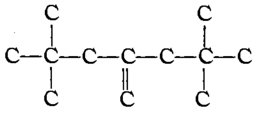
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

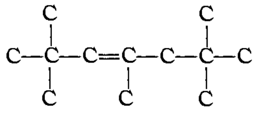
# Polymerization of Olefins. VII.[1] The Isolation and Oxidation of 1,1-Dineopentylethylene

BY FRANK C. WHITMORE AND J. D. SURMATIS

The publication on this subject by Bartlett and his associates,[2] prompted us to assemble work done with this substance during the studies of the triisobutylenes in this Laboratory.[3]

Fractional distillation of triisobutylene obtained by the action of acid catalysts on isobutylene or on *t*-butyl alcohol gives fractions boiling at about 177 and 185° in a ratio of 9:1. The present work deals with the more abundant lower boiling isomers. These have been shown to be olefins with the skeletons[3]


I


II

In ozonolyses and chromic acid oxidations of the triisobutylenes since 1932 the recovery of unchanged 1,1-dineopentylethylene (I) in 15–20% yields has been observed repeatedly. This agrees with the results obtained by Bartlett with permanganate.[2] Disregarding smaller runs, a total of 200 kg. of triisobutylene has been oxidized by various workers in this Laboratory during the past nine years. Because of our need for dineopentylacetic acid[4] for other studies, the accumulated 33 kg. of 1,1-dineopentylethylene has now been oxidized by sodium dichromate and sulfuric acid at 50–60° to give the following percentage yields: dineopentylacetic acid, 25; dineopentyl ketone, 1.9; unchanged 1,1-dineopentylethylene, 46. Other products were trimethylacetic acid, *t*-butylacetic acid, methyl neopentyl ketone and 300 g. of higher ketones which are being studied further.

## Experimental

**Equipment.**—The oxidations were carried out in a 50-gal. Pfaudler glass-lined jacketed kettle provided with an anchor type stirrer, thermocouple and an efficient condenser fitted to serve either for reflux or take-off. The jacket could be supplied with high pressure steam, cold water or mixtures of water and steam.

**Special Still.**—The column had a jacketed electrically heated Pyrex pipe section 10 ft. by 2 in. packed with 0.5 in. carbon rings. It was attached to a 10-gal. stainless steel electrically heated pot. The column was equivalent to 15 theoretical plates.

**Oxidation of Triisobutylene.**—Eight runs were made at various times; a typical one is described. The sodium dichromate, 40 kg., was placed in the kettle with 75 liters of water. The triisobutylene, 25 kg., $n^{20}_{\rm D}$ 1.4325, from Röhm and Haas Company of Philadelphia, was added to the kettle and oxidized at 50–60° by adding 40 liters of concentrated sulfuric acid with stirring over a period of twelve hours. The stirring was continued for two additional hours. The mixture was then steam distilled by introducing high pressure steam at 140° into the jacket. The distillation was continued until a solid appeared in the distillate. The separated oil was freed from organic acids by alkali extraction, water washed and fractionated through the large capacity 15-plate column. Among the products of oxidation was obtained 4.5 kg. of 1,1-dineopentylethylene, b. p. 112–113° at 100 mm., $n^{20}_{\rm D}$ 1.4288.

**Oxidation of 1,1-Dineopentylethylene.**—To the kettle was added 80 liters of water, 36 kg. of sodium chromate and 35 liters of concentrated sulfuric acid. The dineopentylethylene, 33.6 kg., 200 moles, b. p. 112–113° at 100 mm., $n^{20}_{\rm D}$ 1.4288 was added in portions to the oxidizing mixture over a period of thirty-two hours at 50–60° with stirring. The temperature was then raised to 80° by introducing steam into the jacket and the stirring was continued for an additional thirty-five hours. The oxidation products were then steam distilled until a solid appeared in the distillate. The contents of the kettle were cooled and the solid crystalline layer that formed was removed mechanically through an opening in the top of the kettle. This on recrystallization from methanol gave pure dineopentylacetic acid, m. p. 93–94°, 9.9 kg., a yield of 24.7%.

The oil obtained as steam distillate was freed of organic acids by extracting with a solution of 800 g. of sodium hydroxide in 20 kg. of the water layer from the steam distillate. The oil was then siphoned off and water washed. There was obtained 17.5 kg. of oil, $n^{20}_{\rm D}$ 1.4289. On fractionation through the 15-plate column, there were obtained fractions 6–53, 15.7 kg., 46.7% of unoxidized 1,1-dineopentylethylene, b. p. 112–113° at 100 mm., $n^{20}_{\rm D}$ 1.4288. Fractions 1–5 inclusive, on refractionation through a smaller 15-plate column, gave 185 g. of methyl neopentyl ketone b. p. 123–124° at 740 mm., $n^{20}_{\rm D}$ 1.4038, along with 140 g. of material b. p. 148–150° at 730 mm., $n^{20}_{\rm D}$ 1.4160–70, which gave a 2,4-dinitrophenylhydrazone, m. p. 164–165°. Fractions 54–56 on refractionation through a 15-plate column and then refractionation through a 25-plate column gave 650 g., 1.9% yield of dineopentyl ketone, b. p. 183–185° at 740 mm., $n^{20}_{\rm D}$ 1.4210, along with 150 g. of a higher boiling residue.

The water layer from the alkali extraction of the oil, on

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[1] Whitmore and Meunier, THIS JOURNAL, **63**, 2197 (1941).

