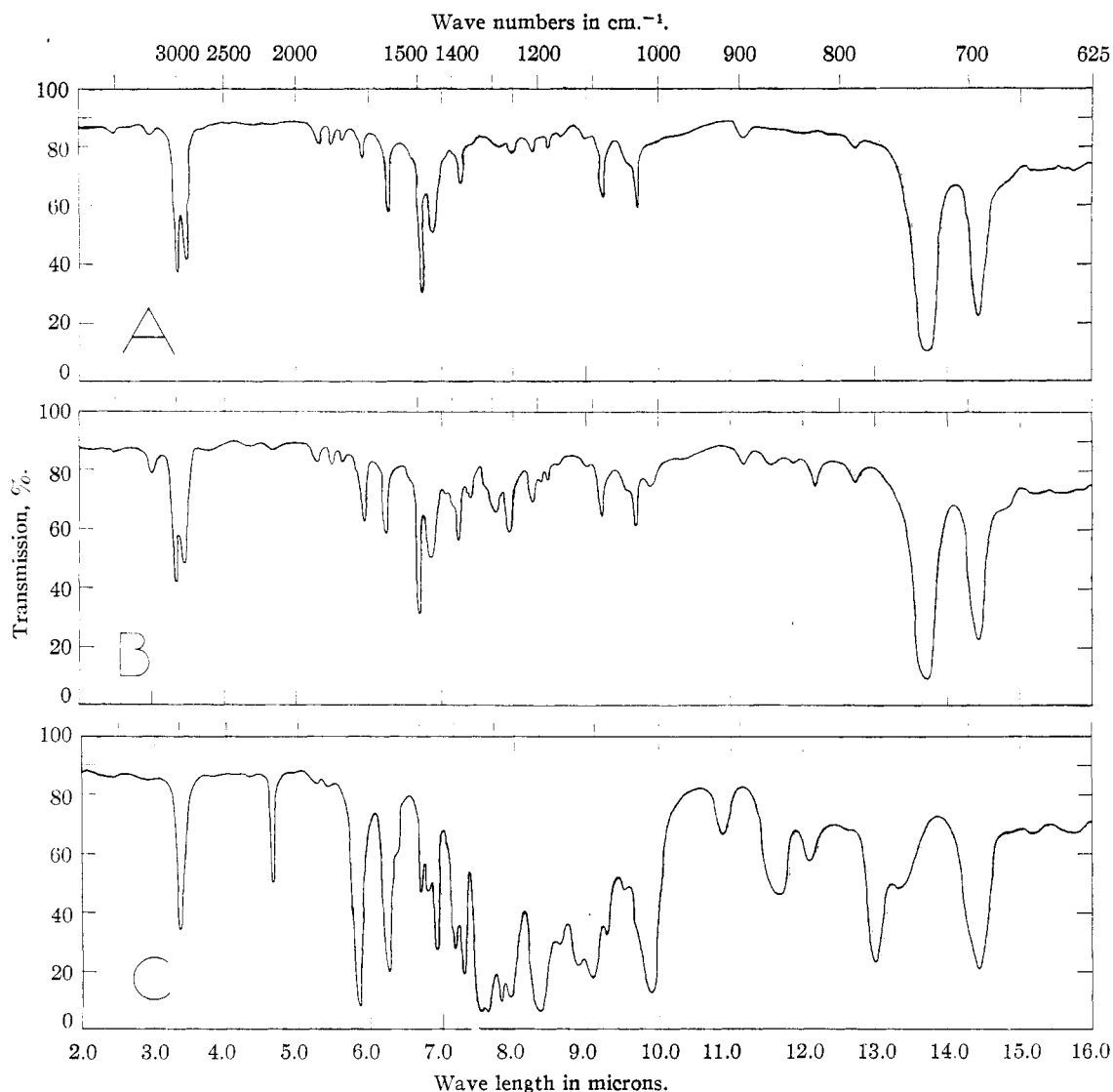


Fig. 1.—Infrared spectrograms: A, ethyl *o*-methyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamate (nujol mull); B, ethyl *p*-methyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamate (nujol mull); C, ethyl  $\beta$ -cyano- $\alpha$ -ethoxycinnamate (pure liquid). Measurements by Jane Hucks.

