LETTERS TO THE EDITOR

Preparation of N,N-Dibutyl-9(10)-dibutylphosphonooctadecanamide by Ultraviolet Initiated Addition of Dibutyl Phosphite to N,N-Dibutyloleamide

Sir: The free radical addition of dibutyl phosphite to terminal and internal double bonds of monounsaturated amides has been initiated by exposure to γ radiation from cobalt-60 with reported yields of ca. 90% (Mod, Harris, Arthur, Magne, Sumrell, and Novak, JAOCS 49:634 [1972]). Addition of dibutyl phosphites to olefins containing terminal and nonterminal double bonds also has been initiated by the presence of peroxides or UV light with reported yields of ca. 45-75% (Stiles, Vaughan, and Rust, J. Amer. Chem. Soc. 80:714 [1958]; Sasin, Olszewski, Russell, and Swern, Ibid. 81:6275 [1959]; Swern, Palm, Sasin, and Witnauer, Chem. Eng. Data 5:484 [1960]). However, attempts to initiate the reaction of dibutyl phosphite with alkyl oleates by exposure to UV light from a high pressure quartz mercury-arc lamp were unsuccessful, and the reactants were recovered unchanged (Sasin, Olszewski, Russell, and Swern, J. Amer. Chem. Soc. 81:6275 [1959]). We, therefore, wish to report that the reaction of internal double bonds in these systems was initiated by exposure to UV light with wavelengths absorbed by the reactants to give substituted amides in high yields.

N,N-Dibutylphosphonooctadecanamide was prepared from a mixture of N,N-dibutyloleamide (1 mol) and dibutyl phosphite (3 mol). Ca. 10 g mixture were placed in a quartz tube, mixed, and exposed to UV light, 21-35 watts at 50 C. The maximum absorption of UV light by dibutyl phosphite was 2200 Å, and that of amide, ca. 2700 Å. After irradiation the mixtures were removed from the photochemical reactor, dissolved in Skelly B, passed through a column of activated alumina to remove excess dibutyl phosphite, and then stripped of Skelly B.

The IR spectra of the products established the presence of phosphonates and the absence of phosphites. NMR spectra confirmed the presence of phosphonate and amide.

The initiation of the addition of the reactants on exposure to UV light from lamps with maximum wavelengths of ca. 2537 Å for ca. 17 hr gave products in ca. 90% yield. These lamps also would emit UV light with wavelengths that had maximum absorption by the reactants. After exposure of the reactants to UV light from eight lamps (2537 Å), plus eight lamps (3500 Å), for 17 hr, the product formed in ca. 98% yield and had elemental analyses for N,N-dibutyl-9(10)-dibutylphosphonooctadecanamide as follows: C: found 69.55%, calculated 69.46%; H: found 12.14, calculated 12.01; N: found 2.28, calculated 2.38; and P: found 5.17, calculated 5.27.

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Potential Hazards of $HClO_4$ in Heated Systems Where Esters are Involved

Sir: This letter is prompted by concern for the safety of those who might use the $HClO_4$-catalyzed method for transesterification of triglycerides reported by P.J. Mavrikos and G. Eliopoulos (JAOCS 50:174 [1973]). Considerable experience with $HClO_4$, particularly with organic compounds, leads me to conclude that the value of $HClO_4$, particularly in heated systems where esters are involved, is far overshadowed by its potential hazards. In the acidic nonaqueous medium described, perchloratoesters of the glycerine (or partial glycerides) may form. Such esterifications are acid-catalyzed. The resulting esters are highly unstable; they are sensitive to both heat and shock, and are particularly sensitive to trituration. For example, the monoperchloratoester of ethylene glycol is thermally and shock sensitive; it explodes at the slightest provocation. The diester has not been successfully prepared. No perchlorate esters of glycerine have been prepared intentionally to my knowledge. I would expect them to be similarly hazardous, however. The use of methyl alcohol provides further jeopardy. Since ethyl perchlorate is also a highly explosive material, I would expect methyl perchlorate to be equally as bad.

Other strong acid catalysts, which are just as effective and yet reasonably inexpensive, include p-toluenesulfonic acid; fluorosulfonic acids; and 2,4,6-trinitrobenzenesulfonic acid. Ample articles in various literature describe their safe, effective use.

Transesterification procedures are used widely, often in routine applications by people with only modest chemical training. To minimize possible problems for those who want to use this procedure, I recommend that, if $HClO_4$ is to be used, the reaction be carried out behind a sturdy safety shield and that all materials be disposed of in an appropriate fashion, such as dilution with water and flushing down the drain with copious amounts of water.

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