

*Anal.* Calcd. for  $C_9H_{18}O_6$ :  $OCH_3$ , 41.9. Found:  $OCH_3$ , 40.0.

(b) An acid acetone solution (72 cc.) containing 1.927 g. of the product from treatment (a) showed the following changes in specific rotation.

Time, min.	5	14	19	24	30	101
$[\alpha]_D$	+36.4°	+40.2°	+43.1°	+40.2°	+39.3°	+37.4°

The 1,4,6-trimethylfructose monoacetone isolated distilled at 100° (0.2 mm.) (bath temperature).

*Anal.* Calcd. for  $C_{12}H_{22}O_6$ :  $OCH_3$ , 35.5. Found:  $OCH_3$ , 34.4.  $n_D$  1.4464;  $[\alpha]_D$  in acetone +17.8° for  $c = 1.85$ .

The purified specimen of 1,4,6-trimethylfructose (0.790 g.) recovered by the hydrolysis of 1.319 g. of the monoacetone derivative showed:  $n_D$  1.4639;  $[\alpha]_D$  in chloroform +29.7° (final value) for  $c = 2.13$ .

The author wishes to express his thanks to Principal Sir James C. Irvine, LL.B., F.R.S., for

his help and advice, and to acknowledge his indebtedness to the Carnegie Trust for the Universities of Scotland for the award of a Research Fellowship.

### Summary

1. Positive and unquestionable evidence has been obtained proving that inulin on methylation and subsequent hydrolysis yields only one trimethylfructose.

2. Two interesting closely related isomeric trimethyl sugars, 3,4,6- and 1,4,6-trimethyl- $\gamma$ -fructose, have been synthesized.

3. The capability of 3,4,6-trimethylfructose monoacetone of existing in isomeric forms has been demonstrated.

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## The Reactivity of Atoms and Groups in Organic Compounds. XIII. The Influence of Structure on the Pyrolysis of Esters of Triphenylacetic Acid<sup>1</sup>

BY JAMES F. NORRIS AND ARTHUR CRESSWELL

It has been shown in this Laboratory that when the members of a series of homologous compounds are heated under fixed conditions the temperatures at which the several compounds first show signs of decomposition at a particular bond vary with the nature of the radicals present.<sup>2</sup>

When ethers of the type  $(C_6H_5)_3C-OR$  were heated<sup>2a</sup> the temperatures at which the bond between the triphenylmethyl radical and the oxygen atom broke indicated the relative labilizing influence toward heat of different alkyl radicals on a carbon-oxygen linkage transmitted through an oxygen atom to which the radical was joined.

In order to gain additional information in regard to the influence of radicals on activating bonds toward heat the temperatures at which the alkyl esters of triphenylacetic acid begin to decompose were studied. In the case of these compounds,  $(C_6H_5)_3C-COO-R$ , the products of pyrolysis, except with the methyl and benzyl esters, are almost exclusively triphenylmethane,

(1) From a part of the thesis of Arthur Cresswell presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

(2) (a) Norris and Young, *THIS JOURNAL*, **52**, 753 (1930); (b) *ibid.*, **52**, 5066 (1930); (c) Norris and Thomson, *ibid.*, **53**, 3108 (1931); (d) Norris and Tucker, *ibid.*, **55**, 4697 (1933).

carbon dioxide, and an olefin.<sup>3</sup> In the pyrolysis of these esters the bonds indicated by lines in the above formula are broken.