All of the *p*-alkyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates underwent cyclization to the 4-alkylphenylpyrrolidinetriones without entry of bromine into the ring (Table III). As the number of methyl groups

in place of hydrogen in the *o*-methyl radical (II) was increased the tendency for bromine to enter the ring appeared to decrease. Bromine did not enter the ring of either the *o*-ethyl- or the *o*-isopropyl derivative when the customary amount of chloroform was used as solvent. In the mini-

TABLE III

R	M.p., °C.	Nitrogen, %	
		Calcd.	Found
2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> - <sup>10</sup>	186-187		
2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	155-156	6.45	6.31
2-iso-C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> -	186-187	6.05	5.92
4-BrC <sub>6</sub> H <sub>4</sub> - <sup>10</sup>	239-240		
4-Br-2-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> - <sup>10</sup>	237.5-238.5		
4-Br-2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>3</sub> -	179-180	4.70	4.82
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> - <sup>10</sup>	263-264		
4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	246-247	6.45	6.52
4-iso-C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> -	232-233	6.05	5.96
4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> -	249-250	5.71	5.62

TABLE IV

R	M.p., °C.	Nitrogen, %		M.p. °C. acid, °C.
		Calcd.	Found	
2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	128-129	8.55	8.37	83-84 <sup>a</sup>
2-iso-C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> -	121-122	7.91	7.84	58-59
4-Br-2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	143-144	5.65	5.73	87-88
4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	199-200	8.55	8.48	89-90 <sup>b</sup>
4-iso-C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> -	172-173	7.91	7.89	51-52 <sup>c</sup>
4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> -	129-130	7.32	7.32	78-79 <sup>d</sup>

<sup>a</sup> F. Mayer and F. A. English, *Ann.*, 417, 60 (1918).

<sup>b</sup> M. T. Bogert and G. S. Stamatoff, *Rec. trav. chim.*, 52, 584 (1933). <sup>c</sup> "Beilstein," Vol. 9, p. 561. <sup>d</sup> R. Berg, *Roczniki Chem.*, 14, 1249 (1934).

imum amount of this solvent the yield of the brominated *o*-ethyl- derivative was 47% and that of the brominated *o*-isopropyl derivative was almost negligible. The pyrrolidinetriones were hydrolyzed to the amides (Table IV) which were then hydrolyzed to the known alkylacetic acids. The melting points were identical with those previously reported. The unknown acids were converted to the corresponding phthalic acids.

### Experimental

**Chloromethylation.**—In a typical experiment 230 g. (1.91 moles) of isopropylbenzene, 46.5 g. (1.55 moles) of paraformaldehyde and 46.4 g. (0.34 mole) of zinc chloride were allowed to react in the usual way with stirring in a rapid stream of hydrogen chloride for four hours at 50–55°. After washing several times with ice-cold water with the addition of petroleum ether to aid in the separation of the layers the ethereal solution was neutralized with sodium hydroxide. It was then washed again, finally with the addition of small portions of anhydrous sodium sulfate to break the emulsion. The organic layer was then shaken with an excess of anhydrous calcium chloride to which 0.5 cc. of saturated sodium hydroxide solution had been added. Distillation of the dried product yielded three fractions exclusive of unreacted hydrocarbon: (1) 84 g. (32%) of monochloromethylisopropylbenzenes, b.p. 116–120° (19 mm.); (2) 9 g., b.p. 150–170°, (3) residue 38.0 g. When formalin was used according to the procedure for the chloromethylation of toluene the yield was only 20% after a reaction period of 15 hours.

Ethylbenzene (6.00 moles), paraformaldehyde (2.43 moles) and zinc chloride (0.53 mole) when reacting for two hours at 55° gave (1) 155 g. (43%) of monochloromethyl-ethylbenzenes, b.p. 104–108° (16 mm.); (2), 32 g., b.p. 180–185° (16 mm.); (3) residue, 50 g. If only 3.00 moles of ethylbenzene reacted with 2.43 moles of paraformaldehyde and 0.53 mole of zinc chloride for 30 minutes at 60° the weights of the respective fractions were as follows: (1) 115 g. (32%); (2) 58 g.; (3) 50 g. *t*-Butylbenzene (3.25 moles), paraformaldehyde (1.33 moles) and zinc chloride (0.29 mole) when reacting at 50° for 90 minutes gave (1) 179 g. (74%) of monochloromethyl-*t*-butylbenzenes, b.p. 119–121° (16.5 mm.); (2) 16 g., b.p. 150–160° (16 mm.); (3) residue, 5.5 g.

