Blum[10] and Tsuji and Ohno[11] recently reported the decarbonylation of acyl chlorides and bromides by tris(triphenylphosphine)rhodium chloride.

We wish now to report our observation on the decarbonylation of aroyl fluorides and in particular, observations relating to catalytic decarbonylation.

Decarbonylation of benzoyl fluoride by tris(triphenylphosphine)rhodium chloride was observed in reactions carried out either in excess, neat benzoyl fluoride, or using solvents like benzene, toluene, *o*-xylene, and α-methylnaphthalene. Best results were obtained either in reactions in neat benzoyl fluoride or in *o*-xylene as solvent. Reactions were carried at 80–120° heating the reaction mixture for 1 hr, then distilling off products and analyzing by glpc, infrared, and nmr spectroscopy. Decarbonylation of aroyl fluorides is a fairly general reaction. Besides benzoyl fluoride, *p*-toluoyl fluoride, *m*-chloro-, *p*-chloro-, and *p*-fluorobenzoyl fluoride yielded the corresponding substituted fluorobenzenes. The decarbonylations are quantitative, based on the amount of aryl fluorides formed and tris(triphenylphosphine)rhodium chloride used.

It was also found that the reactions are catalytic to the degree that 280–580% mole equiv of fluoroaromatic compounds can be formed (Table I) before the activity of the rhodium chloride "catalyst" is lost.

TABLE I

DECARBONYLATION OF AROYL FLUORIDES TO ARYL FLUORIDES BY TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE

| Aroyl fluoride | Product aryl fluoride | % conversion before deactivation of catalyst |
|---|---|---|
| Benzoyl | Fluorobenzene | 580 |
| *p*-Toluoyl | *p*-Fluorotoluene | 470 |
| *m*-Toluoyl | *m*-Fluorotoluene | 530 |
| *p*-Chlorobenzoyl | *p*-Chlorofluorobenzene | 350 |
| *m*-Chlorobenzoyl | *m*-Chlorofluorobenzene | 280 |
| *p*-Fluorobenzoyl | *p*-Difluorobenzene | 340 |

In a typical experiment, a mixture of 2.5 ml of *m*-toluoyl fluoride, 0.5 g of tris(triphenylphosphine)rhodium chloride, and 0.1 g of *o*-xylene (as internal reference standard) were heated for 3 hr at reflux temperature in 10 ml of toluene. The red color of the original reaction mixture changes to yellow and a precipitate forms. After filtration the solution was analyzed by glpc (using a Perkin-Elmer Model F-11 vapor fractometer equipped with a 12-ft Carbowax M-20 filled column). From the ratio of the *m*-fluorotoluene/*o*-xylene peaks the yield of *m*-fluorotoluene found was 0.37 g (530%), based on the amount of catalyst used. Product identification was also achieved by collecting, under semipreparative conditions, gc samples and obtaining their infrared and nmr spectra which were identical with those of pure *m*-fluorotoluene. Longer reaction times and higher temperatures did not further increase yield and catalyst was found to become inactive. Blum[10] was able to show that decarbonylation of aroyl chlorides and bromides is catalytic, according to the reversibility of the reaction of the rhodium carbonyl compound with triphenylphosphine liberating CO and regenerating the active catalyst.

$$RhCl[(C_6H_5)_3P]_3 + CO \rightleftharpoons RhCl(CO)[(C_6H_5)_3P]_2 + P(C_6H_5)_3$$

(10) J. Blum, *Tetrahedron Letters*, 1605, 3041 (1966).

(11) J. Tsuji and K. Ohno, *ibid.*, 4731 (1966).

The fast deactivation of the same catalyst in the reactions with aroyl fluorides in our view is a consequence of a halogen exchange reaction producing tris(triphenylphosphine)rhodium fluoride, which itself is inactive in decarbonylation reactions.

$$[(Ph)_3P]_3RhCl + ArCOF \longrightarrow [(Ph)_3P]RhF + ArCOCl$$

Aroyl chlorides were identified in the reaction mixtures proving the halogen exchange.

Whereas our work demonstrated the feasibility of the decarbonylation of aroyl fluorides to aryl fluorides, so far the reaction was achieved only by using tris(triphenylphosphine)rhodium chloride as decarbonylating agent. Because rapid chlorine–fluorine exchange deactivates the catalyst, the method is limited at the present time. We are continuing efforts to find a decarbonylating catalyst which would not be deactivated by aroyl fluorides.

