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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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Jordanka Petrova^a; Snejana Momchilova^a; Nikolay G. Vassilev^a

^a Faculty of Chemistry, Sofia University, Sofia, Bulgaria

To cite this Article Petrova, Jordanka , Momchilova, Snejana and Vassilev, Nikolay G.(1992) 'STEREOSELECTIVITY OF THE WITTIG-HORNER REACTION WITH BENZYLPHOSPHONATE CARBANIONS AND ALDEHYDES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 68: 1, 45 — 52

To link to this Article: DOI: 10.1080/10426509208038370

URL: <http://dx.doi.org/10.1080/10426509208038370>

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STEREOSELECTIVITY OF THE WITTIG-HORNER REACTION WITH BENZYLPHOSPHONATE CARBANIONS AND ALDEHYDES

JORDANKA PETROVA, SNEJANA MOMCHILOVA and
NIKOLAY G. VASSILEV*

Sofia University, Faculty of Chemistry, 1 A. Ivanov Av., 1126 Sofia, Bulgaria

(Received November 18, 1991; in final form December 6, 1991)

The interaction of Li-diethylbenzylphosphonate **1**-Li with aldehydes **2** is studied at different reaction conditions, the corresponding β -hydroxyethanephosphonate **3** being isolated. It is found that in these cases the aldol stage of the HWE reaction is not stereoselective or threo isomers predominate. The elimination stage leads only to trans-alkene due to the electron and steric influence of the substituents at the phosphorus atom.

Key words: Stereoselectivity; benzylphosphonate carbanion; reaction with aldehydes; threo/erythro ratio; 2-hydroxyphosphonates.

INTRODUCTION

It is known from the literature that the Wittig-Horner reaction with arylstabilized phosphonates usually supplies a high proportion of (E)-alkene.¹ (Z)-Alkenes can be obtained by stereospecific thermal decomposition of the corresponding erythro β -hydroxyphosphonamide adducts^{2,3} as well as by olefination of β -hydroxyphosphine oxide adducts (as alkali metal salts).^{4,5} Seyden-Penne and Bottin-Strzalko⁶ have shown that the base induced decomposition of threo and erythro β -hydroxyphosphonate of the reaction between benzylphosphonic ester and benzaldehyde leads always to (E)- and never to (Z)-stilbene.

It was interesting to study in more details the interaction of benzylphosphonate carbanions and aldehydes with respect to the stage of addition as well as to that of elimination.

RESULTS AND DISCUSSION

We have studied the reaction of the lithium derivative of the diethyl ester of benzylphosphonic acid **1**-Li and benzaldehyde **2a** in THF at -70°C (Scheme 1) and we have established that regardless of whether the reaction time is 1 min or 5 hrs at the same temperature, a constant erythro-**3a**/threo-**3a** ratio is achieved (18:82 and 17:83, respectively; Table I), i.e., threo-**3a** is the product of kinetic control. The erythro-**3a**/threo-**3a** ratio increases to 36:64 when the reaction temperature is allowed to room temperature for 30 min (the yields of **3a** in the two experiments are almost the same, 51% and 54%, respectively), thus suggesting that the equilibrium shift to the direction of the erythro-isomer, but the difference in the thermodynamic stability of both isomers is small. This conclusion is confirmed