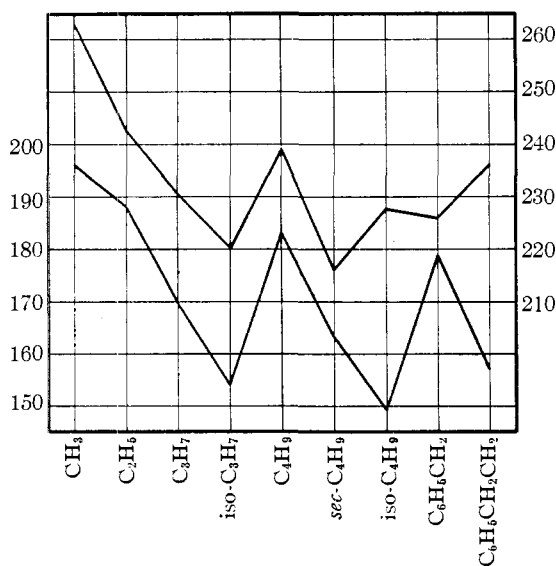
In determining the cracking temperatures of the ethers the compounds were heated at the rate of one degree per minute in the presence of air. In the study of the esters, reported here, different conditions were used to determine whether the order of activating influence was affected by the conditions. The esters were heated in tubes sealed to a small U-shaped mercury manometer and evacuated to about 3 mm. pressure. The tubes were held at a constant temperature for one hour and any change in pressure noted. The temperature at which the first observable increase in pressure (0.1 mm.) occurred after heating for one hour was taken as the cracking temperature.

In order to determine the effect of pressure on the cracking temperature, the normal butyl and the isopropyl esters were heated at constant temperatures in the presence of air at atmospheric pressure and the temperature of cracking determined by the measurement of a bead of mercury in a tube attached to the apparatus in the way

(3) Schmidlin and Hodson, *Ber.*, **41**, 438 (1908), have shown that ethyl triphenylacetate yields, when heated, triphenylmethane, carbon dioxide and ethylene.

already described.<sup>2a</sup> The results were in agreement with those obtained under diminished pressure.

The influence of time of heating was studied with the following results. One gram of isobutyl triphenylacetate (cracking temperature in vacuum 149°) was heated in an evacuated tube connected with a manometer for eighteen hours at 140°, eight hours at 145°, and one hour at 147°. No increase in pressure was observed. At 149° the increase in pressure was 0.5 mm. at the end of one hour. These results show that in the case of these esters heating for a long time is necessary to obtain observable cracking appreciably below the temperatures found by the use of the procedure described above. The differences in the cracking temperatures of the several esters are such that a comparison between them is justified.



Upper curve: cracking temperatures of ethers  $(C_6H_5)_3C-OR$ ; temperatures on the right side of plot.

Lower curve: cracking temperatures of esters  $(C_6H_5)_3CCOOR$ ; temperatures on the left side of plot.

Fig. 1.

The results are shown in the accompanying plot, together with those obtained with the triphenylmethyl ethers containing the same alkyl radicals, to illustrate the relationship between the effects of the several alkyl radicals on the cracking temperatures of the two classes of compounds.

It is evident from the results obtained with the radicals from methyl to secondary butyl that the activating influence of these radicals on the lability toward heat of the bonds broken is similar

in the two series of compounds. This result is unexpected because different types of bonds are broken in the two classes of compounds. In the case of the esters,  $R'-OR$ , it was shown<sup>2a</sup> that the cracking temperatures bore a relationship to the chemical reactivity of the hydrogen-oxygen bond,  $H-OR$ , in the alcohols containing the same alkyl radical. The radical exerted its influence on the labile bond through an oxygen atom.

In the case of the esters,  $R'-COO-R$ , the  $O-R$  bond is broken, and its influence on the carbon-carbon bond which breaks is exerted through an oxygen atom and a carbon atom linked to oxygen. No exact data on the lability of the  $O-R$  bond are available. It is known, however, that as the chemical reactivity of the hydrogen atom in the lower primary aliphatic alcohols decreases the reactivity of the hydroxyl radical also decreases. The results given here indicate that the labilizing influence of the  $O-R$  bond changes progressively with that of the  $-OR$  bond in the case of the first six radicals listed.

