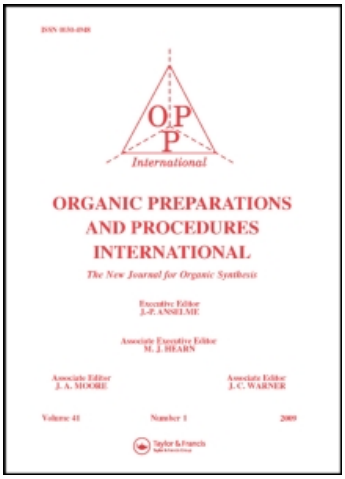

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Rolland M. Waters[a]; N. Wakabayashi[a]; E. S. Fields[a]
[a] Agricultural Environmental Quality Institute Agricultural Research Service USDA, Beltsville, Maryland

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BECKMANN REARRANGEMENTS USING THE CARBON TETRACHLORIDE-TRIPHENYLPHOSPHINE REAGENT

Rolland M. Waters*, N. Wakabayashi, and E. S. Fields

Agricultural Environmental Quality Institute
Agricultural Research Service, USDA[1]
Beltsville, Maryland 20705

The Beckmann rearrangement of ketoximes to amides is well known.[2] The vigorous conditions[3] such as concentrated acids or free halogens[4] generally required are not universally applicable. We have found that the carbon tetrachloride-triphenylphosphine reagent[5] will effect the Beckmann rearrangement on a variety of alkanone oximes. The rearrangement proceeds under mild, neutral conditions to give amides in yields of 50-70%.

$$R_2C{=}NOH + PPh_3 + CCl_4 \xrightarrow{(H_2O)} RNHCOR + Ph_3PO + CHCl_3 + HCl$$

Conditions varied from room temperature (THF solvent) to the reflux temperatures of CCl_4 and THF. No special handling precautions appeared to be necessary, although the rearrangements were run under reasonably anhydrous conditions to prevent oxidation of the phosphine to its oxide by the action of water and CCl_4.[6] Reaction times varied from 2.0 hr (refluxing CCl_4 and THF) to 94 hr (room temperature, THF). One special relationship was noted namely, if an excess of the reagent was used in THF, the yield was critically dependent on time of reaction, and IR monitoring [disappearance of the 3325 cm^{-1} band (N-OH), appearance of the 1665 cm^{-1} band (C=O)] was necessary; however, if nearly equivalent amounts of reagents were used, no such monitoring was needed. The results are summarized in Table I.

Table I. Beckmann Rearrangement of Alkanones

	OXIME	AMIDE (Major isomer)	Solv.	TEMP C°	TIME Hrs	REAGENT OXIME	YLD[a] %
1	$Me_2C{=}CH(CH_2)_2\overset{Me}{C}{=}N{\sim}OH$	$Me_2C{=}CH(CH_2)_2NHCOMe$	CCl_4	Refl.	4.0	1.2:1	50
2	"	"	THF	"	2.0	2:1	60-70[b,c]
3	"	"	"	"	8.0	1.1:1	60[d] 70
4	"	"	"	25	94	1.1:1	70[b]
5	$\underline{n}\text{-}C_6H_{13}\overset{Me}{C}{=}N{\sim}OH$	$\underline{n}\text{-}C_6H_{13}NHCOMe$	"	Refl.	6.0	1.1:1	80
6	"	"	CCl_4	"	6.0	1:1	80
7	"	"	"	"	3.0	1.5:1	68
8	$\underline{n}\text{-}C_4H_9\overset{Et}{C}{=}N{\sim}OH$	$\underline{n}\text{-}C_4H_9NHCOEt$	"	"	1.5	1.1:1	80[e]
9	$\underline{n}\text{-}C_3H_7\overset{Me}{C}{=}N{\sim}OH$	$\underline{n}\text{-}C_3H_7NHCOMe$	THF	"	6.0	1.2:1	40
10	$\underline{i}\text{-}C_3H_7\overset{Me}{C}{=}N{\sim}OH$	$\underline{i}\text{-}C_3H_7NHCOMe$	"	"	6.0	1.2:1	60-70[b]

a. All yields by glpc unless otherwise noted; b. Yield by IR analysis; c. Decreased to 20% by 8.0 hrs; d. Distilled; e. The isomeric amides did not separate under our glpc conditions.

Mechanistic details were not investigated. The fact that the amide apparently formed directly and the expected imidoyl chloride was not observed first indicated the probable presence of water despite our precautions. Nevertheless, the similarity between our results and those of Yamato et al.,[7] reinforces our belief that the fundamental mechanism operant here is essentially the same as theirs although the intermediacy of the N-chloroimine has not been proven. The oximes were mixtures.

The ratio of syn/anti forms of the methyl ketoximes were determined (glpc, nmr), to be 70-84/30-16. (Syn-meaning the hydroxy and methyl groups are cis). In these cases, the products appeared (nmr, glpc) to consist mainly (96:4) of the amides derived from the syn-oximes.

The fate of the anti-isomer was not determined. The IR indicated complete loss of the 3325 cm^{-1} band (N-OH) and hence a transformation of the anti-isomer. The less than 100% yield of amide (based on total oxime mixture) and the 96:4 ratio of isomeric amides produced suggests that the anti-isomer was converted neither in any quantity to its corresponding amide nor to the amide derived from the syn-isomer.

EXPERIMENTAL

All product amides were known compounds. In addition, they were prepared by independent routes and checked by nmr, ir, and glpc. The nmr was a Varian T-60, the IR a Perkin-Elmer 137, the glpc analyses were performed using 5% Carbowax 20M-TPA on base-washed 80-100 mesh Chromosorb G in a Varian 600-D with FID.

Beckmann Rearrangements in CCl_4.- To a 100 ml round bottom flask equipped with a reflux condenser (drying tube), magnetic stirrer, and heating mantle, was introduced a mixture of 1.4 g (10 mmole) of 2-octanone oxime, 5.25 g (20 mmole) Ph_3P, and 50.0 ml CCl_4. The reaction mixture was stirred and brought to gentle reflux for 2.0 hr. Normally, solids appeared in 15-30 min and stirring was continued to prevent bumping. After cooling and filtering, glpc and IR analyses showed the formation of N-n-hexylacetamide in 60-70% yield. Removal of excess solvent by water aspirator and distillation of the semi-solid residue gave 0.7-0.85 g (50-60%) final product, bp. 84-86°/0.1 mm.

Beckmann Rearrangements in THF. - Moderate Reagent Excess. The apparatus was the same. The reaction mixture was composed of 1.4 g (10 mmole) 2-octanone oxime, 2.8 g (11 mmole) Ph_3P, 1.7 g (11.5 mmole) CCl_4 and 50.0 ml dry THF. The solids precipitated slowly. After cooling, IR and glpc

analyses again showed a 60-70% yield. Distillation normally gave 50-60% of product.

Excess Reagent.- The reaction mixture was composed of 1.4 g (10 mmole) 2-octanone oxime, 5.25 g (20 mmole) Ph_3P, and 3.0 g (20 mmole) CCl_4 in 50.0 ml dry THF. Solids normally precipitated in 15-20 min and it was necessary to cool and filter before IR monitoring. Sampling at 1/2 hr intervals normally showed the reaction to be complete in 2 hr with yields ranging from 60-70% (glpc and IR).

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* To whom inquiries should be directed.

1. Mention of a commercial or proprietary product in this paper does not constitute an endorsement of this product by the U.S. Department of Agriculture.

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