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Note

Sensitive gas chromatographic determination of lower aliphatic carbonyl compounds as their pentafluorophenylhydrazones

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For the derivatization of carbonyl compounds, the reaction with 2,4-dinitrophenylhydrazine to form the corresponding solid, water-insoluble 2,4-dinitrophenylhydrazones has been widely used. The analysis of 2,4-dinitrophenylhydrazones by gas chromatography (GC) with high column temperatures had been widely reported¹⁻¹⁴. In addition, the reaction of carbonyl compounds with pentafluorophenylhydrazine has been reported by Attal *et al.*¹⁵ and Mead *et al.*¹⁶. However, these methods have been applied only to high-molecular-weight carbonyl compounds.

This paper describes the sensitive and selective GC analysis of lower aliphatic carbonyl compounds with column temperatures lower than those used in the GC analysis of 2,4-dinitrophenylhydrazone derivatives. The carbonyl compounds are converted into the corresponding pentafluorophenylhydrazones, which are detected using an electron-capture detector (ECD).

EXPERIMENTAL

Reagents

The lower aliphatic carbonyl compounds used in this work were as described earlier¹⁴. Pentafluorophenylhydrazine (purity 97%) was obtained from Aldrich (Milwaukee, Wisc., U.S.A.). Methanol, obtained from Katayama (Osaka, Japan), was fractionally distilled twice over 2,4-dinitrophenylhydrazine (Katayama) (5 g/l added to methanol with the further addition of 10 ml of concentrated hydrochloric acid) in order to remove all traces of the lower carbonyl compounds. All reagents were of laboratory or analytical-reagent grade.

Pentafluorophenylhydrazone derivative formation

The procedure for the preparation the pentafluorophenylhydrazone derivatives was as follows. An amount of $0.5 \cdot 10^{-3}$ mole of lower aliphatic carbonyl compound was added, with a $100-\mu$ l Terumo MS-100 microsyringe, to 1 ml of methanol containing $1.01 \cdot 10^{-3}$ mole of pentafluorophenylhydrazine and the mixture was allowed to react overnight at room temperature. The extent of the reaction was determined from

the carbonyl compounds remaining after the reaction period. A $1-\mu l$ volume of the sample solution was injected (with a $10-\mu l$ Hamilton 701-N microsyringe) into Ethofat or SE-30 columns, and a flame-ionization detector (FID) and a thermal conductivity detector (TCD) were used for detection.

Gas chromatography

The gas chromatographs used were a Shimadzu Model GC5AP₅TF equipped with a TCD, an FID and a digital integrator (Shimadzu Model ITG-2A) for the determination of the extent of the pentafluorophenylhydrazone derivative formation reaction, and a Shimadzu Model GC5AIE equipped with an ECD.

The GC conditions were as follows: (A) analytical column, $3 \text{ m} \times 3 \text{ mm}$ I.D.,

TABLE I

RETENTION TIMES AND EXTENTS OF REACTION FOR 27 PENTAFLUOROPHENYL-HYDRAZONE DERIVATIVES

3-m column, 5% SE-30.

