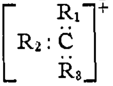
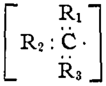
The stability of the spatial arrangement of the groups in tricovalent carbonium ions,  $\left[\begin{array}{c} R_1 \\ R_2:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} \\ R_3 \end{array}\right]^+$ has been studied, and evidence has been submitted which indicates that in the absence of a special mechanism which leads to Walden inversion such configurations are optically unstable.

The optical instability of free radicals  $\left[\begin{array}{c} R_1 \\ R_2:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}\cdot \\ R_3 \end{array}\right]$ has been demonstrated: by the loss of optical activity when *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was allowed to react with triphenylmethyl; by the production of an inactive hydrocarbon in the electrolysis of *l*- and *d*-potassium methylethylacetate; and by the production of an inactive hydrocarbon by the action of metallic sodium on *d*- and *l*-α-bromobibenzyl and *d*-2-bromobutane.

A discussion of these results is given in the light of certain theories which have been proposed for the constitution of these tricovalent compounds.

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Radical Interchange on the Part of Certain Alkyl Orthoformates[1]

BY HOWARD W. POST AND EDWIN R. ERICKSON

Early work on aliphatic ortho esters, while outlining their preparation and properties, has mentioned as well their instability. Triethyl orthoformate for example is not as stable as are the orthoformates of the higher aliphatic alcohols, but no further suggestions have been advanced on this point to date. Compounds of this type have been prepared from the corresponding alcoholate[2] and from the alcohol and hydrogen cyanide.[3]

It was our original purpose to test the relative reactivity of some alcoholates of simple aliphatic alcohols by mixing one mole of chloroform with three moles each of two different alcoholates and determining the identities of the products but the problem soon resolved itself into a study of the reaction

$$HC(OR)_3 + HC(OR')_3 \rightleftharpoons HC(OR)_2OR' + HC(OR')_2OR \qquad (1)$$

The Reaction of Chloroform with Alcoholate Mixtures.—One equivalent of chloroform was added to a mixture of 1.5 equivalents each of two

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[1] Presented at the Spring Meeting, American Chemical Society, March, 1933, at Washington, D. C.

[2] Deutsch, *Ber.*, **12**, 117 (1897); Claisen, *ibid.*, **31**, 1010 (1898); Sah and Ma, THIS JOURNAL, **54**, 2964 (1932); "Organic Syntheses," Vol. V, 1925, p. 55.

[3] Pinner, *Ber.*, **16**, 356 and 1643 (1883).

aliphatic alcoholates, the system being stirred gently. These proportions gave better yields than 1:3:3. The results are summarized below.

TABLE I

$CHCl_3 + RONa + R'ONa$

	R	R'	$HC(OR)_3$, %	$HC(OR)_2OR'$, %	$HC(OR')_2OR$, %	$HC(OR')_3$, %	Total yield, %
1	C_3H_7-	C_4H_9-	27.4	26.0[a]	31.6[a]	15.0	55.0
2	C_3H_7-	i-C_5H_{11}-	28.0	29.8	32.3	9.9	41.0
3	C_3H_7-	C_5H_{11}-	23.9	32.3[a]	30.9[a]	12.9	50.2
4	C_2H_5-	C_4H_9-	12.6	42.1[a]	35.9[a]	9.4	42.1
5	C_2H_5-	C_3H_7-	2.7	41.9	39.5	16.1	34.0

[a] Identified by boiling point only.

It will be noted that in any reaction such as indicated in Equation 1 using the alcoholates specified in Table I there is a strong tendency for the mixed esters to form at the expense of those whose alkyl radicals are all alike.

The physical constants of these simple and mixed orthoformates may be found in the literature[2] and for purposes of identification we confined ourselves to determinations of boiling points, refractive indices and densities. It was found necessary to determine refractive index and density immediately after distillation to obtain consistent results.

TABLE II

PHYSICAL DATA

Ester	B. p., °C.	n^{20}_D	d^{23}_4	Mol. wt.	
				Calcd.	Found
$HC(OC_2H_5)_3$	145 (747 mm.) 60 (30 mm.)	1.3915	0.8964	148.13	148.6
$HC(OC_2H_5)_2OC_3H_7$	165 (747 mm.) 81 (30 mm.)	1.3989	.8813	162.1	160.6
$HC(OC_2H_5)_2SC_2H_5$	76–80 (17 mm.)	1.4397	.9451 (20°/4°)	164.2	165.7
$HC(OC_3H_7)_3$	190–191 (745 mm.) 93 (30 mm.)	1.408	.879	190.2	189.9
$HC(OC_3H_7)_2OC_2H_5$	184 (745 mm.) 93 (30 mm.)	1.4031	.8973 (22°/4°)	176.2	175.5
$HC(OC_3H_7)_2OC_5H_{11}$-i	124–130 (24 mm.)	1.415	.8647	218.2	216.0
$HC(OC_5H_{11}$-$i)_3$	166 (25 mm.)	1.4242	.858	274.3	272.2
$HC(OC_5H_{11}$-$i)_2OC_3H_7$	140–147 (30 mm.)	1.4194	.8626	246.2	244.4

Using the formula $N = M(n^2 - 1)/d(n^2 + 2)$.

After standing for thirty days samples of mixed esters when distilled gave fractions which identified by boiling points, refractive indices and densities represented all four possibilities—$HC(OR)_3$, $HC(OR)_2OR'$, $HC(OR')_2OR$ and $HC(OR')_3$. This reaction took place in the case of every mixed ester prepared during the course of this work.

