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# Unsaturated Ketones. I. The Preparation and Polymerization of Perfluoroalkyl Propenyl Ketones[1]

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A series of perfluoroalkyl propenyl ketones has been prepared and their preparation has been described in detail along with the infrared and ultraviolet absorption spectra. Some polymerizations and copolymerizations of these new monomers have been described and the properties of a variety of new copolymers have been recorded.

This Laboratory has undertaken a study of the preparation and polymerization of $\alpha,\beta$-unsaturated ketones. This paper deals with the synthesis and polymerization reactions of a series of three perfluoroalkyl propenyl ketones.

**Monomer Synthesis.**—It has been shown previously that Grignard reagents react readily with perfluorocarboxylic acids to give alkyl perfluoroalkyl ketones in good yields.[2] Therefore, it was assumed that $\beta,\gamma$-unsaturated ketones could be prepared by treating perfluorocarboxylic acids with allylmagnesium bromide and that these ketones could be rearranged to the $\alpha,\beta$-unsaturated derivatives.

Accordingly, three moles of allylmagnesium bromide were added to one mole of $C_3F_7CO_2H$ or to two moles of $C_3F_7CO_2Li$ in ether to yield fraction I (b.p. 100–115°) and fraction II (b.p. 116.7°). Infrared absorption spectra of the two fractions showed that fraction I had two sharp carbonyl absorption bands, on eat 5.64 $\mu$ and the other at 5.78 $\mu$, while fraction II had a single carbonyl absorption band at 5.78 $\mu$. Both fractions showed a strong C=C band at 6.11 $\mu$. Haszeldine[3] has reported that fluorine-containing ketones having the structure $R_fCOCH_2$– have a strong carbonyl absorption frequency at 5.65 $\mu$. Fraction I, therefore, contains $C_3F_7COCH_2CH{=}CH_2$ (A) accounting for the absorption frequency at 5.64 $\mu$. Since the number of possible hyperconjugation structures is two for A and three for $C_3F_7COCH{=}CHCH_3$ (B), the $\alpha,\beta$–$\beta,\gamma$ equilibrium of the unsaturated ketone should favor the $\alpha,\beta$-derivative.[4] Therefore, A should isomerize to the conjugated system B, thus shifting the carbonyl absorption frequency to the longer wave length 5.78 $\mu$. Refractionation of fraction I after standing several weeks yielded almost entirely fraction II (B). The conjugated structure of B has been confirmed by nuclear magnetic resonance spectrum. Therefore, the reaction of $C_3F_7CO_2H$ or its lithium salt with allylmagnesium bromide produces the $\beta,\gamma$-unsaturated ketones which rearrange slowly to the $\alpha,\beta$-unsaturated derivatives. Compound B was obtained in 40–50% yields using both procedures. Similar yields were obtained using both $CF_3CO_2H$ and $n$-$C_7F_{15}CO_2H$. These $\alpha,\beta$-unsaturated ketones also showed the strong carbonyl absorption frequency at 5.78 $\mu$ and the C=C absorption frequency at 6.11 $\mu$. The physical constants of the $\alpha,\beta$-unsaturated ketones are shown in Table I.

As shown in Table II, the fluorine-containing ketones have the characteristic ultraviolet absorption spectra of unfluorinated vinyl ketones.

It can be seen that as the electron-attracting power of the terminal group R increases, the K- and R-bands are displaced to longer wave lengths. However, the K-band is only displaced to 237 m$\mu$ when R is $CF_3$ while $n$-$C_3F_7$ and $n$-$C_7F_{15}$ causes a shift to 242 m$\mu$. This indicates that the electron-withdrawing effect of $n$-$C_3F_7$ and $n$-$C_7F_{15}$ are about equal but greater than that of $CF_3$. Henne and Fox[5] have previously shown by determining the ionization constants of $C_3F_7CO_2H$ and $CF_3CO_2H$ that the $C_3F_7$ group is more electron withdrawing than the $CF_3$ group.

**Polymerization.**—Homopolymerization of the fluorine-containing unsaturated ketones could not be accomplished using either bulk, solution or emulsion recipes. These ketones did, however, undergo copolymerization with a variety of vinyl monomers such as acrylonitrile, ethyl acrylate, styrene and vinyl acetate. Properties of these copolymers are listed in Table III.