**Acknowledgment.**—Support of this work by a grant of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

## Preparation of Alkyl 2,2-Dialkoxypropanoates[1]

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Alkyl 2,2-dialkoxypropanoates have been prepared in one step by treatment of pyruvic acid with dialkoxypropanes in alcohols as shown in eq 1.

$$2CH_3\overset{\displaystyle OR}{\underset{\displaystyle OR}{|}}{C}CH_3 + CH_3\overset{\displaystyle O}{\overset{\|}{C}}CO_2H \xrightarrow[\text{TosOH}]{\text{ROH}} CH_3\overset{\displaystyle OR}{\underset{\displaystyle OR}{|}}{C}CO_2R + 2CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + ROH \quad (1)$$

R = $CH_3$, $C_2H_5$, *n*-$C_3H_7$, allyl, *n*-$C_4H_9$, *i*-$C_4H_9$, *n*-$C_5H_{11}$, *i*-$C_5H_{11}$

The required dialkoxypropanes were readily made from 2,2-dimethoxypropane and the proper alcohol by the method of Lorette and Howard.[2]

$$CH_3\overset{\displaystyle OCH_3}{\underset{\displaystyle OCH_3}{|}}{C}CH_3 + 2ROH \xrightarrow{\text{TosOH}} CH_3\overset{\displaystyle OR}{\underset{\displaystyle OR}{|}}{C}CH_3 + 2CH_3OH \quad (2)$$

Table I summarizes the yields obtained in the preparation of the ketal esters. In general the yields were

(1) (a) This investigation was supported by Public Health Service Grant GM12399 from the National Institute of General Medical Sciences. (b) Presented at the Great Lakes Regional Meeting of the American Chemical Society, Chicago, Ill., June 16–17, 1966.

(2) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).

TABLE I

PREPARATION OF ALKYL 2,2-DIALKOXYPROPANOATES[a]

| Derivative | Reacn time, hr | Reacn temp, °C | Yield, % |
|---|---|---|---|
| Methyl | 12 | 65 | 68 |
| Ethyl | 30 | 78 | 64 |
| *n*-Propyl | 30 | 96 | 67 |
| Allyl | 14 | 100 | 72 |
| *n*-Butyl | 30 | 114 | 66 |
| Isobutyl | 30 | 106 | 62 |
| *n*-Pentyl | 69 | 128 | 65 |
| Isopentyl | 72 | 124 | 61 |

[a] $CH_3COCO_2H$, 0.062 mole; $(RO)_2C(CH_3)_2$, 0.20 mole; ROH, 0.30 mole; TosOH, 1.1 mmoles.

60–70%. The reaction time was long in most cases. The reaction was followed by gas chromatography. When the amount of product leveled off, the reaction was quenched with sodium alkoxide, the mixture was distilled, and the product was finally isolated by preparative gas chromatography. The reaction times listed, therefore, are reasonably accurate. Table I shows the reaction temperature varied from one derivative preparation to the next. Also, no common solvent was used from one preparation to another. No conclusions can be reached from these data, then, regarding the effect of structure on reactivity.

However, some knowledge of the reaction path was gained by studying the formation of the methyl derivative in detail by gas chromatography. When the reactants and catalyst were combined, a rapid production of acetone and decrease in dialkoxypropane occurred. No other change was observed. This implies that the product formed in addition to acetone did not elute from the gas chromatographic column. The most reasonable coproduct was the ketal acid