A mixture of pure $HC(OC_3H_7)_3$ and pure $HC(OC_5H_{11}$-$i)_3$ in equimolar amounts was set aside to stand for one month at room temperature. At the end of that time fractional distillation at low pressures showed that an interchange of radicals had taken place but that the two middle fractions were not present in as large amount as the first and fourth

$$HC(OC_3H_7)_3 + HC(OC_5H_{11}\text{-}i)_3 \rightleftharpoons HC(OC_3H_7)_2OC_5H_{11}\text{-}i + HC(OC_5H_{11}\text{-}i)_2OC_3H_7 \quad (2)$$

Diethyl propyl orthoformate reacted in the presence of phosphorus pentoxide to give all four possible orthoformates. It may seem at first that the interaction of two molecules of this ester under these conditions may have been catalyzed by hydrogen ion, but this can hardly be so because the pure orthoformates containing like alkyl groups did not hydrolyze when similarly treated. With only a small amount of water present, hydrolysis does take place, however.

Propyl orthoformate reacted with absolute ethyl alcohol to give four possibilities as well as the two alcohols

$$HC(OC_3H_7)_3 + C_2H_5OH \rightleftharpoons C_3H_7OH + HC(OC_3H_7)_2OC_2H_5\text{, etc.} \quad (3)$$

Yields were: $HC(OC_2H_5)_3$ 2.1%, $HC(OC_2H_5)_2OC_3H_7$ 42.0%, $HC(OC_3H_7)_2OC_2H_5$ 40.0% and $HC(OC_3H_7)_3$ 15.9%. Of course it is probable here that as soon as more than one orthoformate appears it may react with some other orthoformate as well as with one of the alcohols.

Ethyl mercaptan was allowed to stand in contact with triethyl orthoformate in a sealed tube at room temperature for one week. On distillation triethyl orthoformate and monothiotriethyl orthoformate came over. There was a higher boiling fraction but we were not able to isolate anything therefrom

$$HC(OC_2H_5)_3 + C_2H_5SH \rightleftharpoons C_2H_5OH + HC(OC_2H_5)_2SC_2H_5 \quad (4)$$

Experimental Part

Preparation of the Mixed Esters.—The alcohols were purchased from the Eastman Kodak Co. and then dehydrated. To prepare the alcoholates 3 equivalents of clean sodium was dissolved in an excess of the desired alcohol, and the two solutions of alcoholates were mixed. To this system a solution of chloroform in a little mixed alcohols was added dropwise with gentle stirring. All outlets of the system were closed with calcium chloride tubes. Care must be taken lest the temperature rise too high. The reaction was completed in about an hour and a half but it was found that the yield could be increased by allowing the mixture to stand several hours longer. Half a gram of hydroquinone acts as an inhibitor of oxidation here.

Sodium chloride was removed by suction, excess alcohols distilled at atmospheric pressure and the mixture of products fractionated at reduced pressures, generally 30 mm. Refractionations gave pure products.

Reactions of Esters.—The reactions of the mixed esters were brought about simply by allowing them to stand as already described.

Molecular refractions were calculated from the values for the various atoms found in the current literature.[4]

Discussion

We have shown that an equilibrium is immediately set up when two different orthoformates are mixed at room temperatures. This equilibrium reaction consists of the interconversion of the four esters $HC(OR)_3$, HC-

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(4) Landolt and Börnstein, "Physikalisch-chemische Tabellen," Vol. II, p. 985 (5th ed.).

$(OR')_2OR$, $HC(OR)_2OR'$ and $HC(OR')_3$. Only a small amount of the two mixed esters is obtained when propyl orthoformate and isoamyl orthoformate are mixed, as compared with a larger amount of the two mixed compounds using esters of lower molecular weights. This may be explained by assuming that reaction is preceded by decomposition into fragments, this decomposition being known to be less rapid in the case of the higher homologs. Similar reactions with alcohols and mercaptans seem to involve transfer of OR rather than R.

Summary

1. At room temperatures the mixed orthoformates thus far investigated isomerize to a mixture of all four possible esters, this reaction taking place almost instantaneously over phosphorus pentoxide.

2. At room temperatures two orthoformates react with interchange of radicals, the yield of products varying, as far as observation has gone, inversely as the radical weights involved.

3. Tripropyl orthoformate reacts with absolute ethyl alcohol, giving a mixture of the four possible orthoformates and two alcohols. Ethyl mercaptan reacts with triethyl orthoformate giving the mono thio compound.

BUFFALO, N. Y.

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Polymerization of Diolefins with Olefins. II. Function of Pentene-2 in the Polymerization of Isoprene

BY CHAS. ALLEN THOMAS AND WM. H. CARMODY

In the previous paper[1] it was reported that when pure isoprene, in which there was no appreciable amount of olefin present, was placed in contact with anhydrous aluminum chloride, there was no temperature rise or any other obvious chemical reaction, even when a considerable proportion of anhydrous aluminum chloride had been added. It was shown that an olefin, such as pentene-2, added to the isoprene–aluminum chloride mix, started the reaction immediately; and that in polymerizing isoprene and pentene-2 by aluminum chloride, there were two solid polymers formed, one insoluble and the other soluble in hydrocarbon solvents. The amount of the soluble polymer formed is proportional to the pentene-2 present, while the amount of the insoluble polymer varies inversely with the amount of pentene-2 present.

The purer the isoprene, the more inert it is toward aluminum chloride. Very pure isoprene can be obtained by converting it into the tetrabromide

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[1] Thomas and Carmody, THIS JOURNAL, **54**, 2480 (1932).