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## Note

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### Liquid chromatography of dinitro-*p*-xylenes

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This paper is an example of the application of high-speed liquid chromatography (HSLC) to separate isomers obtained from a common reaction. The preparative separation provided quantities of pure reaction products that could not be obtained by conventional separation techniques. Also, the utility of HSLC in the investigation of common reactions is demonstrated.

#### EXPERIMENTAL

##### *Liquid chromatography*

The chromatograph used in these studies was constructed from two Model 314 Isco pumps, a modified Valco Model CV-6-Hpax injection valve, a Waters Model 401 refractometer, and an Isco Model UA-5-UV detector. Pressure was indicated on a Bourden gauge of 0-3,000 lbs. Columns used for the preparative separations were a 100 × 2.5 cm glass column (Chromatronix) packed with Porasil A and two 25 × 1.0 cm stainless-steel columns (Altex) slurry-packed with Partisil 10. Analytical separations were performed on a 25 cm × 2.6 mm stainless-steel column slurry-packed with Partisil 10. Components were joined by using 1/16 in. O.D. stainless-steel tubing and Swagelok fittings. All fittings used downstream from injections were zero dead volume and the tubing was 0.009 in. I.D. A SGE 5BL-RD-3 syringe was used for analytical injections.

Preparative separations of 3-g samples on Porasil A were accomplished using hexane-acetone (7:1) at a flow-rate of 325 ml/h. Detection was performed with the RI detector. Chromatographic conditions for other separations are given in the legends to Figs. 1 and 2.

##### *Nitration conditions*

Mononitro-*p*-xylene (2.0 g) was mixed with H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> and heated in an oil bath. The times, temperatures, and ratio of HNO<sub>3</sub> to mononitro-*p*-xylene that were used are shown in Table I. After nitration the reaction products were poured onto ice and the mixture was extracted once with benzene and then four times with chloroform. The combined organic layers were evaporated to dryness on a flash

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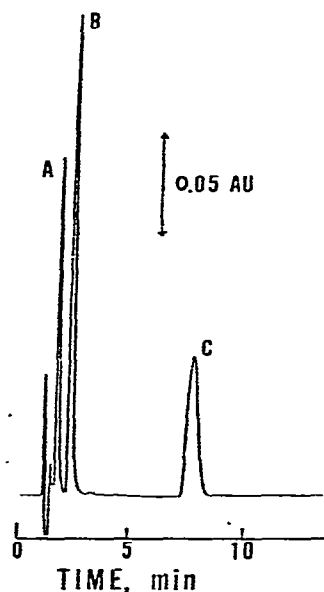


Fig. 1. HSLC separation of dinitro-*p*-xylenes. Column, 25 cm  $\times$  2.6 mm, packed with Partisil 10; solvent, hexane-ethyl acetate (7:1); flow-rate, 1.0 ml/min; pressure, 350 lb./in.<sup>2</sup>; sample size, 15.0  $\mu$ g in 5  $\mu$ l; detection, UV, 280 nm. Peaks: (A) 2,5-dinitro-*p*-xylene; (B) 2,6-dinitro-*p*-xylene; (C) 2,3-dinitro-*p*-xylene.

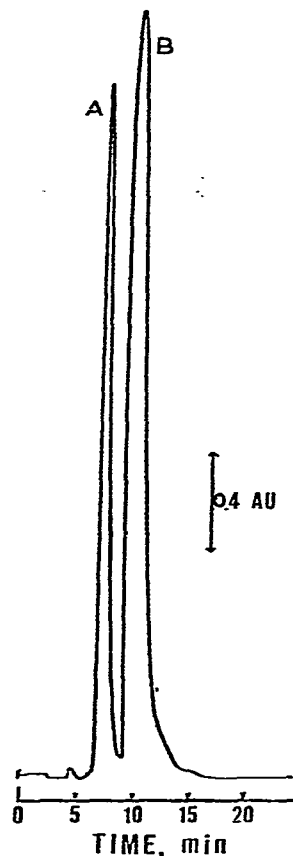


Fig. 2. Preparative separation of 2,5-dinitro-*p*-xylene (A) and 2,6-dinitro-*p*-xylene (B). Column, two 25 cm  $\times$  1.0 cm columns packed with Partisil 10; solvent, hexane-ethyl acetate (9:1); flow-rate, 325 ml/h; pressure, 200 lb./in.<sup>2</sup>; sample size, 50 mg in 270  $\mu$ l; detection, UV, 365 nm.

evaporator. Samples for analysis were prepared by dissolving 15 mg in 5 ml of methylene chloride.