TABLE II

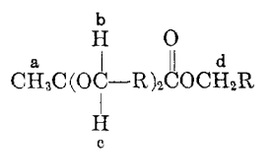
ANALYSIS AND PHYSICAL PROPERTIES OF ALKYL 2,2-DIALKOXYPROPANOATES

$CH_3C(OR)_2CO_2R$

| R | Registry No. | Bp, °C (mm) | $n^{25}D$ | $d^{25}_4$ | Formula | Carbon, % Calcd | Carbon, % Found | Hydrogen, % Calcd | Hydrogen, % Found | Sapon equiv Calcd | Sapon equiv Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 10076-48-9 | 62–63 (12) | 1.4092 | 1.0600 | $C_6H_{12}O_4$ | 48.64 | 48.85 | 8.16 | 8.18 | 148 | 148 |
| $C_2H_5$ | 7476-20-2 | 70–71 (10) | 1.4112 | 0.9728 | $C_9H_{18}O_4$ | 56.82 | 57.08 | 9.54 | 9.60 | 190 | 188 |
| *n*-$C_3H_7$ | 10076-50-3 | 88–89 (4) | 1.4200 | 0.9382 | $C_{12}H_{24}O_4$ | 62.04 | 62.31 | 10.41 | 10.43 | 232 | 230 |
| Allyl | 10076-51-4 | 102–103 (4) | 1.4497 | 0.9899 | $C_{12}H_{18}O_4$ | 63.70 | 64.09 | 8.02 | 7.90 | 226 | 224 |
| *n*-$C_4H_9$ | 10076-52-5 | 110–111 (10) | 1.4302 | 0.9213 | $C_{15}H_{30}O_4$ | 65.66 | 65.72 | 11.02 | 11.01 | 274 | 273 |
| *i*-$C_4H_9$ | 10076-53-6 | 105–106 (3) | 1.4210 | 0.9057 | $C_{15}H_{30}O_4$ | 65.66 | 65.85 | 11.02 | 10.96 | 274 | 273 |
| *n*-$C_5H_{11}$ | 10076-54-7 | 133–134 (3) | 1.4344 | 0.9112 | $C_{18}H_{36}O_4$ | 68.31 | 68.65 | 11.47 | 11.33 | 316 | 317 |
| *i*-$C_5H_{11}$ | 10076-55-8 | 138–139 (4) | 1.4328 | 0.9039 | $C_{18}H_{36}O_4$ | 68.31 | 68.55 | 11.47 | 11.20 | 316 | 317 |

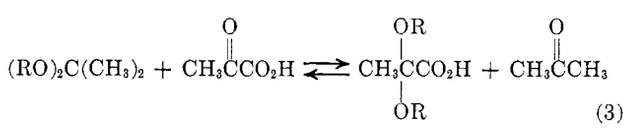
TABLE III

CHARACTERISTIC NMR ABSORPTION[a]



| R | Assignment | Chemical shift, ppm | Multiplicity[b] | Assignment | Chemical shift, ppm | Multiplicity[b] |
|---|---|---|---|---|---|---|
| H | a | 1.58 | 1 | b | 3.42 | 1 |
| H | c | | | d | 3.96 | 1 |
| $CH_3$ | a | 1.53 | 1 | b | 3.57 | 4 |
| $CH_3$ | c | 3.57[c] | 4 | d | 4.27 | 4 |
| $C_2H_5$ | a | 1.57 | 1 | b | 3.45 | m |
| $C_2H_5$ | c | 3.48 | m | d | 4.17 | 3 |
| $CH_2$=CH | a | 1.60 | 1 | b | 4.07 | m |
| $CH_2$=CH | c | 4.10 | m | d | 4.70 | m |
| *n*-$C_3H_7$ | a | 1.55 | 1 | b | 3.48 | m |
| *n*-$C_3H_7$ | c | 3.52 | m | d | 4.22 | 3 |
| *i*-$C_3H_7$ | a | 1.53 | 1 | b | 3.23 | m |
| *i*-$C_3H_7$ | c | 3.27 | m | d | 3.96 | 2 |
| *n*-$C_4H_9$ | a | 1.53 | 1 | b | *Ca.* 3.5 | m |
| *n*-$C_4H_9$ | c | *Ca.* 3.5 | m | d | 4.20 | 3 |
| *i*-$C_4H_9$ | a | 1.53 | 1 | b | 3.50 | m |
| *i*-$C_4H_9$ | c | 3.53 | m | d | 4.23 | 3 |

[a] When R = alkyl, absorption with complex splitting was observed at approximately 0.7–2 ppm. When R = vinyl, absorption and complex splitting was observed at 5–6.3 ppm. [b] *m* = multiple. [c] Chemical shift from b barely discernible.



shown in eq 3. Like pyruvic this acid would not be expected to elute from the column. Thus, at least part of the ketal ester product probably arises by way of a ketal acid.

Table II presents analytical results and physical properties of the alkyl 2,2-dialkoxypropanoates. The physical properties of the methyl and ethyl derivatives, the only ketal esters reported previously, agree with published values.[3,4] However, no proof of structure was reported previously. Elemental analysis and the method of preparation indicated only two possible isomers, the alkyl 2,2-dialkoxypropanoate and the alkyl orthopyruvate. Ortho esters are generally not saponifiable. The products prepared as described above were saponifiable.

