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TRIMETHYLSILYL POLYPHOSPHATE (PPSE). A USEFUL REAGENT FOR THE BECKMANN REARRANGEMENT

Tsuneo Imamoto*, Hideki Yokoyama, and Masataka Yokoyama
Department of Chemistry, Faculty of Science, Chiba University,
Yayoi-cho, Chiba City, Japan

Summary: Various oximes were rearranged smoothly to the corresponding amides in trimethylsilyl polyphosphate (PPSE) which was conveniently prepared from phosphorus pentoxide and hexamethyldisiloxane.

The Beckmann rearrangement is one of the most important reactions for the preparation of amides and has wide spread synthetic applications.[1] Therefore, a number of experimental procedures involving reagents have been developed.[1-6] Among them, readily available polyphosphoric acid (PPA) has been frequently used for the rearrangement.[3,7-9] This reagent, however, is a viscous liquid and has low solvent power at room temperature, so that the reaction in this medium should be usually carried out at elevated temperatures.

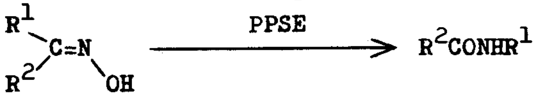
We intended to exploit a new reagent for the Beckmann rearrangement, which is easily prepared and has good solvent power at room temperature. After many trials, it was found that phosphorus pentoxide (10 g) dissolved within a short time (ca. 1 h) in a refluxing mixture of hexamethyldisiloxane (21 ml) and organic solvent (40 ml) such as dichloromethane, chloroform, or benzene under argon atmosphere. The solution thus resulted was colorless, volatile liquid, and had a good solvent power to dissolve many kinds of organic substances.

Using this new reagent, trimethylsilyl polyphosphate (polyphosphoric acid trimethylsilyl ester: PPSE),[10] we tried the rearrangement of oximes. A typical experimental procedure is as follows; acetophenone oxime (201 mg, 1.49 mmol) was dissolved in a benzene solution (4.5 ml) of PPSE at room temperature. After 6 h, the reaction mixture was treated with water (7 ml) and then extracted with dichloromethane. The combined extracts were dried over Na_2SO_4, and evaporated under reduced pressure. The crystalline material obtained was purified by thin layer chromatography on silica-gel to afford acetanilide (193 mg, 96%).

In a similar manner, various oximes were converted into the corresponding amides in good yields. The results are listed in Table 1. A noteworthy fact is that 4,4-diethoxycarbonyl-3,5-diphenylcyclohexanone oxime was rearranged without hydrolysis of ester moiety (Entry 9).

The reagent (PPSE) is, different from PPA, essentially aprotic, and is similar to ethyl polyphosphate (PPE).[11,12] In order to compare both reagents,

Table 1. The Beckmann rearrangement of oximes using PPSE



Entry	R^1	R^2	Solvent	Reaction time (h)	Yield (%)
1	C_6H_5	CH_3	C_6H_6	6	96
2	C_6H_5	C_6H_5	C_6H_6	20	94
3	C_6H_5	$C_6H_5CH_2$	C_6H_6	18	92
4	C_6H_5	$C_6H_5CH=CH-$	CH_2Cl_2	0.5	57
5	C_6H_5		CH_2Cl_2	20	76
6	$4\text{-}ClC_6H_4$	CH_3	CH_2Cl_2	3.5	92
7	$C_6H_5CH_2$	$C_6H_5CH_2$	C_6H_6	38	76
8	$-(CH_2)_5-$		C_6H_6	15	69
9	$-CH_2CH(C_6H_5)C(CO_2C_2H_5)_2CH(C_6H_5)CH_2-$		CH_2Cl_2	12	63
10	$-(CH_2)_7-$		C_6H_6	15	52

we next tried the Beckmann rearrangement of several oximes listed in Table 1, using a chloroform solution of PPE.[13] In any cases, the reaction proceeded smoothly at room temperature, and the corresponding amides were isolated in satisfactory yields (78-97%).

Both reagents gave similar results, but PPSE is superior to PPE with respect to the preparation of the reagent. The former reagent can be easily obtained, while the preparation of the latter one needs long time.[11,12]

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