When the radicals present in the ethers and esters were isobutyl, phenylmethyl and  $\beta$ -phenylethyl, the effects on cracking temperatures were opposite from those in the cases of the other radicals. It is known in the case of the two aromatic alcohols that the reactivity of the hydroxyl group does not decrease with that of the hydrogen atom.  $\beta$ -Phenylethyl alcohol has the more reactive hydrogen and phenylmethyl alcohol the more reactive hydroxyl group. It is also known that the hydroxyl group of isobutyl alcohol is not very reactive. From these considerations it is understandable why the radicals in these three alcohols lead to different results from those obtained with the others studied.

It should be noted in the comparison of the cracking temperatures of the methyl and ethyl derivatives in the two series that in the case of the ethers the two derivatives break almost exclusively at the alkoxy bond  $RO-$ ,<sup>4</sup> whereas in the case of the esters it is shown in this paper that the methyl derivative cracks largely at this bond while the ethyl ester cracks at the bond between the radical and oxygen  $C_2H_5-O$ .

### Experimental Details

**Preparation of Compounds.**—Triphenylacetic acid was prepared by the action of carbon dioxide on triphenylmethylmagnesium chloride.<sup>5</sup> In the preparation of the

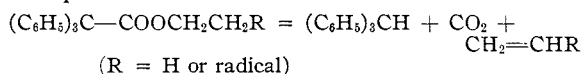
(4) Norris and Cresswell, *THIS JOURNAL*, **55**, 4946 (1933).

(5) Schmidtlin, *Ber.*, **39**, 236 (1906).

latter compound the method of Gilman and Zoellner<sup>6</sup> was used. When 74 g. of triphenylmethyl chloride was used the yields of acid obtained varied from 67 to 82%.

**Triphenylacetyl Chloride.**—This compound was prepared from the acid by the action of thionyl chloride, after experience had shown that the older methods in which the halides of phosphorus were used gave a product difficult to purify. Twenty grams of the crude acid, dried in a vacuum and finely ground, was refluxed for two hours in an all-glass apparatus with 50 cc. of the chloride. At the end of this time the acid had dissolved. The excess of thionyl chloride was distilled off under diminished pressure and the residue dissolved in benzene and refluxed with 0.5 g. of norite. The solution was filtered, evaporated until crystals began to form and allowed to cool. The acyl chloride after washing with petroleum ether and drying in a vacuum weighed 18 g. The yields varied between 83 and 95%. The chloride was sparingly soluble in boiling ligroin, from which it crystallized in thick white needles that melted at 123.5–124°. Schmidlin and Hodson<sup>5</sup> record the melting point 128° after several recrystallizations.

dioxide, carbon monoxide, olefins, and saturated hydrocarbons. Carbon monoxide was found only in the cases noted in Table III. The hydrocarbons were not identified. The pyrolysis takes place, almost exclusively, except in the case of the methyl and benzyl esters, according to the equation



In determining the amount of olefin present the strength of sulfuric acid used in the absorption was that required to react quantitatively with the compound formed. In the case of all the esters, with the exception of the benzyl compound, triphenylmethane was shown to be the chief solid product formed. The hydrocarbon was identified by its melting point and a mixed melting point with a sample of the pure triphenylmethane. The results are given in Table II.

It will be seen from Table II that the decomposition of the methyl and benzyl esters was different from that involved in the pyrolysis of the other esters. The formation