TABLE II

¹H NMR spectral data of the adducts **3** in CDCl₃

Erythro-3a		δ 0.95(t, $^3J = 7.0$ Hz, 3H) and 1.28(t, $^3J = 7.0$ Hz, 3H, OCH ₂ CH ₃), 3.22(dd, $^2J_{\text{H}^a\text{P}} = 23.0$ Hz, $^3J_{\text{H}^a\text{H}^b} = 3.9$ Hz, 1H, H ^a), 3.52–4.13(m, 5H, OCH ₂ +OH), 5.50(dd, $^3J_{\text{H}^b\text{P}} = 6.5$ Hz, $^3J_{\text{H}^a\text{H}^b} = 3.9$ Hz, 1H, H ^b), 7.12–7.26(m, 10H, Ph).
Threo-3a		δ 1.12(t, $^3J = 7.0$ Hz, 3H) and 1.22(t, $^3J = 7.0$ Hz, 3H, OCH ₂ CH ₃), 3.43(dd, $^2J_{\text{H}^a\text{P}} = 19.7$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.3$ Hz, 1H, H ^a), 3.79–4.10(m, 4H, OCH ₂), 4.81(s, 1H, OH), 5.26(dd, $^3J_{\text{H}^b\text{P}} = 11.6$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.3$ Hz, 1H, H ^b), 7.06–7.27(m, 10H, Ph).
Threo-3h		δ 1.06(t, $^3J = 7.0$ Hz, 3H) and 1.13(t, $^3J = 7.0$ Hz, 3H, OCH ₂ CH ₃), 3.48–4.01(m, 4H, OCH ₂), 3.77(s, 3H, OCH ₃), 3.78(dd, $^2J_{\text{H}^a\text{P}} = 16.0$ Hz, $^3J_{\text{H}^a\text{H}^b} = 7.4$ Hz, 1H, H ^a), 4.55(d, $^3J_{\text{H}^b\text{H}^g} = 7.4$ Hz, 1H, OH), 5.45(ddd, $^3J_{\text{H}^b\text{H}^g} = 7.4$ Hz, $^3J_{\text{H}^b\text{H}^d} = 18.2$ Hz, $^3J_{\text{H}^a\text{H}^b} = 7.4$ Hz, 1H, H ^b), 6.74(d, $^3J_{\text{H}^f\text{H}^e} = 8.2$ Hz, 1H, H ^f), 6.84(dd, $^3J_{\text{H}^d\text{H}^c} = 7.5$ Hz, $^3J_{\text{H}^d\text{H}^e} = 6.5$ Hz, 1H, H ^d), 7.14(dd, $^3J_{\text{H}^f\text{H}^e} = 8.2$ Hz, $^3J_{\text{H}^d\text{H}^e} = 6.5$ Hz, 1H, H ^e), 7.27(d, $^3J_{\text{H}^d\text{H}^c} = 7.5$ Hz, 1H, H ^c), 7.09–7.33(m, 5H, Ph).
Threo-3c		δ 1.17(t, $^3J = 7.0$ Hz, 3H) and 1.24(t, $^3J = 7.0$ Hz, 3H, OCH ₂ CH ₃), 3.35(dd, $^2J_{\text{H}^a\text{P}} = 19.7$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.4$ Hz, 1H, H ^a), 3.83–4.13(m, 4H, OCH ₂), 4.81(s, 1H, OH), 5.23(dd, $^3J_{\text{H}^b\text{P}} = 11.1$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.4$ Hz, 1H, H ^b), 7.06–7.27(m, 10H, Ph).
Threo-3d		δ 1.22(t, $^3J = 7.0$ Hz, 3H) and 1.24(t, $^3J = 7.0$ Hz, 3H, OCH ₂ CH ₃), 3.34(dd, $^2J_{\text{H}^a\text{P}} = 19.8$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.3$ Hz, 1H, H ^a), 3.92–4.14(m, 4H, OCH ₂), 5.03(d, $^3J_{\text{H}^b\text{H}^e} = 2.2$ Hz, 1H, OH), 5.34(ddd, $^3J_{\text{H}^b\text{H}^e} = 2.2$ Hz, $^3J_{\text{H}^b\text{P}} = 11.6$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.3$ Hz, 1H, H ^b), 7.10–7.21(m, 5H, Ph), 7.32(d, $^3J_{\text{H}^d\text{H}^c} = 8.8$ Hz, 2H, H ^c +H ^{c'}), 8.01(d, $^3J_{\text{H}^d\text{H}^c} = 8.8$ Hz, 2H, H ^d +H ^{d'}).