HCHO1302.49100CH_3CHO3.9380 $C_{2}H_{3}CHO$ 5.50100 $n-C_{3}H_{7}CHO$ 9.30100 $iso-C_{3}H_{7}CHO$ 6.8890 $n-C_{4}H_{9}CHO$ 23.91100 $iso-C_{4}H_{9}CHO$ 11.27100 $n-C_{4}H_{9}CHO$ 22.92100 $CH_{2}=CHCHO$ 6.06100 $CH_{3}CH_{2}=CHCHO$ 6.06100 $CH_{3}CO-C_{4}H_{5}$ 7.99100 $CH_{3}COC_{2}H_{5}$ 7.99100 $CH_{3}CO-r_{4}H_{9}$ 14.92100 $CH_{3}CO-r_{5}o-C_{3}H_{7}$ 10.03100 $CH_{3}CO-re_{4}H_{9}$ 14.92100 $CH_{3}CO-re_{4}H_{9}$ 12.45100 $C_{3}H_{5}CO-re_{4}H_{9}$ 12.45100 $C_{3}H_{5}CO-re_{4}H_{5}$ 11.3880 $C_{5}H_{5}CO-re_{4}H_{5}$ 11.3880 $C_{5}H_{4}CHO$ 19.28100 $c_{5}H_{4}(CH_{3})CHO$ 19.73100 $c_{5}H_{4}(CH_{3})CHO$ 19.73100 $c_{5}H_{4}(CH_{3})CHO$ 7.80100 $c_{5}H_{4}O_{2}$ 7.24100 $c_{6}H_{10}O$ 7.80100 $c_{6}H_{10}OCCH_{5}$ 13030100 $CH_{3}COCCH_{5}$ 13030100	Compound	Temperature (°C)	Retention time (min)	Extent of reaction* (%)
CH ₃ CHO 3.93 80 C ₂ H ₅ CHO 5.50 100 $n-C_3H_7CHO$ 9.30 100 $iso-C_3H_7CHO$ 6.88 90 $n-C_4H_5CHO$ 23.91 100 $iso-C_4H_5CHO$ 23.91 100 $iso-C_4H_5CHO$ 23.91 100 $iso-C_4H_5CHO$ 22.92 100 $n-C_3H_{11}CHO$ 22.92 100 $CH_2=CHCHO$ 6.06 100 CH_3COCH_3 5.44 100 $CH_3COC_4H_5$ 7.99 100 $CH_3CO{150}-C_3H_7$ 10.03 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 14.92 100 $C_3H_5CO{145}$ 11.38 80 $C_2H_5COC_3H_5$ 11.38 80 $C_4H_4(CH_3)CHO$ 19.73 100 $o-C_6H_4(CH_3)CHO$ 19.73 100 $o-C_6H_4(CH_3)CHO$ 19.73 100 $o-C_6H_4(CH_3)CHO$ 7.80 100 $c_5H_4O_2$ 7.24	нсно	130	2.49	100
C_2H_5CHO 5.50 100 $n-C_3H_7CHO$ 9.30 100 $iso-C_3H_7CHO$ 6.88 90 $n-C_4H_9CHO$ 23.91 100 $iso-C_3H_1CHO$ 21.91 100 $iso-C_4H_9CHO$ 11.27 100 $n-C_5H_{11}CHO$ 22.92 100 $CH_2=CHCHO$ 6.06 100 $CH_3CH=CHCHO$ 12.04 100 CH_3COCH_3 5.44 100 $CH_3COC_4H_5$ 7.99 100 $CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_4H_9$ 19.45 100 $CH_3CO-secC_4H_9$ 14.92 100 $C_4H_5COC_3H_5$ 11.38 80 $C_5H_5COC_3H_5$ 11.38 80 $C_5H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $c_5H_4O_2$ 7.24 100 $c_6H_4OCH_3$ 16.76 100 $c_6H_4OCH_3$ 16.76 100 $C_8H_4OCCH_3$ 16.76	CH ₃ CHO		3.93	80
$n-C_3H_7CHO$ 9.30 100 $iso-C_3H_7CHO$ 6.88 90 $n-C_4H_9CHO$ 23.91 100 $iso-C_3H_1CHO$ 21.91 100 $n-C_3H_{11}CHO$ 22.92 100 $n-C_3CH_{11}CHO$ 22.92 100 $CH_2=CHCHO$ 6.06 100 $CH_3CH=CHCHO$ 12.04 100 CH_3COCH_3 5.44 100 $CH_3COC_2H_5$ 7.99 100 $CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_4H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $C_3H_4COC_3H_5$ 11.38 80 C_5H_5CHO 170 12.96 100 $c-C_6H_4(CH_3)CHO$ 19.73 100 $o-C_6H_4(CH_3)CHO$ 19.73 100 $c-C_6H_4(CH_3)CHO$ 19.73 100 $c-C_6H_4(CH_3)CHO$ 19.78 100 $c-C_6H_4(CH_3)CHO$ 7.80 100	C₂H₅CHO		5.50	100
$iso-C_3H_7CHO$ 6.88 90 $n-C_4H_9CHO$ 23.91 100 $iso-C_4H_9CHO$ 11.27 100 $n-C_3H_{11}CHO$ 22.92 100 $CH_2=CHCHO$ 6.06 100 $CH_3CH=CHCHO$ 12.04 100 CH_3COCH_3 5.44 100 $CH_3COC_2H_5$ 7.99 100 $CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_3H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $C_3H_5CO-iso-C_4H_9$ 12.45 100 $C_4H_5COC_3H_5$ 11.38 80 C_5H_5CHO 170 12.96 100 $c_2H_5COC_3H_5$ 100 100 100 $c_5H_4(CH_3)CHO$ 19.73 100 100 $c_5H_4O_2$ 7.24 100 100 $c_5H_4O_2$ 7.80 100 100 $c_5H_4O_2$ 7.80 100 100 $c_6H_1_5COCH_3$	n-C ₃ H ₇ CHO		9.30	100
$n-C_4H_9CHO$ 23.91 100 $iso-C_4H_9CHO$ 11.27 100 $n-C_3H_{11}CHO$ 22.92 100 $CH_2 = CHCHO$ 6.06 100 CH_3COCH_3 5.44 100 $CH_3COC_2H_5$ 7.99 100 $CH_3COC_2H_5$ 7.99 100 $CH_3COC_2H_5$ 7.99 100 $CH_3CO-r.C_4H_9$ 19.45 100 $CH_3CO-r.C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 12.45 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_4H_5COC_2H_5$ 100 100 $C_4H_5COC_2H_5$ 100 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_2H_5COC_2H_5$ 100 100 $C_2H_5COC_1H_5$ 170 12.96 100 $c_2H_4(CH_3)CHO$ 19.28 100 100 $c_5H_4O_2$ 7.24 100 100 100 $c_5H_4O_2$ 7.80 100 100 100 100 c_6H_1OO 7.80 100 100 1	iso-C ₃ H ₇ CHO		6.88	90