**Ethyl Alkyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates.**—The mixtures of nitriles were obtained in the usual way from the monochloromethyl derivatives (1.20 moles), 188 cc. of alcohol, sodium cyanide (1.53 moles) and 68 cc. of water. The alcoholic solution of the chlorides was added in 45 minutes with mechanical stirring and the refluxing was continued for five hours. Ethylphenylacetoneitriles, yield 88%, b.p. 140–143° (19 mm.); isopropylphenylacetoneitriles, yield 84.4%, b.p. 134–137° (14.5 mm.); *t*-butylphenylacetoneitriles, yield 90.5%, b.p. 143–146° (15 mm.). The corresponding alkyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates were prepared in the same general way as previously described,<sup>1a</sup> but the separation of the isomers was more tedious and required separate techniques.

**Separation of Ethyl Ethyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates.**—The ethereal solution of the esters from 1.06 moles of the nitriles gave 231 g. of residue after removal of the last of the solvent, finally with a capillary under diminished pressure at 95–100°. This was dissolved in 100 cc. of toluene and 125 cc. of petroleum ether was stirred in. After standing in an ice-bath for several hours the crystals were filtered with suction and washed first with a 1:1 mixture of toluene and petroleum ether and then with petroleum ether; weight 115 g., m.p. 77–83°. The product was dissolved in 57 cc. of toluene and thoroughly cooled in a salt-ice-bath. The white crystalline product was filtered with suction and washed with an ice-cold 1:1 mixture of toluene and petroleum ether; para isomer: 101 g., m.p. 82–83°.

The removal of the solvent from the first filtrate left a viscous residue which largely solidified after standing two weeks. The liquid was then practically all removed by suction for two days with the aid of a rubber dam. The crystalline portion (76.5 g.) was dissolved in 15 cc. of hot alcohol and allowed to stand in a refrigerator for two weeks; yield, 34.5 g., m.p. 53–59°. Further refrigeration yielded,

in addition, 18.5 g., m.p. 50–60°. The combined product was recrystallized from toluene-petroleum ether mixtures several times. As the purification proceeded the solution would tolerate the addition of more petroleum ether without precipitation of an oil. Ortho isomer: 23.4 g., m.p. 66–67°.

In another experiment 102 g. of material (m.p. 53–58°) was isolated by freezing, finally with Dry Ice in acetone, of a solution of the viscous residue from the para isomer in 25 cc. of toluene plus 25 cc. of petroleum ether. It was now dissolved in 25 cc. of hot alcohol, cooled in a salt-ice-bath and filtered cold with the aid of a rubber dam; yield 37.5 g., m.p. 59–62°. This was dissolved in 18 cc. of hot toluene, cooled in ice, filtered cold with suction and washed first with a mixture of toluene and petroleum ether, then with petroleum ether; yield 21 g., m.p. 66–67°.

**Separation of Ethyl Isopropyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates.**—In this case the mixture of esters from 150 g. of isopropylphenylacetoneitriles was initially obtained by addition of 50 cc. of ether plus 125 cc. of petroleum ether to the acidified reaction mixture, 201 g., m.p. 60–71°. The viscous oil (31.8 g.) from the filtrate after standing in a refrigerator largely solidified. The solid yielded more of the para isomer (m.p. 78–79°). The crude crystalline product was dissolved in 200 cc. of hot toluene to which, after cooling somewhat, was added an equal volume of petroleum ether. The para isomer crystallized at room temperature as fine needles, m.p. 78–79°. The solvents were removed from the filtrate and the process was repeated several times. After the yield of pure product amounted to 112 g. a finely divided precipitate appeared in the solution at room temperature. This was filtered immediately (3.0 g., m.p. 115.5–116.5°). The solvents were removed from the filtrate and the process was repeated several times. The combined crops of the ortho isomer were recrystallized from toluene. After removal of this amount of the ortho isomer 20.9 g. more of the para isomer could be obtained. Para isomer: yield 132.9 g., m.p. 78–79°; ortho isomer: yield 11.9 g., m.p. 115.5–116.5°.

In another preparation, after no more relatively pure para isomer separated, it was found helpful to dissolve further crops, m.p. 68–72°, in two-fifths of their weight of hot alcohol. This ice-cold solution deposited the para isomer which was filtered with suction, using a rubber dam. This facilitated the crystallization of the ortho isomer from the toluene-petroleum ether solution of the residual mixture.