TABLE II (Continued)

Threo-3e	$ \begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{CH}_2\text{O})_2\text{P}-\text{CH}^a-\text{C}_6\text{H}_5 \\ \\ \text{HO}-\text{CH}^b-\text{CH}^c-\text{CH}_3^d \\ \\ \text{CH}_3^e \end{array} $	δ 0.79(d, $^3J_{\text{H}^d\text{H}^c} = 6.7$ Hz, 3H, H^d), 0.96(d, $^3J_{\text{H}^e\text{H}^c} = 6.9$ Hz, 3H, H^e), 1.16(t, $^3J = 7.0$ Hz, 3H) and 1.27(t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 1.49(dtt, $^3J_{\text{H}^b\text{H}^c} = 2.2$ Hz, $^3J_{\text{H}^e\text{H}^c} = 6.7$ Hz, 1H, H^b), 3.22(dd, $^2J_{\text{H}^a\text{P}} = 20.6$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.8$ Hz, 1H, H^a), 3.80-4.14(m, 4H, OCH_2), 3.93(s, 1H, OH), 4.18(ddd, $^3J_{\text{H}^b\text{H}^c} = 2.2$ Hz, $^3J_{\text{H}^b\text{P}} = 11.8$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.8$ Hz, 1H, H^b), 7.06-7.27(m, 10H, Ph).
Threo-3f	$ \begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{CH}_2\text{O})_2\text{P}-\text{CH}^a-\text{C}_6\text{H}_5 \\ \\ \text{HO}-\text{CH}^b-\text{CH}_2^{\text{c,c'}}-\text{CH}^d-\text{CH}_3^e \\ \\ \text{CH}_3^{\text{c'}} \end{array} $	δ 0.80(d, $^3J_{\text{H}^e\text{H}^d} = 6.8$ Hz, 3H, H^e), 0.83(d, $^3J_{\text{H}^{\text{c,c'}}\text{H}^d} = 6.8$ Hz, 3H, $\text{H}^{\text{c,c'}}$), 1.03(ddd, $^3J_{\text{H}^d\text{H}^c} = 14.0$ Hz, $^2J_{\text{H}^c\text{H}^{\text{c'}}} = 10.2$ Hz, $^3J_{\text{H}^c\text{H}^b} = 2.3$ Hz, 1H, H^c), 1.13(t, $^3J = 7.0$ Hz, 3H) and 1.29(t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 1.33(dd, $^2J_{\text{H}^c\text{H}^{\text{c'}}} = 10.2$ Hz, $^3J_{\text{H}^{\text{c,c'}}\text{H}^d} = 3.8$ Hz, 1H, $\text{H}^{\text{c,c'}}$), 1.86(ddqq, $^3J_{\text{H}^e\text{H}^d} = 6.8$ Hz, $^3J_{\text{H}^e\text{H}^{\text{c,c'}}} = 6.5$ Hz, $^3J_{\text{H}^c\text{H}^d} = 14.0$ Hz, $^3J_{\text{H}^{\text{c,c'}}\text{H}^d} = 3.8$ Hz, 1H, H^d), 3.08(dd, $^2J_{\text{H}^a\text{P}} = 20.2$ Hz, $^3J_{\text{H}^a\text{H}^b} = 8.9$ Hz, 1H, H^a), 3.76-4.17(m, 4H, OCH_2), 3.92(s, 1H, OH), 4.32(ddd, $^3J_{\text{H}^b\text{H}^c} = 2.3$ Hz, $^3J_{\text{H}^b\text{P}} = 10.5$ Hz, $^3J_{\text{H}^a\text{H}^b} = 8.9$ Hz, 1H, H^b), 7.24-7.35(m, 5H, Ph).
Threo-3g	$ \begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{CH}_2\text{O})_2\text{P}-\text{CH}^a-\text{C}_6\text{H}_5 \\ \\ \text{HO}-\text{CH}^b-\text{C}^c=\text{C}^d-\text{O}^e \end{array} $	δ 1.12(t, $^3J = 7.1$ Hz, 3H) and 1.25(t, $^3J = 7.1$ Hz, 3H, OCH_2CH_3), 3.59-4.11(m, 4H, OCH_2), 3.74(dd, $^2J_{\text{H}^a\text{P}} = 20.2$ Hz, $^3J_{\text{H}^a\text{H}^b} = 8.7$ Hz, 1H, H^a), 4.60(s, 1H, OH), 5.28(dd, $^3J_{\text{H}^b\text{P}} = 15.1$ Hz, $^3J_{\text{H}^a\text{H}^b} = 8.7$ Hz, 1H, H^b), 6.12(d, $^3J_{\text{H}^d\text{H}^c} = 3.1$ Hz, 1H, H^c), 6.14(dd, $^3J_{\text{H}^d\text{H}^c} = 3.1$ Hz, $^3J_{\text{H}^e\text{H}^d} = 1.7$ Hz, 1H, H^d), 7.18-7.26(m, 6H, Ph+ H^e).
Threo-3h	$ \begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{CH}_2\text{O})_2\text{P}-\text{CH}^a-\text{C}_6\text{H}_5 \\ \\ \text{HO}-\text{CH}^b-\text{C}^c=\text{C}^d-\text{O}^e-\text{CH}_2^f \end{array} $	δ 1.17(t, $^3J = 7.1$ Hz, 3H) and 1.26(t, $^3J = 7.1$ Hz, 3H, OCH_2CH_3), 3.37(dd, $^2J_{\text{H}^a\text{P}} = 19.6$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.6$ Hz, 1H, H^a), 3.90-4.12(m, 4H, OCH_2), 4.61(s, 1H, OH), 5.19(dd, $^3J_{\text{H}^b\text{P}} = 10.3$ Hz, $^3J_{\text{H}^a\text{H}^b} = 9.6$ Hz, 1H, H^b), 5.84(s, 2H, H^f), 6.54(s, 2H, H^dH^e), 6.75(s, 1H, H^c), 7.15(m, 5H, Ph).

