

Note

Thin-layer chromatographic decomposition of the picrates and trinitrobenzates of polycyclic hydrocarbons and other organic compounds

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In a previous paper¹, decomposition of picrate, trinitrobenzate and styphnate derivatives of polycyclic hydrocarbons in a chromatographic column containing basic alumina, used in the purification of these compounds, was reported to occur. In this paper is described the thin-layer chromatographic decomposition on silica gel (with a fluorescent indicator) of the picrates and trinitrobenzates of polycyclic hydrocarbons and other representative organic compounds (dibenzofuran, β -naphthol, α -naphthylamine). Such derivatives are used as intermediates in the purification and identification of these compounds. For the identification of the compounds and evaluation of the degree of purification obtained, the melting points and ultraviolet spectra of the products were determined.

EXPERIMENTAL

Apparatus

Melting points were determined on a Kofler hot stage and are uncorrected. UV absorption spectra were measured in ethanol with a Beckman DB instrument. Desaga equipment was used for thin-layer chromatography.

Preparation of derivatives

The picrates and trinitrobenzates of naphthalene (I), β -methyl-naphthalene (II), anthracene (III), phenanthrene (IV), chrysene (V), pyrene (VI), acenaphthene (VII), fluorene (VIII), dibenzofuran (IX), β -naphthol (X) and α -naphthylamine (XI) were prepared by heating for 10 min on a water bath equimolecular solutions of the compounds (I–XI) and either picric acid or trinitrobenzene in solvents or solvent mixtures as indicated in Tables I and II. Subsequent crystallization was carried out at room temperature. The compounds were purified by recrystallization from the same solvents or solvent mixtures. Chrysene picrate is unstable² and could not be prepared with the same solvents and procedures as the other compounds. For this preparation an equimolecular mixture of picric acid and V in light petroleum (b.p. 80–100°C) were heated for 10 min, adding the minimum amount of benzene until total dissolution occurred. The solution was allowed to cool and a bright orange crystalline product was obtained (m.p. 160–164°C). On recrystallization from the same solvents mixture it melted at 169–170°C.

TABLE I
PREPARATION AND DECOMPOSITION OF THE PICRATES

| Compound | Picrates | | | Purified compounds | | |
|----------|----------------------|----------|-------------|--------------------|-------------|-----------|
| | M.p. (°C) | Solvent* | Weight (mg) | M.p. (°C) | Weight (mg) | Yield (%) |
| I | 149-151 | E | 198 | 79-80 | 64 | 89 |
| II | 116-118 | E | 206 | 34-35 | 79 | 95 |
| III | 138-139 | B-LP | 200 | 215-216 | 69 | 80 |
| IV | 142-144 | E | 148 | 100-101 | 58 | 90 |
| V | 169-170 | LP**-B | 180 | 255-256 | 72 | 81 |
| VI | 220-222 | E | 193 | 155-156 | 66 | 75 |
| VII | 160-161 | E | 200 | 93-94 | 64 | 80 |
| VIII | 78-79 | B-LP | 165 | 116-117 | 64 | 94 |
| IX | 98-99 | B-LP | 252 | 86-87 | 79 | 76 |
| X | 160-162 | B | 274 | 123-124 | 82 | 86 |
| XI | 170-172 (decomp.) | B | 210 | 50-51 | 70 | 88 |

* E = ethanol; B = benzene; LP = light petroleum (b.p. 60-80°C).

** LP (80-100)-B.

TABLE II
PREPERATION AND DECOMPOSITION OF THE TRINITROBENZOLATES

| Compound | Trinitrobenzolates | | | Purified compounds | | |
|----------|--------------------|----------|-------------|--------------------|-------------|-----------|
| | M.p. (°C) | Solvent* | Weight (mg) | M.p. (°C) | Weight (mg) | Yield (%) |
| I | 153-154 | E | 183 | 79-80 | 66 | 96 |
| II | 125-127 | E | 159 | 33-34 | 52 | 81 |
| III | 164-166 | B-LP | 179 | 214-215 | 67 | 82 |
| IV | 159-160 | E | 200 | 101-102 | 70 | 80 |
| V | 187-188 | B-LP | 220 | 254-255 | 107 | 95 |
| VI | 244-246 | E | 199 | 156-157 | 87 | 92 |
| VII | 168-170 | B-LP | 274 | 91-92 | 93 | 82 |
| VIII | 105-106 | B-LP | 211 | 114-115 | 79 | 86 |
| IX | 96-97 | B-LP | 275 | 85-86 | 113 | 94 |
| X | 160-162 | B | 212 | 124-125 | 80 | 94 |
| XI | 218-220 | B | 219 | 49-50 | 73 | 83 |

* See Table I.