Perfluoropropyl propenyl ketone has also been copolymerized with $m$-trifluoromethylstyrene and 1,1-dihydroperfluorobutyl acrylate. Products were a white powder and a sticky gum, respectively. Incorporation was confirmed by infrared analysis. No further characterization was made. An attempted copolymerization of the perfluoropropyl propenyl ketone with benzalacetophenone in a bulk recipe failed to give any polymeric product. $n$-Butyl vinyl ether copolymers could not be prepared using either bulk or emulsion recipes. In the attempted copolymerization of the perfluoroalkyl propenyl ketones with maleic anhydride only maleic acid was isolated. An attempted Diels–Alder reaction yielded the same product.

As a group, the perfluoroalkyl propenyl ketones exhibit polymerization reactivity similar to that of other $\beta$-substituted-$\alpha,\beta$-unsaturated ketones such as benzalacetophenone and its analogs.[6] Incorporation of the ketones with acrylonitrile and ethyl acrylate is small, whereas large amounts of ketone are incorporated with styrene. One noticeable difference between the fluorine-containing ketones and benzalacetophenone or benzalacetone is the

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[1] Presented before the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956.

[2] K. T. Dishart and R. Levine, THIS JOURNAL, **78**, 2268 (1956).

[3] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

[4] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1950, p. 281.

[5] A. L. Henne and C. J. Fox, THIS JOURNAL, **73**, 2323 (1951).

[6] (a) C. S. Marvel, W. R. Peterson, H. K. Inskip, J. E. McCorkle, W. K. Taft and B. G. Labbe, *Ind. Eng. Chem.*, **45**, 1542 (1953); (b) C. S. Marvel, J. Quinn and J. S. Showell, *J. Org. Chem.*, **18**, 1730 (1953); (c) C. S. Marvel, L. E. Coleman, Jr., and G. P. Scott, *ibid.*, **20**, 1785 (1955).

TABLE I

PHYSICAL PROPERTIES OF UNSATURATED KETONES, $R_fCOCH{=}CHCH_3$

| $R_f$ | B.p. °C. | B.p. Mm. | $n^{20}D$ | $d^{20}_4$ | $AR_f$ | Analyses[a] Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Fluorine, % Calcd. | Fluorine, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_3$ | 85–86 | 757 | 1.3583 | 1.189 | 1.33 | 43.45 | 43.32 | 3.62 | 3.40 | 41.30 | 41.40 |
| $n$-$C_3F_7$ | 116.7 | 745 | 1.3400 | 1.366 | 1.37 | 35.29 | 35.39 | 2.10 | 2.18 | 55.88 | 55.68 |
| $n$-$C_7F_{15}$ | 55.0–55.5 | 5 | 1.3340 | 1.624 | 1.30 | 30.14 | 30.13 | 1.14 | 1.20 | 65.07 | 65.10 |

[a] Analysis were carried out by the Schwartzkopf Microanalytical Laboratory, Woodside, N. J.

TABLE II

ULTRAVIOLET SPECTRA OF $\alpha,\beta$-UNSATURATED KETONES, $RCOCH{=}CHCH_3$

| R | K-band λmax | K-band E | R-band λmax | R-band E |
|---|---|---|---|---|
| $CH_3$ | 224 | 9.750 | 313.5 | 38 |
| $CF_3$ | 237 | 1.800 | 322 | 20 |
| $n$-$C_3F_7$ | 242 | 5.600 | 322 | 45 |
| $n$-$C_7H_{15}$ | 242 | 5.800 | 322 | 50 |