**Attempted Separation of Ethyl *t*-Butyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamates.**—The esters from 284.6 g. of *t*-butylphenylacetoneitriles were obtained as an oil. The oil was dissolved in 120 cc. of hot toluene and 287 cc. of petroleum ether was stirred into the partially cooled solution. The product which separated by cooling in an ice-salt-bath was filtered, washed first with toluene-petroleum ether then with petroleum ether (188.7 g., m.p. 70–75°). After removal of the solvents and repeating with 70 cc. of toluene and 140 cc. of petroleum ether 130 g. more of crystalline product (m.p. 72–74°) was obtained. By reworking the filtrate four times with smaller quantities of the mixed solvents and allowing to stand in a refrigerator the total yield of crude crystalline product was increased to 369.7 g. This by recrystallization from a 1:2 mixture of toluene and petroleum ether in a salt-ice-bath gave the pure para isomer in the form of granular crystals, m.p. 74–75°. The residual oil from the crude product weighed 72.4 g. So far, it has been impossible to isolate the ortho isomer from this.

**Hydrolysis of the Esters.**—The pure esters (0.150 mole), when stirred and heated with a solution of sodium hydroxide (0.160 mole) in 200 cc. of water, completely dissolved at 50–70°. Heating was discontinued when precipitation began at 70–80°. After separation of the nitriles with ether the water layer was treated with 1.6 g. of sodium hydroxide and heated again. All were obtained as colorless liquids, with pleasant odors and therefore presumably free from isonitriles (Table II). The pure alkylphenylacetoneitriles were hydrolyzed to the alkylphenylacetic acids in 85–95% yields by refluxing the nitrile (0.100 mole) and 13 g. of 40% aqueous sodium hydroxide in 75 cc. of alcohol for five hours.

**4-Arylpyrrolidinetriones.**—The yields of unbrominated phenylpyrrolidinetriones obtained under previously described conditions<sup>1a</sup> were as follows: *p*-ethyl-, 80%; *p*-isopropyl-, 81%; *p*-*t*-butyl-, 58%. The crude products which separated from the chloroform were filtered and then crystallized from hot alcohol for analysis (Table III). The ortho compounds behaved less uniformly.

Ethyl *o*-ethyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamate (0.020 mole) was reacted with bromine (0.021 mole) and water (0.020 mole) in 16 cc. of chloroform at 50° for six hours and then allowed to stand at room temperature for two days. No precipitate separated. Concentration of the solution gave 3.7 g. of yellow crystals, m.p. 149–153°. After crystallization from chloroform this unbrominated compound melted at 155–156°. When the same amounts of reagents were dissolved in the minimum amount of chloroform the reaction product soon separated as a solid. The minimum amount of hot chloroform now needed to dissolve this product after standing two days was 50 cc. Fractional crystallization gave 2.8 g. (47%) of very insoluble 4-(4-bromo-2-ethylphenyl)-pyrrolidinetrione and 1.3 g. (29%) of very soluble 4-(2-ethylphenyl)-pyrrolidinetrione.

Ethyl *o*-isopropyl- $\beta$ -cyano- $\alpha$ -hydroxycinnamate (0.020 mole) in 16 cc. of chloroform by similar treatment gave no solid precipitate. The viscous residue after removal of the chloroform under diminished pressure could then be crystallized from chloroform to give 4.5 g. of crude lemon-yellow product melting at 171–174° with some decomposition. After several crystallizations the 4-(2-isopropylphenyl)-pyrrolidinetrione melted at 186–187°. When the experiment was repeated using the minimum amount of solvent (6 cc.) crystals separated much more slowly (one day) and in smaller amount (1.0 g.) than in the case of the *o*-ethyl derivative. This product contained bromine. After repeated crystallization from chloroform the amount diminished to 0.1 g., and the melting point of the lemon-

yellow crystals was still rising at 194–196°. This is probably the brominated pyrrolidinetrione but it was not further investigated on account of insufficient material.

**Characterization of Pyrrolidinetriones.**—4-(4-Ethylphenyl)-pyrrolidinetrione (6.51 g.) was dissolved in a mixture of 1.84 g. of potassium hydroxide and 20 cc. of water, heated to boiling and then allowed to cool. The weight of 4-ethylphenylacetamide was 2.4 g. By reheating the filtrate twice the yield of crude product was increased to 4.9 g. The pure product was obtained by recrystallization from boiling alcohol, m.p. 199–200°. It was identified by alkaline hydrolysis to 4-ethylphenylacetic acid which was crystallized from hot alcohol, m.p. 89–90°. Similarly, amides from other pyrrolidinetriones (Table IV) were identified in the case of known acids.

4-Bromo-2-ethylphenylacetamide (0.5 g.) was refluxed three hours with 0.16 g. of sodium hydroxide in 10 cc. of alcohol to give 4-bromo-2-ethylphenylacetic acid, m.p. 87–88° (from ligroin). This gave 4-bromo-*o*-phthalic acid,<sup>10</sup> m.p. 176–178°, by oxidation with alkaline permanganate.