## RESULTS

It has been reported that the nitration of mononitro-*p*-xylene affords the 2,3-dinitro- and 2,6-dinitro-*p*-xylenes, but none of the 2,5-dinitro-*p*-xylene, under appropriate experimental conditions<sup>1</sup>. Since the 2,3-dinitro-*p*-xylene was required for synthetic purposes, the nitration of mononitro-*p*-xylene was repeated as previously described to obtain this isomer. However, the desired product was not recovered from the nitration mixture by the fractional crystallization procedure thus reported. Thin-

layer chromatography (silica gel) of the reaction mixture in a number of solvent systems revealed only two components. On the other hand, HSLC on Partisil 10 revealed the presence of a third component, as shown in Fig. 1. Because of the large differences in retention times of the first two peaks as compared to the third, a two-step preparative procedure was chosen for the separation of the three components. Chromatography on Porasil A provided a good separation of compound C from the two fast moving components (A and B). The fast moving components A and B (which eluted as a single peak on Porasil A) were then separated on Partisil 10 (Fig. 2). The identities of the three compounds were established by melting points and proton magnetic resonance spectra. Component B was 2,6-dinitro-*p*-xylene, component C was 2,3-dinitro-*p*-xylene, and component A was 2,5-dinitro-*p*-xylene, which had not been found in the previous report<sup>1</sup>. The purity of the separated isomers is shown in Fig. 3.