Conclusive evidence that the ketal esters were indeed the products of the pyruvic acid reaction was obtained by nmr. The methyl ortho ester would have had two peaks in a 3:1 intensity ratio, whereas the methyl ketal ester would have three peaks in ratios 1:2:1. The latter type of spectrum was found. The methyl derivative peaks were then used to identify absorptions in the spectra of the other seven derivatives. The identifiable peaks are listed in Table III. All intensity ratios agreed with those for the structures claimed.

Nmr offers one other kind of evidence for the ketal ester structural assignment. The two $\alpha$ protons of the ketal alkoxy groups in the higher derivatives should have been nonequivalent[5] and, therefore, have dif-

(3) L. Claisen, *Ber.*, **29**, 2931 (1896).
(4) K. Auwers, *ibid.*, **44**, 3514 (1911).
(5) P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **47**, 49 (1961).

ferent chemical shifts and additional splitting, whereas the $\alpha$ protons would be equivalent in the ortho ester. What was actually observed was a chemical shift difference and complex splitting of the $\alpha$ protons.

Table IV lists the principal infrared peaks of the alkyl 2,2-dialkoxypropanoates that are characteristic and identifiable. Broad absorption owing to C—O stretching was observed in the 8.5- to 9.0-$\mu$ region. The broadness was probably the result of overlap of the ketal and ester C—O stretching bands. The absorption in the 13.1-$\mu$ region was present in all of the derivatives and could be the most useful in identifying these ketal esters. It has been tentatively assigned to ester stretching.

TABLE IV
CHARACTERISTIC INFRARED BANDS ($\mu$)

| Derivative | C=O stretch[a] | Ester[a] | C—O stretch, ester and ketal (very broad)[a,b] | Ester[c] |
|---|---|---|---|---|
| Methyl | 5.67 | 7.73 | 8.20–9.00 | 13.11 |
| Ethyl | 5.70 | 7.77 | 8.35–9.00 | 13.14 |
| *n*-Propyl | 5.72 | 7.80 | 8.50–9.00 | 13.14 |
| Allyl | 5.72 | 7.81 | 8.48–9.02 | 13.10 |
| *n*-Butyl | 5.70 | 7.80 | 8.50–9.00 | 13.10 |
| Isobutyl | 5.70 | 7.80 | 8.52–8.98 | 13.10 |
| *n*-Pentyl | 5.75 | 7.84 | 8.60–9.00 | 13.16 |
| Isopentyl | 5.72 | 7.80 | 8.60–9.00 | 13.17 |

[a] Strong. [b] Occasionally resolved slightly into more than one band. [c] Medium to weak; tentative assignment.

### Experimental Section[6]

**Preparation of 2,2-Dialkoxypropanes.**—The dialkoxypropanes were prepared according to the method of Lorette and Howard.[2] Redistilled Eastman 2,2-dimethoxypropane and alcohols were used. Three new 2,2-dialkoxypropanes were prepared.

**2,2-Diisobutoxypropane** had bp 56–57° (4 mm), $d^{25}_4$ 0.8205, $n^{25}D$ 1.4036. *Anal.* Calcd for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.11; H, 12.50.

**2,2-Di-*n*-pentoxypropane** had bp 79–80° (4 mm), $d^{25}_4$ 0.8337, $n^{25}D$ 1.4170. *Anal.* Calcd for $C_{13}H_{28}O_2$: C, 72.17; H, 13.05. Found: C, 72.20; H, 13.11.

**2,2-Diisopentoxypropane** had bp 71–72° (4 mm), $d^{25}_4$ 0.8259, $n^{25}D$ 1.4136. *Anal.* Calcd for $C_{13}H_{28}O_2$: C, 72.17; H, 13.05. Found: C, 71.71; H, 12.71.

**Preparation of Alkyl 2,2-Dialkoxypropanoates.**—Eastman pyruvic acid was carefully distilled under vacuum, and an anhydrous fraction was taken for further work. The quantities of reactants, solvent, and catalyst shown in Table I were combined in a 250-ml, round-bottom flask. One drop of methyl sulfoxide was added[7] and the solution was refluxed. Periodically samples were removed and analyzed on an Aerograph Model 90 CS gas chromatograph with the use of a 5 ft × 0.25 in. 8% Dow 702 silicone on 60–80 mesh Celite column. When gas chromatography showed reaction was complete, the mixture was distilled slowly until approximately 25 ml was collected. A 10% sodium alkoxide solution was added until the reaction mixture was alkaline to wet litmus. Distillation was continued at reduced pressure and the alkyl 2,2-dialkoxypropanoate was collected over the boiling point range shown in Table II. The product was further purified by preparative gas chromatography with the use of the instrument mentioned above and a 5 ft × 0.5 in. 20% SE30 silicone on 60–80 mesh Celite column.