TABLE I  
PROPERTIES OF THE ESTERS OF THE FORMULA  $(C_6H_5)_3CCOOR$

Radical	Heated, hours	Yield, %	M. p., °C.	Crystal form	Notes
CH <sub>3</sub>	10	81	184–185	Rect. plates	9.5 g. chloride, 150 cc. CH <sub>3</sub> OH; 150 cc. C <sub>6</sub> H <sub>6</sub> added to dissolve ester. Cryst. on cooling
C <sub>2</sub> H <sub>5</sub>	8	80	116–117	Fib. needles	8.5 g. chloride, 100 cc. C <sub>2</sub> H <sub>5</sub> OH. V. s. C <sub>2</sub> H <sub>5</sub> OH, C <sub>6</sub> H <sub>6</sub> and ligroin
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	10	..	98–99	Feath. needles	V. s. ligroin
<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	12	56	83.5–84.5	Large hex. plates	From 10 g. chloride. 4 g. triphenylacetic acid formed as by-product. Much less sol. than normal ester
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	8	87	99–99.6	Fib. needles	V. s. Dist. slight dec. 81–82° at 7 mm.
<i>iso</i> -C <sub>4</sub> H <sub>9</sub>	10	93	88–89	Rhomb. needles	V. s. in usual solvents
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	10	57	101–102	Needles	Less s. than normal ester
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	10	30	76–76.5	Silky needles	V. s. C <sub>6</sub> H <sub>6</sub> , CCl <sub>4</sub> , lig.
<i>iso</i> -C <sub>5</sub> H <sub>11</sub>	10	..	77.5–78	Asbestos-like needles	V. s. in usual solvents
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Sev.	..	84–84.5	Silky needles	V. s. in lig.
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	20	..	99–99.5	Rect. needles	5 g. chloride, 10 cc. C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH used. V. s. C <sub>6</sub> H <sub>6</sub> , CCl <sub>4</sub> , M. s. lig.
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	20	63	92.5–93	Light yellow prisms	Decol. norite

**Preparation of Esters of Triphenylacetic Acid.**—The esters were prepared by refluxing triphenylacetyl chloride with an excess of the pure anhydrous alcohol, in the proportion of 10 g. of the former to 50 cc. of the latter unless otherwise stated in the tabulation. The time of refluxing varied and was dependent on the rate at which the acyl chloride dissolved. The excess of solvent was distilled off under diminished pressure and the residue of ester was crystallized from ligroin (b. p. 70–95°). The preparation and properties of the following esters have not been reported, *n*-C<sub>3</sub>H<sub>7</sub>, *iso*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *iso*-C<sub>4</sub>H<sub>9</sub>, *sec*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>, *n*-C<sub>6</sub>H<sub>13</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>. All of these were analyzed for carbon and hydrogen. Duplicate analyses checked closely and were in excellent agreement with the calculated values.

**Pyrolysis of the Esters of Triphenylacetic Acid.**—The esters (from 0.5 to 2 g.) were heated rapidly to boiling and the gases formed measured and analyzed for carbon

of formaldehyde from the methyl ester indicates that the bond of the alkoxyl group is broken as is the case when the methyl ether  $(C_6H_5)_3C-OCH_3$  decomposes and produces the aldehyde. The high percentage of carbon monoxide formed from the benzyl ester indicates that it too breaks at the similar bond. It is probable that benzaldehyde was a product of the pyrolysis.<sup>7</sup> The results in these two cases are in line with other observations which show that when there is the opportunity to form an olefin from a radical that contains two carbon atoms the pyrolysis of an ester will take place in this way.

**Determination of Cracking Temperatures.**—The esters were heated in glass tubes of 10 mm. internal diameter with a capacity of 5 cc. A small U-manometer containing mercury was sealed to each tube. The ester was carefully melted to release adsorbed gas and the tube was evacuated to a pressure of about 3 mm. and then sealed.

(7) Hurd, "Pyrolysis of Carbon Compounds," p. 538, has shown that benzyl benzoate gives benzaldehyde as one product of pyrolysis.

(6) Gilman and Zoellner, THIS JOURNAL, 51, 3493 (1929).

TABLE II  
PRODUCTS OF PYROLYSIS OF THE ESTERS (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCOOR

Radical	CO <sub>2</sub> in gaseous	Olefin products, %	Remarks
CH <sub>3</sub>	12	0	Gas contained 8% CO. 61.9% absorbed in H <sub>2</sub> O (formald.) and 18% satd. HC.
C <sub>2</sub> H <sub>5</sub>	46.7	41	Resid. satd. gas burned pale blue flame
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	50	49.5	Vol. of gas equiv. to 80% dec.
iso-C <sub>3</sub> H <sub>7</sub>	46	53	83% decomposition
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	40	40	Ester heated two days at 270-300°. Resid. gas air
iso-C <sub>4</sub> H <sub>9</sub>	47	47	Resid. gas burned pale blue flame; 84% dec.
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	50.7	41.1	8.2% gas burned pale blue flame
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	37	..	42.4% CO. Resid. gas air
β-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	76	..	1.7% CO. Residual gas air. 0.5 g. pyrolyzed. Gas coll. over Hg with trap to condense vol. liquids. 0.2 cc. liquid. Micro b. p. 143°. Index refr. at 25° 1.566. Styrene, b. p. 144°. Index at 20°, 1.547