*o*-Isopropylphenylacetamide (0.5 g.) was incompletely (50–60%) hydrolyzed, under the above conditions after refluxing five hours, to the acid, m.p. 58–59° (from ligroin). Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: neut. equiv., 178. Found: neut. equiv., 170. This acid by oxidation with alkaline permanganate gave *o*-phthalic acid, m.p. 208–210°, which was isolated and purified as previously described.<sup>10</sup>

NEWARK, DEL.

RECEIVED NOVEMBER 14, 1950

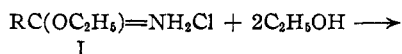
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## The Thermal Decomposition of Iminoester Salts and the Cleavage of Orthoesters by These Salts

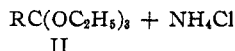
By S. M. McELVAIN AND BRYCE E. TATE\*

The thermal decomposition of iminoester hydrohalides (I) into the corresponding amide (III) and alkyl halide in chloroform or *t*-butyl alcohol solution follows first order kinetics as determined by the rate of disappearance of the chloride ion. The rate data are shown to be consistent with either a first order intramolecular decomposition of the un-ionized salt (reaction (1)) or an ionic mechanism (reactions (2) and (3)) involving a bimolecular, rate determining step. The relative rates of cleavage of orthoesters to the corresponding normal esters and an alkyl halide (reaction (6)) by iminoester hydrohalides have been determined in chloroform solution. Some relationships between the structures of the reactants and the rates of cleavage are discussed and a mechanism for the cleavage reaction (reactions (6) and (7)) is proposed. An alternative reaction, which would yield the normal ester and ether in an alcohol solution (reaction (8)), is shown to be insignificant.

The alcoholysis of iminoester hydrochlorides (I) derived from straight chain carboxylic acids gives the corresponding orthoesters (I) in yields of 60–80%.<sup>1</sup> The presence of a single negative  $\alpha$ -substituent such as chloro,<sup>1</sup> ethoxyl,<sup>2</sup> phenyl,<sup>3</sup> carbethoxyl<sup>4</sup> or cyano<sup>4</sup> in the iminoester hydrochloride usually does not appreciably change these yields. However, the presence of two  $\alpha$ - or  $\beta$ -substituents in the iminoester hydrochlorides usually lowers the yield of the orthoester to 20–30% or less.<sup>1,5</sup>



I



II

While alcoholysis of each of the three types of iminoester hydrochlorides gives some amide (III) as a side product, amide formation becomes quite

important in the alcoholysis of disubstituted compounds where the yields of this side product may approach 50%.<sup>5a</sup> The normal ester and the nitrile from which the iminoester hydrochloride is derived have also been found to be products of the alcoholysis.<sup>5a</sup> Normal ester and nitrile formation have not been observed in the straight chain series, but some normal ester is formed when the single  $\alpha$ -substituent is phenyl,<sup>6</sup> and much larger amounts of normal ester are formed when the iminoester has two  $\alpha$ - or  $\beta$ -substituents.<sup>1,5</sup>

This paper reports the results of work initiated for the purpose of determining the mechanisms of the reactions by which amides and normal esters are formed during the alcoholysis of iminoester hydrochlorides. The conclusions which have been drawn are based on the relationships of structure to the rates of thermal decomposition of iminoester salts in solution and the cleavage of orthoesters by these salts.

**The Thermal Decomposition of Iminoester Salts.**—Although the decomposition of an iminoester hydrochloride (I) to an amide (III) and alkyl chloride was first observed many years ago,<sup>7</sup> no

(\*) E. I. du Pont de Nemours and Company Research Assistant, 1949–1950.

(1) S. M. McElvain and W. Nelson, *THIS JOURNAL*, **64**, 1825 (1942).

(2) S. M. McElvain and P. M. Walters, *ibid.*, **64**, 1963 (1942).

(3) S. M. McElvain and C. L. Stevens, *ibid.*, **68**, 1917 (1946).

(4) S. M. McElvain and J. P. Schroeder, *ibid.*, **71**, 40 (1949).

(5) S. M. McElvain and (a) R. L. Clarke, *ibid.*, **69**, 2661 (1947);

(b) C. L. Stevens, *ibid.*, **69**, 2663 (1947).

(6) S. M. McElvain and J. T. Venerable, *ibid.*, **72**, 1664 (1950).

(7) A. Pinner and F. Klein, *Ber.*, **10**, 1892 (1877).