TABLE III

BULK POLYMERIZATIONS OF PERFLUOROALKYL PROPENYL KETONES WITH VINYL MONOMERS

| Comonomer | Polym. time, hr. | Conversion, % | Inherent viscosity (benzene) | Softening point, °C. | Change ratio ketone/comonomer | Fluorine, % | Ketone incorp. wt. % | Appearance of polymer |
|---|---|---|---|---|---|---|---|---|
| | | | Perfluoromethyl propenyl ketone | | | | | |
| Acrylonitrile | 7 | 35 | 0.8[a] | >275 | 40/60 | Trace | 5[b] | Powder |
| Ethyl acrylate | 7 | 25 | | | 30/70 | 3.7 | 9 | Gum |
| Vinyl acetate | 48 | 25 | 0.9 | 90–95 | 40/60 | 23.6 | 57 | Powder |
| Styrene | 7 | 55 | 0.5 | 145–150 | 40/60 | 14.0 | 34 | Powder |
| | | | Perfluoropropyl propenyl ketone | | | | | |
| Acrylonitrile | 7 | 40 | 0.85[a] | >275 | 40/60 | Trace | 5[b] | Powder |
| Ethyl acrylate | 7 | 25 | | | 30/70 | 7.5 | 13 | Gum |
| Vinyl acetate | 48 | 40 | 0.57 | 83–88 | 40/60 | 36.8 | 65 | Powder |
| Styrene | 7 | 50 | 0.30 | 140–145 | 40/60 | 27.5 | 50 | Powder |
| | | | Perfluoroheptyl propenyl ketone | | | | | |
| Acrylonitrile | 7 | 45 | 1.7[a] | >275 | 40/60 | 4.4 | 7 | Powder |
| Ethyl acrylate | 7 | 25 | | | 30/70 | 15.5 | 24 | Gum |
| Vinyl acetate | 48 | 40 | 0.7 | 75–80 | 40/60 | 49.4 | 75 | Powder |
| Styrene | 7 | 50 | 0.3 | 130–135 | 40/60 | 33.6 | 52 | Powder |

[a] Inherent viscosity determined in N,N'-dimethylformamide. [b] Estimated from infrared spectrum.

copolymer formation of the former with vinyl acetate. Benzalacetophenone and similar ketones did not yield copolymers.

In comparing the reactivity of the three ketones described in this paper, it was observed that as the size of the perfluoroalkyl group increased, the reactivity increased and the rate decreased. An estimation of the reactivity ratios of the fluorine-containing ketones with styrene ($M_1$) indicated that the perfluoropropyl- and perfluoroheptyl-derivatives were similar ($r_1$ = 0.5–0.7; $r_2$ = 0) while the perfluoromethyl propenyl ketone ($r_1$ = 1.0; $r_2$ = 0) was less reactive. On an over-all basis, perfluoropropyl propenyl ketone indicated optimum utility as a comonomer. A forthcoming paper will discuss the copolymerization of these ketones with various 1,3-dienes.

## Experimental

Three moles of allylmagnesium bromide in two liters of diethyl ether was prepared in a cyclic reactor.[7]

One mole of perfluorocarboxylic acid in an equal volume of ether was added dropwise with stirring to the Grignard reagent which was cooled in an ice-bath. After stirring overnight at room temperature, the reaction mixture was hydrolyzed by pouring into ice–concentrated hydrochloric acid. The ether layer was separated and the water layer extracted with three 100-ml. portions of ether. The combined ether layers were dried over Drierite and distilled to remove the ether; the residual liquid was then dried over phosphoric anhydride and fractionally distilled through an efficient column. In each case, a lower boiling fore-cut was obtained which upon redistilling after several weeks of standing yielded additional propenyl ketone.

An alternate procedure for the ketone preparation was accomplished by treating equivalents of perfluorocarboxylic acid and metallic lithium in a small quantity of ether to give the lithium perfluorocarboxylate. After addition of one liter of ether to two moles of the lithium salt, the solution was cooled in an ice-bath and three moles of allylmagnesium bromide in three liters of ether was added dropwise with stirring. The reaction was run overnight at room temperature and the mixture was worked up as described above. Using either procedure, the yields of the perfluoroalkyl propenyl ketones were 40–50%.

**Polymerization.**—Bulk, solution and emulsion recipes were used. Bulk polymerizations were run at 60° with benzoyl peroxide as catalyst. For solution polymerization, benzene or N,N'-dimethylformamide was used as solvent. The emulsion recipes consisted of Office of Synthetic Rubber soap, potassium persulfate as initiator and dodecyl mercaptan as modifier. Occasionally Dupanol ME was used as an emulsifier. Reactions were run at 50°. In all cases, screw cap bottles were used with Buna N type gaskets.

The incorporation of the propenyl ketones into copolymers was determined by elemental analysis and confirmed by the infrared absorption frequency of the ketone carbonyl band which shifted from 5.78 $\mu$ in the monomer to 5.65–5.70 $\mu$ in the polymer.

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(7) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 23.