$iso-C_4H_9CHO$ 11.27 100 $n-C_3H_{11}CHO$ 22.92 100 $CH_2=CHCHO$ 6.06 100 CH_3COCH_3 5.44 100 $CH_3COC_4H_5$ 7.99 100 $CH_3COC_2H_5$ 7.99 100 $CH_3COC_4H_9$ 19.45 100 $CH_3CO-r.C_4H_9$ 19.45 100 $CH_3CO-r.C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 12.45 100 $CH_3CO-secC_4H_9$ 12.45 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_4H_5COC_3H_5$ 170 12.96 100 $C_2H_5COC_3H_5$ 170 12.96 100 c_2H_5CHO 170 12.96 100 $c_5H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $c_5H_4O_2$ 7.24 100 $c_5H_4O_2$ 7.80 100 $c_6H_5COCH_3$ 16.76 100 $C_8H_5COCH_3$ 130 30 100 CH_3COCOCH_4 5.83 100<	n-C₄H₀CHO		23.91	100
$n-C_3H_{11}CHO$ 22.92 100 $CH_2=CHCHO$ 6.06 100 $CH_3CH=CHCHO$ 12.04 100 CH_3COCH_3 5.44 100 $CH_3COC_2H_5$ 7.99 100 $CH_3CO_iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_3H_7$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 12.45 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_4H_5COC_3H_5$ 170 12.96 100 $C_2H_5COC_3H_5$ 170 12.96 100 $c-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $c-C_6H_4(CH_3)CHO$ 19.73 100 $C_5H_4O_2$ 7.24 100 $c_6H_5COCH_3$ 16.76 100 CH_3COCCH_3 100 CH_3COCCH_3 100 CH_4COCCH_3 130 30 100 CH_3COCH_3 100 CH_3COCH_3 100	iso-C₄H₀CHO		11.27	100
$CH_2 = CHCHO$ 6.06 100 $CH_3CH = CHCHO$ 12.04 100 CH_3COCH_3 5.44 100 $CH_3COC_2H_5$ 7.99 100 $CH_3COC_3H_7$ 10.03 100 $CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_4H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 14.90 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_4H_5COC_3H_5$ 11.38 80 C_5H_5CHO 170 12.96 100 $o^2-C_8H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $c_3H_4O_2$ 7.24 100 C_6H_10O 7.80 100 $C_6H_5COCH_3$ 16.76 100 $CH_3COCOCH_3$ 130 30 100 $CH_3COCCH_2COCH_3$ 5.83 100	<i>n</i> -C₅H ₁₁ CHO		22.92	100
CH_3CH=CHCHO12.04100CH_3COCH_35.44100CH_3COC_2H_57.99100CH_3CO-iso-C_3H_710.03100CH_3CO-n-C_4H_919.45100CH_3CO-iso-C_4H_914.92100CH_3CO-secC_4H_914.92100CH_3CO-secC_4H_912.45100CH_3CO-tertC_4H_911.3880C_5H_5COC_3H_517012.96100 $c-C_6H_4(CH_3)CHO$ 19.28100 $m-C_6H_4(CH_3)CHO$ 19.73100 $c_3H_4O_2$ 7.24100 $C_6H_5COCH_3$ 16.76100CH_3COCOCH_313030100CH_3COCOCH_45.83100	CH ₂ =CHCHO		6.06	100
CH_3COCH_3 5.44 100 $CH_3COC_2H_5$ 7.99 100 $CH_3COC_3H_7$ 10.03 100 $CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_4H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $C_2H_sCOC_3H_5$ 11.38 80 $C_2H_sCOC_3H_5$ 170 12.96 100 $o-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $c_3H_4O_2$ 7.24 100 C_6H_1OO 7.80 100 $C_6H_5COCH_3$ 16.76 100 $CH_3COCOCH_3$ 130 30 100	CH ₃ CH=CHCHO		12.04	100
$CH_3COC_2H_5$ 7.99 100 $CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-iso-C_4H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $CL_3CO-iso-C_4H_9$ 12.45 100 $C_2H_sCOC_3H_s$ 11.38 80 $C_2H_sCOC_3H_5$ 170 12.96 100 $o-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 19.73 100 $c_5H_4O_2$ 7.24 100 C_6H_1OO 7.80 100 $C_6H_5COCH_3$ 16.76 100 $CH_3COCOCH_3$ 130 30 100	CH ₃ COCH ₃		5.44	100