[2] Bartlett, Fraser and Woodward, *ibid.*, **63**, 495 (1941).

[3] Whitmore, Wilson, Capinjola, Tongberg, Fleming, McGrew and Cosby, *ibid.*, **63**, 2035 (1941).

[4] Whitmore and Wilson, *ibid.*, **56**, 1397 (1934).

acidification with sulfuric acid and extraction with four liters of benzene yielded 337 g. of a liquid acid mixture. On fractionation through a 25-plate column there were obtained fractions 1–10 inclusive, 150 g. of trimethylacetic acid m. p. and mixed m. p. of its anilide 130–131°, and fractions 11–20 inclusive, 109 g. of *t*-butylacetic acid, m. p. and mixed m. p. of its anilide 128–129°. The third component in the mixture was identified as dineopentylacetic acid, m. p. and mixed m. p. of its anilide 165–166°

## Summary

1. The considerable resistance of 1,1-dineopentylethylene to oxidation has been confirmed.

2. 1,1-Dineopentylethylene can be readily obtained in about 15% yields from the oxidation of crude triisobutylene.

3. The oxidation of 1,1-dineopentylethylene by chromic acid mixture gives about 25% of dineopentylacetic acid and 50% of unchanged olefin.

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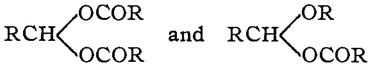
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# Acylals

BY CHARLES D. HURD AND FRANK O. GREEN

Ethers, acetals, esters and acid anhydrides all contain the C–O–C grouping. So also do such compounds as $CH_3CH(OCOCH_3)_2$ and $C_2H_5OCH_2OCOCH_3$, but these belong to none of the above four classifications. The general term "acylal" has been assigned[1] to compounds of this class. In general, an acylal function is a C–O–C grouping wherein one of the two carbons is in the aldehyde state of oxidation and the other is in the acid state of oxidation. For contrast, the C–O–C of acetals is an aldehyde-alcohol combination and that of esters an acid-alcohol combination.

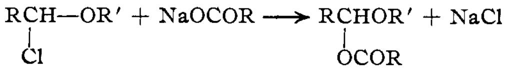
The present study is devoted to the chemistry of acylals of these two general formulas



$$RCH\begin{cases}OCOR\\OCOR\end{cases} \quad \text{and} \quad RCH\begin{cases}OR\\OCOR\end{cases}$$

Strictly speaking the latter contains both acetal and acylal functions but it is convenient to refer to both types as acylals. There is no terminology for this class of substances as yet, but names comparable to those developed for acetals would assist in the visualization of these functional groups. Systematic names will be used in this paper.

1-Alkoxyalkyl chlorides were used in the synthesis of several mixed acetal-acylals in accordance with the equation



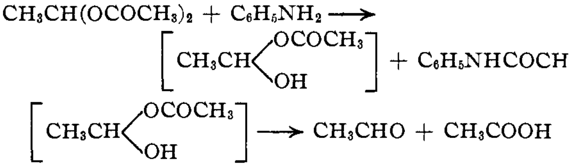
$$\underset{\displaystyle Cl}{RCH}\text{—}OR' + NaOCOR \longrightarrow \underset{\displaystyle OCOR}{RCHOR'} + NaCl$$

Except for 1-ethoxyethyl acetate, $CH_3CH(OC_2H_5)OCOCH_3$, which Claisen[2] made by the reaction of acetic anhydride and ethyl acetal, no simple mixed acylals above the formaldehyde derivatives have been reported. Several such mixed acylals, $CH_2(OR)OCOR$, were prepared by Fife, Clark and Garland.[3] Another substance of this type which has been reported is 2,2,2-trichloro-1-ethoxyethyl acetate,[4] $CCl_3CH(OC_2H_5)OCOCH_3$. It was prepared by the reaction of acetyl chloride and chloral alcoholate. A list of the several acetal acylals formed in the present investigation together with their physical properties is submitted in Table I. Analytical results are included also. All combustions except that for 1-propoxyethyl propionate were carried out by Mr. Ernest Washburn.

Calculation of the molecular refractivities of the fourteen new compounds showed close agreement with the values obtained with the Lorenz-Lorentz formula, $M(n^2 - 1)/d(n^2 + 2)$.

Several new reactions of acylals were investigated. Ethylidene acetate was used throughout since it was the most readily available acylal. The reactions studied were those with aniline, hydroxylamine, and chlorine.

Acetanilide, acetic acid and acetaldehyde were the products of reaction with aniline. From the results it is apparent that only one of the two acetate radicals functions as an acetylating agent and the intermediate hemiacylal decomposes spontaneously.



$$CH_3CH(OCOCH_3)_2 + C_6H_5NH_2 \longrightarrow \left[CH_3CH\begin{cases}OCOCH_3\\OH\end{cases}\right] + C_6H_5NHCOCH_3$$

$$\left[CH_3CH\begin{cases}OCOCH_3\\OH\end{cases}\right] \longrightarrow CH_3CHO + CH_3COOH$$

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[1] Hurd and Cantor, THIS JOURNAL, **60**, 2678 (1938).

[2] Claisen, *Ber.*, **31**, 1018 (1898).

[3] Fife, Clark and Garland, THIS JOURNAL, **47**, 2421 (1925).

[4] Meyer and Dulk, *Ann.*, **171**, 69 (1874).