The tubes were heated to a constant temperature in a vapor-bath for twenty minutes to ensure thermal equilibrium and the manometer was read. The tube was then heated for one hour and any increase in pressure noted. Since the vapor pressure of the ester was constant, any increase in pressure was due to the gaseous products of

cracking. An increase of 1 mm. at 150-200° in a tube of 5 cc. capacity would correspond to approximately 0.003% decomposition of the ethyl, propyl and butyl esters.

Preliminary experiments made by heating tubes in the vapors of several boiling liquids showed the temperature ranges within which decomposition took place. To obtain the intermediate temperatures an apparatus was designed in which the tubes were heated by the vapor of a liquid boiling under a pressure that could be varied. For temperatures between 170 and 210°, nitrobenzene and between 145 and 179.5° *p*-cymene were used. If a tube showed no increase in pressure at the end of one hour, the temperature was raised five degrees. If the tube then showed an increase the temperature was dropped 2° and another reading made. It is believed that the temperatures of decomposition were measured to an accuracy of 2°. The cracking temperatures of the esters were as follows: CH<sub>3</sub> 196°, C<sub>2</sub>H<sub>5</sub> 188°, *n*-C<sub>3</sub>H<sub>7</sub> 169°, iso-C<sub>3</sub>H<sub>7</sub> 154°, *n*-C<sub>4</sub>H<sub>9</sub> 183°, *sec*-C<sub>4</sub>H<sub>9</sub> 163°, iso-C<sub>4</sub>H<sub>9</sub> 149°, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> 179° and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub> 157°.

### Summary

1. The following esters of triphenylacetic acid were prepared: CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, iso-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *sec*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>, iso-C<sub>5</sub>H<sub>11</sub>, *n*-C<sub>6</sub>H<sub>13</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>.

2. The temperatures at which the esters first began to show signs of decomposition when heated for one hour (the cracking temperatures) were determined.

3. The influence of a change in the radical present on the cracking temperatures is compared with another series of compounds containing the same radicals.

CAMBRIDGE, MASS.

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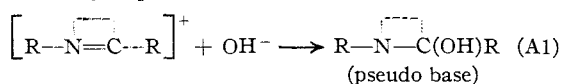
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

## Pseudo Bases. IV. The Mechanism of Formation of Dimolecular Ethers from Pseudo Bases. The Aromatic Nature of Heterocyclic Compounds<sup>1</sup>

BY JOHN G. ASTON AND PERCIVAL A. LASSELLE

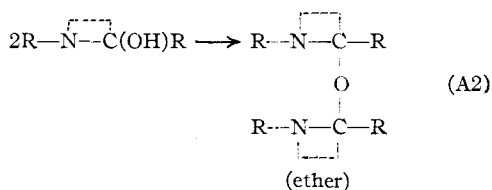
### Introduction

The pseudo basic systems in the quinoline series have long been known to yield dimolecular ethers by loss of a molecule of water from two molecules of the pseudo base. This reaction has been formally represented<sup>2</sup>



(1) Submitted in partial fulfillment of the requirements for the Ph.D. Degree.

(2) Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899).



when  $\overset{\text{---}}{\text{N}}=\overset{\text{---}}{\text{C}}$  represents the quinoline nucleus.

It has been shown<sup>3</sup> that 1,2,5-trimethylpyrazinium hydroxide disappears slowly from its aqueous solution by a reaction of the second order with

(3) Aston, *THIS JOURNAL*, **53**, 1448 (1931).