$CH_3CO-iso-C_3H_7$ 10.03 100 $CH_3CO-n-C_4H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-iso-C_4H_9$ 14.90 100 $CH_3CO-secC_4H_9$ 14.90 100 $CH_3CO-iso-C_4H_9$ 12.45 100 $C_2H_5COC_3H_5$ 11.38 80 C_6H_5CHO 170 12.96 100 $o-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 18.75 100 $o-C_6H_4(CH_3)CHO$ 19.73 100 $C_5H_4O_2$ 7.24 100 C_6H_1OO 7.80 100 $C_6H_5COCH_5$ 16.76 100 $CH_3COCOCH_3$ 130 30 100	CH ₃ COC ₂ H ₅		7.99	100
$CH_3CO-n-C_4H_9$ 19.45 100 $CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 14.90 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_2H_5COC_3H_5$ 11.38 80 C_6H_5CHO 170 12.96 100 $o-C_6H_4(CH_3)CHO$ 19.28 100 $o-C_6H_4(CH_3)CHO$ 18.75 100 $o-C_6H_4(CH_3)CHO$ 19.73 100 $C_5H_4O_2$ 7.24 100 $C_6H_5COCH_3$ 16.76 100 $C_6H_5COCH_3$ 130 30 100	CH ₃ CO- <i>iso</i> -C ₃ H ₇		10.03	100
$CH_3CO-iso-C_4H_9$ 14.92 100 $CH_3CO-secC_4H_9$ 14.90 100 $CH_3CO-secC_4H_9$ 12.45 100 $C_2H_5COC_3H_5$ 11.38 80 C_6H_5CHO 170 12.96 100 $o-C_6H_4(CH_3)CHO$ 19.28 100 $o-C_6H_4(CH_3)CHO$ 18.75 100 $o-C_6H_4(CH_3)CHO$ 19.73 100 $c-C_6H_4(CH_3)CHO$ 19.73 100 $c-C_6H_4(CH_3)CHO$ 19.73 100 $c-C_6H_4(CH_3)CHO$ 19.73 100 $C_5H_4O_2$ 7.24 100 $C_6H_{10}O$ 7.80 100 $C_6H_5COCH_3$ 16.76 100 CH_3COCOCH_4 130 30 100	CH₃CO- <i>n</i> -C₄H9		19.45	100
CH_3CO -sec. $-C_4H_9$ 14.90 100 CH_3CO -tert. $-C_4H_9$ 12.45 100 $C_2H_5COC_2H_5$ 11.38 80 C_6H_5CHO 170 12.96 100 $p-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 18.75 100 $p-C_6H_4(CH_3)CHO$ 19.73 100 $c_5H_4O_2$ 7.24 100 $C_6H_5COCH_3$ 16.76 100 $C_6H_3COCCH_3$ 130 30 100 $CH_3COCCH_2COCH_3$ 5.83 100	CH3CO-iso-C4H9		14.92	100
$CH_3CO-tertC_4H_9$ 12.45 100 $C_2H_5COC_2H_5$ 11.38 80 C_6H_5CHO 170 12.96 100 $o-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 18.75 100 $p-C_6H_4(CH_3)CHO$ 19.73 100 $c_5H_4O_2$ 7.24 100 $C_6H_5COCH_3$ 16.76 100 $C_6H_5COCCH_3$ 130 30 100 $CH_3COCCH_2COCH_3$ 5.83 100	CH₃CO-secC₄H9		14.90	100
$C_2H_5COC_2H_5$ 11.38 80 C_5H_5CHO 170 12.96 100 $P-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 18.75 100 $p-C_6H_4(CH_3)CHO$ 19.73 100 $P-C_6H_4(CH_3)CHO$ 19.73 100 $C_5H_4O_2$ 7.24 100 C_6H_10O 7.80 100 $C_6H_5COCH_5$ 16.76 100 CH_4COCOCH_3 130 30 100 CH_3COCCH_2COCH_3 5.83 100	CH₃CO-tertC₄H9		12.45	100
C_6H_5CHO 170 12.96 100 $p-C_6H_4(CH_3)CHO$ 19.28 100 $m-C_6H_4(CH_3)CHO$ 18.75 100 $p-C_6H_4(CH_3)CHO$ 19.73 100 $p-C_6H_4(CH_3)CHO$ 19.73 100 $c_5H_4O_2$ 7.24 100 C_6H_1OO 7.80 100 $C_6H_5COCH_3$ 16.76 100 CH_3COCOCH_4 130 30 100 CH_3COCH_2COCH_3 5.83 100	C2H5COC2H5		11.38	80
$p - C_6 H_4(CH_3)CHO$ 19.28 100 $m - C_6 H_4(CH_3)CHO$ 18.75 100 $p - C_6 H_4(CH_3)CHO$ 19.73 100 $p - C_6 H_4(CH_3)CHO$ 19.73 100 $C_3 H_4 O_2$ 7.24 100 $C_6 H_{10}O$ 7.80 100 $C_6 H_5 COCH_3$ 16.76 100 CH_3 COCOCH_4 130 30 100 CH_3 COCH_2 COCH_3 5.83 100	C₅H₅CHO	170	12.96	100
$m-C_6H_4(CH_3)CHO$ 18.75 100 $p-C_6H_4(CH_3)CHO$ 19.73 100 $C_3H_4O_2$ 7.24 100 $C_6H_{10}O$ 7.80 100 $C_6H_5COCH_3$ 16.76 100 CH_3COCOCH_3 130 30 100 CH_3COCH_2COCH_3 5.83 100	ρ-C₀H₄(CH₃)CHO		19.28	100
$p-C_6H_4(CH_3)CHO$ 19.73 100 $C_3H_4O_2$ 7.24 100 $C_6H_{10}O$ 7.80 100 $C_6H_5COCH_3$ 16.76 100 CH_4COCOCH_3 130 30 100 CH_3COCCH_2COCH_3 5.83 100	m-C₀H₄(CH₃)CHO		18.75	100
$C_3H_4O_2$ 7.24 100 $C_3H_{10}O$ 7.80 109 $C_8H_5COCH_3$ 16.76 100 CH_4COCOCH_3 130 30 100 CH_3COCH_2COCH_3 5.83 100	σ-C₀H₄(CH₃)CHO		19.73	100
$C_6H_{10}O$ 7.80 100 $C_6H_3COCH_3$ 16.76 100 CH_3COCOCH_3 130 30 100 CH_3COCH_2COCH_3 5.83 100	C₅H₄O₂		7.24	100
C6H3COCH3 16.76 100 CH3COCOCH3 130 30 100 CH3COCH2COCH3 5.83 100	C6H10O		7.80	100
CH ₃ COCOCH ₃ 130 30 100 CH ₃ COCH ₂ COCH ₃ 5.83 100	C6H3COCH3		16.76	100
CH ₃ COCH ₂ COCH ₃ 5.83 100	CH3COCOCH3	130	30	100
	CH ₃ COCH ₂ COCH ₃		5.83	100