TABLE III
 Yields and configuration of the olefins 4

N	Adduct 3	Reaction conditions	Yields of 4(%)	Configuration of 4*
1.	Threo-3a	Method A	88	(E)-4a
2.	Erythro- Threo-3a-Li 1	Method B	72	(E)-4a
3.	Threo-3a	Method D	10	(E)-4a
4.	Erythro/threo- 3a-Li 1:2	Method D	10	(E)-4a
5.	Threo-3a	Method C	5	(E)-4a
6.	Threo-3b	Method A	86	(E)-4b
7.	Threo-3d	Method A	83	(E)-4d

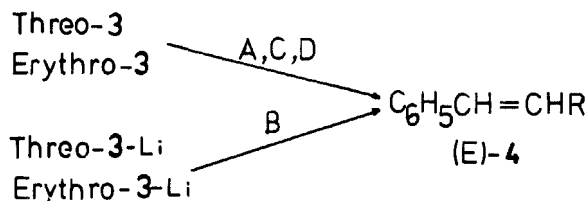
* The product contains traces of (Z)-4

by experiments carried out in ether at -70°C for the reaction time of either 15 sec or 8 hrs: the erythro-3a/threo-3a ratio remains constant (40:60 and 44:56, respectively), the yield of 3a being the same (80%). At room temperature for a reaction time of 1 hr this ratio still remains unchanged and 5 hrs are required for its slight increase (50:50), the yield being however considerably lower in this case (48%).

Traces of olefins (mainly E-stilbene) are detected in all experiments, their amount remaining negligible (up to 5% E-stilbene).