**Nmr and Infrared.**—Nmr spectra were measured on a Varian Model A-60 instrument.[8] The infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer.

(6) Microanalyses by Drs. G. Weiler and F. B. Strauss, Microanalytical Laboratory, Oxford, England.

(7) P. G. Simmonds and A. Zlatkis, *Anal. Chem.*, **37**, 302 (1965).

(8) The authors wish to thank Dr. J. R. Vercellotti for obtaining the spectra.

**Registry No.**—2,2-Diisobutoxypropane, 10076-56-9; 2,2-di-*n*-pentoxypropane, 10076-57-0; 2,2-diisopentoxypropane, 10294-76-5.

## Preparation and Deamination of 6$\beta$-Amino-17$\beta$,19-dihydroxy-3$\alpha$,5$\alpha$-cycloandrostane

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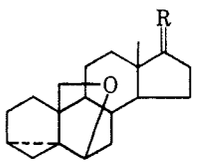
*Received December 1, 1966*

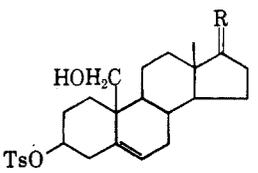
Kinetically controlled solvolyses of steroid $\Delta^5$-3$\beta$-*p*-toluenesulfonates[1] and deaminations of steroid $\Delta^5$-3$\beta$-amines[2] lead to 6$\beta$-substituted 3$\alpha$,5$\alpha$-cyclo steroids[3] *via* homoallylic cation intermediates. It has been shown that the presence of a hydroxyl group at $C_{19}$, which might conceivably effect intramolecular solvation of the $\beta$ face of the homoallylic cation at $C_6$, does not alter the stereochemistry of kinetically controlled hydrolysis.[4]

The present study was undertaken to determine the effect of a 19-hydroxyl group on the stereochemistry of reaction at $C_6$ of a steroid 19-hydroxy-3$\alpha$,5$\alpha$-cyclo-6-carbinyl cation generated under both ammonolysis and deamination conditions.

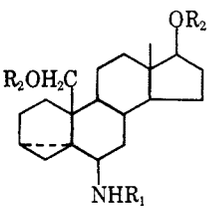
Thermodynamically controlled, acid-catalyzed solvolyses of 6$\beta$,19-oxido-3$\alpha$,5$\alpha$-cyclo steroids have been found to give rise to 19-hydroxy-$\Delta^5$-3$\beta$-substituted steroids in which the 3$\beta$ substituent is derived from the conjugate base of the solvent.[5] In the present work, brief treatment of the 6$\beta$,19-oxido-3$\alpha$,5$\alpha$-cyclo steroids Ia[5a] and Ib with excess *p*-toluenesulfonic acid in an-




Ia, R = O
b, R = 17$\beta$-OH and 17$\alpha$-H




IIa, R = O
b, R = 17$\beta$-OH and 17$\alpha$-H




IIIa, $R_1 = R_2 = H$
b, $R_1 = R_2 = COCH_3$
c, $R_1 = COCH_3$; $R_2 = H$

(1) N. L. Wendler in "Molecular Rearrangements," Part 2, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1075.

(2) J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4615 (1962).

(3) An exception has been noted by L. A. Freiberg, *ibid.*, **30**, 2476 (1965), who found that both 3$\alpha$,5$\alpha$-cyclo-6$\alpha$ and -6$\beta$ azides were formed on treatment of cholesteryl *p*-toluenesulfonate with sodium azide in several solvent systems.

(4) R. M. Moriarty and T. D. J. D'Silva, *Tetrahedron*, **21**, 547 (1965).

(5) (a) K. Tanabe, R. Takasaki, K. Sakai, R. Hayashi, and Y. Morisawa, *Chem. Pharm. Bull.* (Tokyo), **10**, 1126 (1962). (b) J. Tadanier, *J. Org. Chem.*, **28**, 1744 (1963). (c) R. M. Moriarty and T. D. J. D'Silva, *ibid.*, **28**, 2445 (1963).