* The extent of the reaction was determined from the carbonyl compounds remaining after the reaction period with an Ethofat column (GC conditions, A, 90°; from formaldehyde to diethyl ketone, and biacetyl and acetyl acetone) and an SE-30 column (GC conditions, B, 130°; from benzaldehyde to acetophenone).

glass; column packing, 20% Ethofat 60/25 on Shimalite F (20–80 mesh); carrier gas (nitrogen) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min, respectively; column temperature, 90°; injection port and detector (FID) temperature, 100°; (B) analytical column, 3 m × 3 mm I.D., glass; column packing, 5% SE-30 on Chromosorb W (60–80 mesh), acid washed and silanized; carrier gas (nitrogen) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/mif, respectively; column temperature, 130° or 170°; injection port and detector (FID) temperature, 180°; ECD ⁶³Ni (10 mCi) carrier gas (nitrogen) flow-rate, 50 ml/min; column temperature, 130°; injection port temperature, 180°; detector temperature, 250°: pulsed voltage, (voltage 48 V, pulse width 8 μ sec); (C) analytical column, 30 m × 0.25 mm I.D., glass capillary coated with PEG 20M (obtained from Hitachi, Ibaraki, Japan); carrier gas (helium) flow-rate, 0.8 ml/min; purge gas, (helium) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min; air and hydrogen flow-rate, 0.8 ml/min; purge gas, (helium) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min; column temperature, 130°; injection port and detector (FID) temperature, 200°; splitting ratio, 1:96.

