

Results

All compounds were resolved except benzene from ethylcyclohexane, *n*-propylcyclohexane from isopropylcyclohexane, and *sec.*-butylcyclohexane from *n*-butylcyclohexane. Since by simple fragmentation none of the alkylbenzenes studied could give both of these unresolved cyclohexane pairs, lack of resolution was of little consequence. A separate study showed that benzene is only formed in very small relative amounts, so that the detection of products with this retention time was attributed predominantly to ethylcyclohexane. The alkylbenzenes studies are listed in Table I, together with the major reaction products. In all compounds the predicted behaviour was observed, and it was found that, in general, for a given parent compound, the ratio of the amount of an alkylbenzene to the corresponding cyclohexane increased with the number of carbon atoms on the side chain. For example *n*-propylbenzene gave rise to small amounts of cyclohexane and methylcyclohexane, and somewhat greater quantities of ethyl- and propylcyclohexane, ethylbenzene and unreacted parent compound. A chromatogram is shown in Fig. 1.

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The gas chromatography of alkyldinitrophenols and the corresponding anisoles

A recent paper by HRIVŇÁK *et al.*¹ on the GLC separation of nitrophenols and nitroanisoles on polyester columns reports a greater retention time for certain dinitroanisoles than for the corresponding dinitrophenol. Similar behaviour has already been reported by us for some alkyldinitrophenols and alkyldinitroanisoles^{2,3}.

Experimental

The gas chromatographic separations were carried out as previously described^{3,4} using DNOC (6-methyl-2,4-dinitrophenol*) as standard, except that mononitrophenols were examined on the DEGA column at 155° using 2-nitroanisole as standard.

Results and discussion

The three important types of hydrogen bonding in the GLC separation of nitro-

* To simplify discussion this and similar compounds are designated 2,4-dinitrophenols even when the alkyl group is such that 2-alkyl-4,6-dinitrophenol is correct.

phenols and nitroanisoles are: (1) that between phenolic hydroxyl groups and free hydroxyl groups in the stationary phase, (2) intramolecular hydrogen bonding between the hydroxyl and *ortho* nitro groups in the aromatic nucleus, and (3) that between aromatic nitro groups and hydroxyl groups of the stationary phase. This latter (type 3) bonding is much weaker than the others and has a less significant effect on GLC behaviour. Exploitation of type 2 bonding, that is of the so-called "ortho effect", enables separation of free phenols without prior methylation since type 1 bonding is reduced or precluded resulting in a reduction in retention time. This principle was invoked in the analysis of the isomeric octyldinitrophenols obtained from the hydrolysis of "Karathane" where separation of the methyl ethers was not possible, and for other similar separations^{1, 5}.

Retention data for fifteen nitrophenols and their methyl ethers on two stationary phases (DEGA and LAC-2R-446) are listed in Table I. Since all the phenols possess a hydroxyl group *ortho* to a nitro group, type 2 bonding occurs. The present work gave similar results to those of HRIVŇÁK *et al.*¹ in that the 2,4-dinitroanisole/2,4-dinitrophenol relative retention ratio was greater than 3:1 whereas that for the 2,6-dinitro analogues was 1:2. Introduction of an alkyl group into the aromatic nucleus significantly altered these ratios, that for the 6-methyl-2,4-dinitro compounds being approximately 1:1 (Table I). There is little difference in retention time for 2,4-dinitrophenol and the 6-methyl derivative since the effect of increase in molecular weight is offset by strengthening of the intramolecular hydrogen bond due to the electronic effect of the $-CH_3$ group. The significant decrease in the values for the corresponding anisoles may be due to hindering of the rotation of the $-OCH_3$ group by the adjacent

TABLE I

RELATIVE RETENTIONS^a OF NITRO- AND ALKYL DINITROPHENOLS AND THEIR CORRESPONDING ANISOLE ON POLYESTER PHASES

Compound	1% DEGA 0.08% H ₃ PO ₄ 235°		2.5% LAC-2R-446 0.2% H ₃ PO ₄ 215°		Ratio of methyl ether to phenol	
	Phenol	Methyl ether	Phenol	Methyl ether	DEGA	LAC- 2R-446
2-Nitrophenol	0.29 ^b	1.00 ^b	0.04	0.13	3.45	3.00
2-Nitro-6-methylphenol	0.35 ^b	0.38 ^b	0.10	0.10	1.09	1.00
2-Nitroresorcinol	0.53 ^b	3.95 ^b	0.17	0.80	7.5	4.70
2,4-Dinitrophenol	0.94	2.05	1.02	2.9	2.46	2.85
6-Methyl-2,4-dinitrophenol	1.00	1.03	1.00	1.21	1.03	1.21
6- <i>n</i> -Propyl-2,4-dinitrophenol	1.06	1.05	1.24	1.29	0.98	1.04
6- <i>n</i> -Butyl-2,4-dinitrophenol	1.42	1.30	1.59	1.61	0.92	1.01
6- <i>n</i> -Octyl-2,4-dinitrophenol	3.55	3.48	4.40	4.53	0.98	1.03
6-(1-Methylheptyl)-2,4-dinitrophenol	2.25	2.08	2.72	2.62	0.93	0.96
6-(1-Ethylhexyl)-2,4-dinitrophenol	1.85	1.73	2.06	2.06	0.93	1.00
6-(1-Propylpentyl)-2,4-dinitrophenol	1.66	1.50	1.88	1.80	0.90	0.96
6- <i>sec</i> -Butyl-2,4-dinitrophenol	1.05	0.94	1.14	1.19	0.91	1.05
6- <i>tert</i> -Butyl-2,4-dinitrophenol	0.90	0.92	1.03	1.07	1.02	1.04
2,6-Dinitrophenol	1.66	0.84	1.64	0.82	0.50	0.50
4-Methyl-2,6-dinitrophenol	1.69	0.82	1.70	0.90	0.49	0.52

^a Relative to DNOC.

^b 155°, relative to 2-nitroanisole.

—CH₃ group with a resultant lessening of any type 3 bonding which might have occurred. However, many alkyldinitroanisoles are eluted slightly before the corresponding phenol particularly on the DEGA column, since the size and shape of the alkyl substituent in these cases significantly affect type 3 bonding. Thus, with isomeric butyl-2,4-dinitrophenols, maximum steric hindrance (and minimum hydrogen bonding) in the *tert.*-butyl isomer, and the converse with the *n*-butyl one results in relative retentions of 0.90 and 1.42 (DEGA column), the *tert.*-butyl compound having a lower elution time than 2,4-dinitrophenol itself. A similar situation occurs with the four 6-octyl-2,4-dinitrophenol isomers.

2,6-Dinitrophenol has a longer retention time than its 2,4-dinitro analogue whereas, for the methyl ethers, that for 2,6-dinitroanisole is much shorter than for its 2,4-isomer. In 2,6-dinitrophenol, bonding of —OH to two *ortho* nitro groups may result in delocalisation of the hydrogen bond, permitting some bonding to phase and a resultant increase in retention times. Faster elution of 2,6-dinitroanisole may be due to a reduction of type 3 bonding as a result of steric hindrance by the methoxyl group. Substitution of alkyl groups into position 4 of the aromatic nucleus results in the expected steady increase in retention times for succeeding homologues³.

The *ortho* mononitrophenols and anisoles behave in the same manner as the 2,4-dinitro compounds; 2-nitroresorcinol, in which both hydroxyl groups are hydrogen bonded to a nitro group cannot bond to the phase and the phenol is eluted very much faster than the anisole.

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