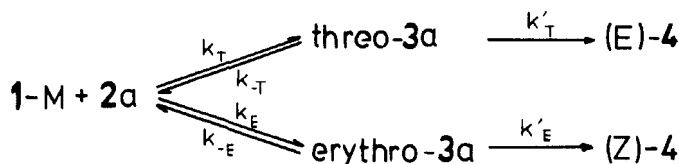
The reaction was carried out with a large number of aldehydes (2b-h), predominantly at low temperature (-70°C). The respective adducts 3 were obtained in good yields (40–80%), the threo-isomer being the prevailing one in all diastereomeric mixtures, that is the stereoselectivity do not depend on the substituents of the aldehyde component. Such a "threo"-diastereoselectivity was observed also in the reaction of 1-Li and unsymmetric ketones.⁷ All new intermediate β -hydroxyphosphonates 3b–h were characterized by elemental analysis and IR-spectroscopy and their relative configuration was determined by ^1H NMR spectroscopy (Table II). In accordance with previous studies of ours⁸ as well as those of Seyden-Penne concerning 3a.⁶ The threo isomers 3a–h are characterized by $J_{\text{HaHb}} = 7\text{--}10$ Hz, $J_{\text{PHa}} = 18\text{--}20$ Hz and $J_{\text{PHb}} = 9\text{--}14$ Hz, which is an indication of their existence in CDCl_3 predominantly in antiperiplanar conformation of the hydrogen atoms.

The formation of olefins from the adducts 3 was also studied. It was established that (E)-4a was the only reaction product regardless of whether the interaction is carried out with pure threo-3a, and NaH at room temperature in DMF (method A), or with a diastereomeric mixture of threo-3a-Li + erythro-3a-Li at the same temperature (method B), the yields being 88% and 72%, respectively. Traces of (Z)-4a were detected in both experiments. We observed similar results when olefinating the diastereomeric mixtures of 3b as well as of 3d with NaH (yields of E-alkene of 86% and 83%, respectively (Table III). Thermolysis of 3a (method C) as well as experiments for olefin formation from threo-3a or diastereomeric mixture-3a in alcoholic solution of hydrochloric acid (method D)⁹ resulted in the isolation of (E)-4a as the sole reaction product in low yield (5–10%), the (Z)-isomer being present in traces.



A: NaH, DMF, 25°C, 3 hrs; B: 25°C, 24 hrs; C: toluene, silicagel, 110°C, 5 hrs; D: hydrochloric acid/ethanol, 25°C, 3 hrs.

We carried out also experiments on the “retro” Wittig-Horner reaction. When metallating pure threo-**3a** with BuLi in THF at -70°C and allowing the reaction mixture to warm to room temperature for 30 min, a diastereomeric mixture of erythro-**3a**/threo-**3a** = 46:54 and 28% of **1** were isolated after hydrolysis. In the same experiment, but with a starting mixture of erythro-**3a**/threo-**3a** = 42:58 at the same conditions the reaction product contains erythro-**3a**/threo-**3a** = 42:58 and 14% of **1**†, while from -70° to 0°C no changes in the starting material were detected. The experiments prove significant reversibility of the HWE reaction at a temperature higher 0°C (THF, counterion Li^+), as well as that the threo-isomer is the product of a kinetic control. On the bases of the quantity of **1** we consider that in the interval $-78^\circ \div 20^\circ\text{C}$ $k_{-T} > k_{-E}$ and $k_T \approx k_E$ (no stereospecific aldol stage).



Analogous experiments with NaNH_2 in THF for 3 hrs at room temperature show the ratio (Z)-**4**/(E)-**4** = 1:99 and 1% of **1** (glc), irrespective of the starting adducts (pure threo-**3a** or mixture erythro-**3a**/threo-**3a** = 42:58), that is $k'_T \gg k'_E \gg k_{-T}$ and k_{-E} .

These results confirm the conclusion of Seyden-Penne that erythro-**3a** does not lead to (Z)-stilbene by the Wittig-Horner-reaction, as well as our previous conclusion for the significance of the surrounding of the PO group for the elimination process.⁷ The possibility of obtaining (Z)-stilbene from erythro- β -hydroxyphosphonamide adduct **5** (by thermolysis or in acidic medium^{3,9} as well as from erythro-**6-Li**¹⁰ confirms that the electron and steric influence of the substituents at phosphorus atom is a reason for their different behavior in the elimination stage in comparison with erythro-**3** (Figure 1).

It was shown recently that there is a distinction in the crystal structure of β -hydroxyphosphinoxide and phosphonate adducts (**3** and **6**) as well.^{10,11} Buss et al.^{10b} reported that in erythro-**6** an intramolecular H-bonding occurs, while the crystal structure of threo-**3** is built up of centrosymmetric dimers of intermolecular hydrogen bonded molecules.¹¹

†By $^1\text{H-NMR}$; the quantity of stilbene **4** in the two experiments is negligible (4–5%, column chromatography).