RESULTS AND DISCUSSION

The retention times and the extent of the derivatization for 27 pentafluorophenylhydrazone derivatives are given in Table I. All of the carbonyl compounds underwent highly quantitative reactions, except for acetaldehyde and diethyl ketone (80%).

Fig. 1(a) shows a typical chromatogram for eight pentafluorophenylhydrazone



Fig. 1. (a) Typical chromatogram of eight pentafluorophenylhydrazone derivatives (SE-30, FID). Peaks of pentafluorophenylhydrazones: $1 = \text{formaldehyde } (0.53 \,\mu\text{g})$; $2 = \text{acetaldehyde } (0.11 \,\mu\text{g})$; $3 = \text{propionaldehyde } (0.12 \,\mu\text{g})$; $4 = \text{acrolein } (1.2 \,\mu\text{g})$; $5 = \text{isobutyraldehyde } (0.13 \,\mu\text{g})$; 6 = nbutyraldehyde $(0.13 \,\mu\text{g})$; $7 = \text{isovaleraldehyde } (0.13 \,\mu\text{g})$; $8 = \text{crotonaldehyde } (0.39 \,\mu\text{g})$. (b) Typical chromatogram of five pentafluorophenylhydrazone derivatives (SE-30, ECD). Peaks of pentafluorophenylhydrazones: $1 = \text{formaldehyde } (0.11 \,\text{ng})$ plus pentafluorophenylhydrazine; 2 = acetaldehyde $(0.11 \,\text{ng})$; $3 = \text{propionaldehyde } (0.12 \,\text{ng})$; $4 = \text{isobutyraldehyde } (0.13 \,\text{ng})$; 5 = n-butyraldehyde $(0.14 \,\text{ng})$. (c) Typical chromatogram of three pentafluorophenylhydrazone derivatives (PEG 20M, glass capillary column, FID). Peaks of pentafluorophenylhydrazones: $1 = \text{acetone } (5 \cdot 10^{-7} \,\text{mole})$; $2 = \text{acrolein } (5 \cdot 10^{-7} \,\text{mole})$; $3 = \text{propionaldehyde } (5 \cdot 10^{-7} \,\text{mole})$.

NOTES

derivatives using an FID with an SE-30 column (GC conditions B). The separation of the peaks of pentafluorophenylhydrazine and the formaldehyde pentafluorophenylhydrazone derivative was incomplete. Fig. 1(b) shows a typical chromatogram for five pentafluorophenylhydrazone derivatives with highly sensitive electron-capture detection (GC conditions B, 130°). The minimum detectable amount from the chromatogram was about 0.01 ng. However, the peak of the formaldehyde pentafluorophenylhydrazone derivative overlapped that of pentafluorophenylhydrazine. (Fig. 1(c) shows a typical chromatogram for the derivatives of the C₃ compounds propionaldehyde, acrolein and acetone obtained with a 30 m \times 0.25 mm I.D. glas capillary column packed with PEG-20M at 130° (GC conditions C). A complete separation was achieved at a lower temperature than that necessary with the 2,4-dinitrophenylhydrazone derivatives¹⁴.

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