Chromatographic decomposition

Weighed amounts of the picrates and trinitrobenzolates were dissolved in minimum amounts of solvent (commonly benzene or ethanol). They were spotted on chromatographic plates [20 × 20 cm; silica gel 60 HF₂₅₄₊₃₆₆ (Merck), thickness 0.50 mm] and were developed (at room temperature, 20 ± 2°C) with the solvents indicated in Tables III and IV. Compounds I-XI, products of the decomposition of the derivatives, were examined under ultraviolet light. The fluorescence observed varied between violet-brown and bluish-brown, except IX (sky blue) and VI (brilliant yellow). The compounds were extracted from the adsorbent with different solvents (acetone for I,

TABLE III
CHROMATOGRAPHIC DECOMPOSITION OF THE PICRATES

| Compound | $R_f \times 100^*$ | | | |
|-------------|--------------------|------|----|-------|
| | LP | LP-T | T | T-C-A |
| I | | 53 | | |
| II | | 77 | | |
| III | 45 | | | |
| IV | 43 | | | |
| V | 28 | | | |
| VI | 42 | | | |
| VII | 53 | | | |
| VIII | 40 | | | |
| IX | 48 | | | |
| X | | | 14 | |
| XI | | | | 53 |
| Picric acid | 0 | 0 | 0 | 0 |

* Eluents: LP = light petroleum (b.p. 60–80°C); LP-T = light petroleum (b.p. 60–80°C)–toluene (98:2); T = toluene; T-C-A = toluene–chloroform–ethyl acetate (7:3:3).

III, IV and IX; benzene for V and VII; ethanol for II, VI, VIII, X and XI), then crystallized from the corresponding solvents (ethanol for I–IV and VI–IX; benzene for V; ethanol–water for X and XI). The melting points and UV spectra of the compounds were then determined.

TABLE IV
CHROMATOGRAPHIC DECOMPOSITION OF THE TRINITROBENZOLATES

| Compound | $R_f \times 100^*$ | | |
|-----------------|--------------------|------|----|
| | LP | LP-T | T |
| I | | | 84 |
| II | | 76 | |
| III | 49 | | |
| IV | | | 87 |
| V | | 73 | |
| VI | 46 | | |
| VII | | 78 | |
| VIII | | | 88 |
| IX | | 85 | |
| X | | | 14 |
| XI | | | 14 |
| Trinitrobenzene | 0 | 0 | 60 |

* Eluents: see Table III.

TABLE V
UV ABSORPTION SPECTRA

| Compound | λ (nm) (log ϵ) | λ_{\max} (nm) (log ϵ) | |
|----------|--|---|------------|
| | | a | b |
| I | <i>p</i> bands: 284 (3.70), 274 (3.86), 264 (3.79), 256 (3.68), 248 (3.44) | 274 (3.60) | 274 (3.86) |
| II | <i>p</i> bands: 266 (3.65), 274 (3.68), 286 (3.54) | 274 (3.45) | 274 (3.68) |
| III | <i>p</i> bands: 373 (3.85), 354 (3.87), 340 (3.77), 322 (3.50), 309 (3.17) | 354 (3.64) | 354 (3.87) |
| IV | <i>p</i> bands: 292 (4.32), 280 (4.22), 272 (4.26) | 292 (4.18) | 292 (4.32) |
| V | <i>p</i> bands: 320 (4.21), 304 (4.19), 292 (4.14), 280 (4.15) | 320 (4.10) | 320 (4.21) |
| VI | <i>p</i> bands: 336 (4.75), 320 (4.50), 306 (4.02), 294 (3.66) | 336 (4.40) | 336 (4.75) |
| VII | 280 (3.80), 288 (3.86), 300 (3.65) 304 (3.34) | 288 (3.60) | 288 (3.86) |
| VIII | α -bands: 300 (4.01), 288 (3.76), <i>p</i> bands: 262 (4.26) | 262 (4.14) | 262 (4.26) |
| IX | 300 (3.68), 298 (3.98), 286 (4.22), 278 (4.26), 273 (4.12), 250 (4.30), 242 (4.12) | 250 (4.16) | 250 (4.30) |
| X | 228 (4.85), 254 (3.40), 260 (3.60), 274 (3.65), 285 (3.50) | 228 (4.60) | 228 (4.85) |
| XI | 243 (4.30), 320 (3.73) | 243 (4.02) | 243 (4.30) |

RESULTS AND DISCUSSION

The results for the picrates and trinitrobenzulates and the melting points and the yields of the different compounds after the purification procedures are given in Tables I and II. In Tables III and IV the eluents used in the chromatographic decomposition procedure and the $R_F \times 100$ values for the purified compounds and the reactants are given. UV absorption bands, fundamentally *p* bands³, of the compounds after the purification process are given in Table V, together with λ_{\max} . (log ϵ) values of the compounds (a) before and (b) after the purification step. For the trinitrobenzulates, the UV spectra of the compounds do not differ appreciably from those indicated in Table V, and have therefore been omitted.

Compounds I–XI were commercial products with melting points (°C) of 75–77 (I), 29–32 (II), 207–210 (III), 95–98 (IV), 230–234 (V), 150–153 (VI), 88–92 (VII), 107–110 (VIII), 80–83 (IX), 117–120 (X) and 40–43.5°C (XI). The melting points of the compounds after the chromatographic process and after recrystallization are given in Tables I and II. These results and those in Tables III–V indicate the degree of purification attained.

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