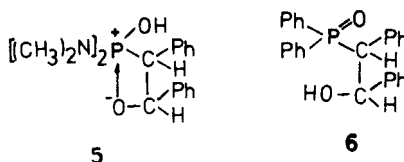


FIGURE 1

EXPERIMENTAL

The reaction of **1** with **2** was carried out under dry argon in anhydrous solvents (THF, ether or ether-pentene 1:1). NMR-spectra of the adducts **3** were recorded on BRUKER WM-250 and JEOL JNM-100 with HMDSO or TMS as internal standard and CDCl_3 as solvent. IR-spectra were registered on Specord-71 IR. The olefins were purified by column filtration on Al_2O_3 with hexane. The qualitative tlc investigations were carried out on Silicagel 60 F_{254} using chloroform-ethylacetate 3:1 as mobile phase (for adducts) or hexane (for olefins). The ratio (Z)-**4**/(E)-**4**/**1** is determined by glc (8% PEGA Chromosorb P/NAW "Perkin-Elmer" SIGMA-3B apparatus).

*Synthesis of esters of 2-aryl(alkyl, furyl)-2-hydroxy-1-phenylethanephosphonic acids **3**.*

General Procedure.⁷ To a solution of **1** (10 mmol) in 20 ml of anhydrous THF, cooled to -70°C , BuLi (10 mmol, 1.6 M in hexane), diluted with 8 ml of THF, is added under argon. After 15 min stirring, the aldehyde **2** is added (10 mmol in 6 ml THF) and the reaction mixture is kept at this temperature (or is allowed to warm to room temperature) for another 15 sec, 300 min. The mixture is hydrolysed, extracted with CH_2Cl_2 and after evaporation of the solvents the crude product **3** is studied by ^1H NMR and tlc.

Conversion of the hydroxyphosphonate adducts **3 or their alkaline salts into olefins **4**.** *A*¹²: The mixture of equimolar quantity **3** and NaH in DMF is stirred 3 hrs at room temperature. After hydrolysis with water and extraction in consecutive order with hexane and ether the solvents are evaporated and the products are purified by column filtration. *B*: The reaction mixture is obtained from **1**-Li and **2** using the general procedure. After keeping it 15 min at -70°C it is allowed to warm to room temperature, kept 24 hrs at this temperature under argon and then treated as in method A. *C*¹³: Thermal olefination of **3** by reflux 5 hrs in toluene. *D*⁹: The mixture of 10 mmol of **3**, 10 ml of anhydrous ethanol and 0.1 ml of conc. hydrochloric acid is refluxed 1 hr with stirring, the solvent is evaporated in vacuum and 3 ml of 10% Na_2CO_3 is added. The residue is extracted with ether, the organic layer is washed with water and dried over MgSO_4 . After evaporation of the solvent, the crude product **3** is treated as in method A.

Experiments on the reversibility of the Wittig-Horner reaction. a) To a solution of 1.17 g (3.5 mmol) of threo-**3a** (respectively mixture of erythro-**3a**/threo-**3a** = 42:58) in 8 ml of THF, cooled to -70°C , BuLi (3.7 mmol, 1.6 M in hexane) is added under argon. After 30 min stirring the reaction mixture is allowed to warm to room temperature for 30 min. After hydrolysis with 0.3 ml of F_3CCOOH and evaporation of the solvents in vacuum the crude product is studied by ^1H NMR and glc. b) To a solution of 0.334 g (1 mmol) of threo-**3a** (respectively mixture of erythro-**3a**/threo-**3a** = 42:58) in 20 ml of THF 0.05-0.10 g of NaH (55–60%) is added under argon. After 3 hrs stirring the reaction mixture is hydrolysed with 0.1 ml of F_3CCOOH , the solvent is evaporated in vacuum and the crude product is studied by glc.

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