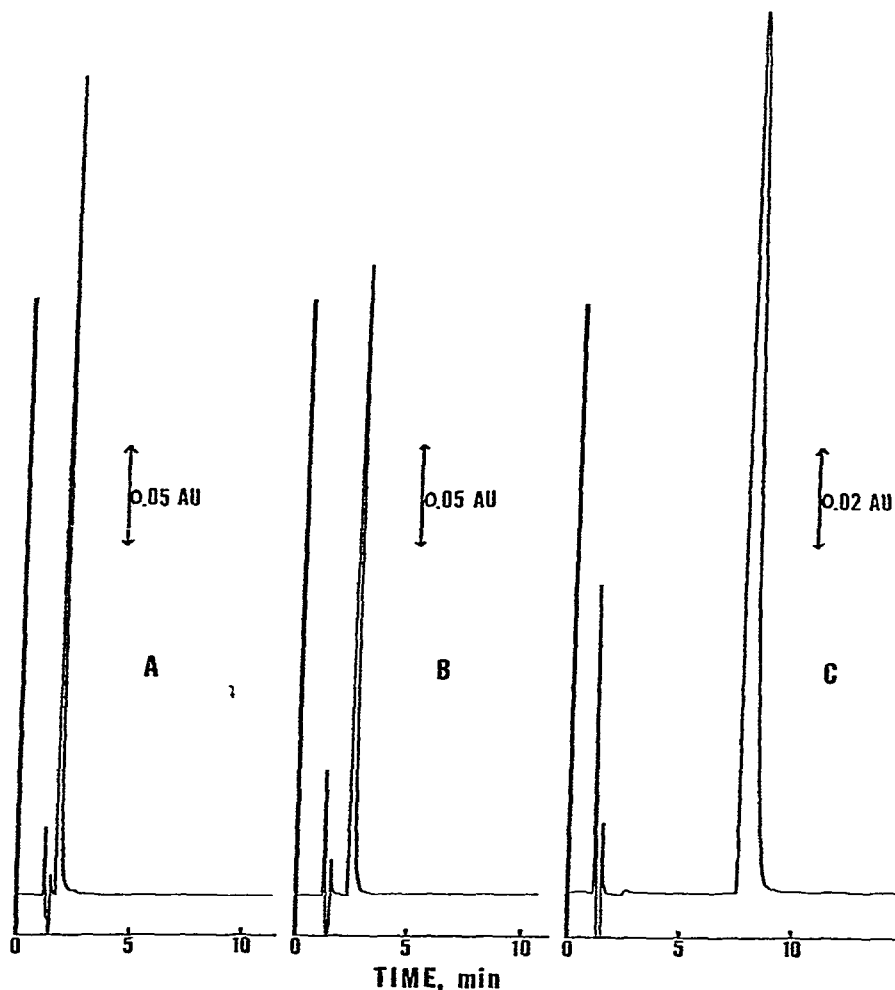


Fig. 3. HSLC of separated dinitroxylenes as an indicator of purity. Chromatographic conditions, same as for Fig. 1. Sample sizes, (A) 4.5  $\mu\text{g}$  in 3  $\mu\text{l}$ ; (B) 7.5  $\mu\text{g}$  in 5  $\mu\text{l}$ ; (C) 15.0  $\mu\text{g}$  in 5  $\mu\text{l}$ .

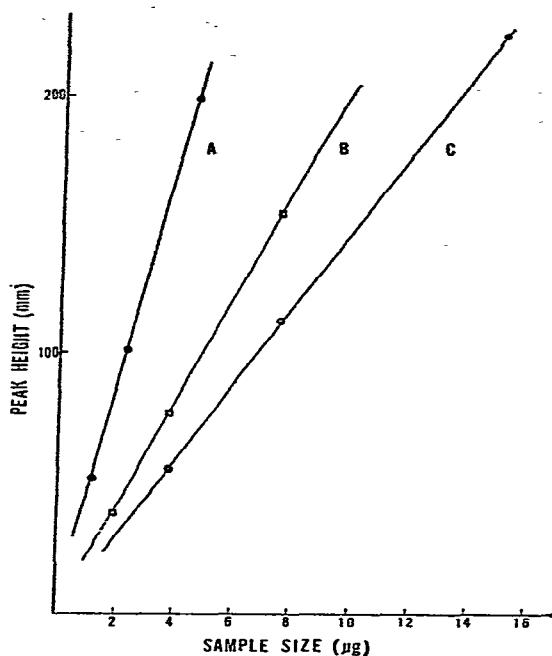


Fig. 4. Calibration curves for dinitro-*p*-xylenes. (A) 2,5-Dinitro-*p*-xylene; (B) 2,6-dinitro-*p*-xylene; (C) 2,3-dinitro-*p*-xylene. A and B, 0.5 a.u.f.s.; (C) 0.2 a.u.f.s.

It was of interest to determine the effect of reaction conditions on the ratio of the three isomers produced in the nitration. Therefore, calibration curves were produced for each of the three isomers, as shown in Fig. 4. The effects upon the ratio of isomers as a function of reaction time and temperature and the ratio of sulfuric to nitric acid were investigated. The data presented in Table I demonstrate that varying reaction conditions produce only small changes in the ratio of the isomers produced in the reaction.

TABLE I  
NITRATION OF MONONITRO-*p*-XYLENE

Sample	Time (min)	Temperature (°C)	$HNO_3$ -mononitro- <i>p</i> -xylene ratio	Percentages of dinitro- <i>p</i> -xylenes from HSLC		
				2,3-	2,6-	2,5-
1	15	70	1.1	48	36	16
2	15	90	1.1	48	35	17
3	10	80	1.1	50	35	15
4	15	80	1.1	50	35	15
5	15	80	1.4	43	40	17
6	20	80	1.1	50	35	16

## ACKNOWLEDGEMENT

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## REFERENCE

- 1 K. A. Kobe and T. B. Hudson, *Ind. Eng. Chem.*, 42 (1950) 356.