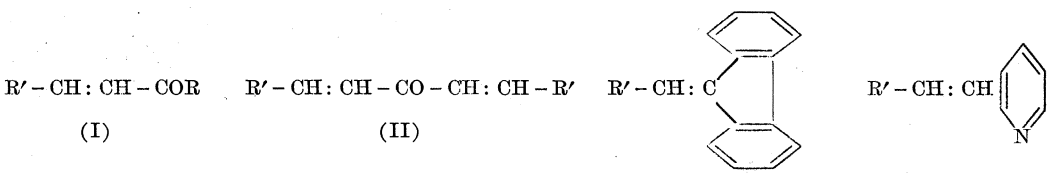
Reactions with 9-Anthraldehyde

Ahmed Mustafa

Chemistry Department, Faculty of Science, Fouad I University, Abbassia-Cairo, Egypt

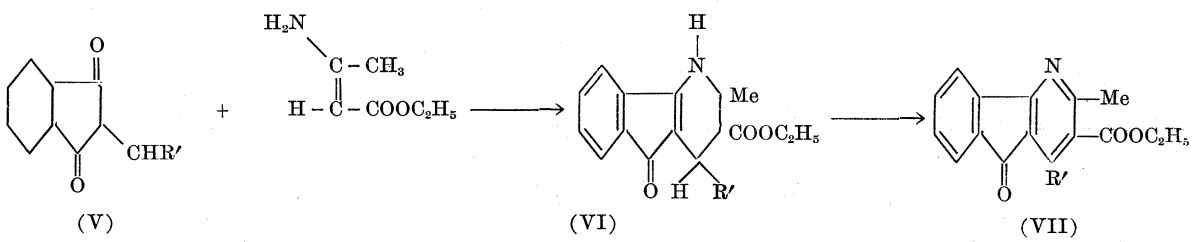
9-Anthraldehyde reacts readily with the reactive methylene group in malonic acid (*1*). A number of other condensation reactions have been studied, all leading to colored substances characterized by extended conjugated systems (*5*). With various methyl ketones, (9-anthrylidene)-compounds of the type (I) have been obtained.



(R′ = anthryl, $C_{14}H_9$)

9-Anthrylidene acetone (1,R = CH_3), mp 115°, yellow crystals from alcohol (Found: C, 87.8; H, 5.6; M (micro-Rast), 236. $C_{18}H_{14}O$ requires C, 87.8; H, 5.7%; M, 246), and di-9-anthrylidene-acetone (II), mp above 250° from xylene (Found: C, 91.1; H, 5.0; M (micro-Rast) 425. This last compound condenses with ethyl 2-amino crotonate in glacial acetic acid to give violet crystals from acetic acid, mp above 260° of ethyl-1-anthryl-3-methyl-1: 4-dihydro-4-azofluorenone-2-carboxylate (VI) (Found: C, 80.6; H, 5.3; N, 3.3. $C_{30}H_{23}O_3N$ requires C, 80.9; H, 5.1; N, 3.1%) in nearly quantitative yield. Oxidation of (VI) with chromic acid in acetic acid afforded ethyl-1-anthryl-3-methyl-4-azofluorenone-2-carboxylate (VII), yellow crystals from tetralin, mp above 270° (Found: C, 81.3; H, 4.5; N, 3.1. $C_{30}H_{21}O_3N$ requires C, 81.3; H, 4.7; N, 3.2%).

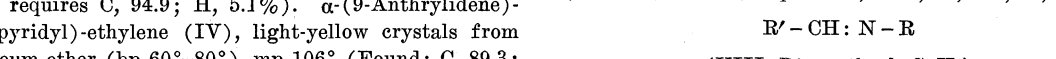
The condensation of 9-anthraldehyde with *o*-, *m*-, and *p*-nitroaniline (*2*) leads to the formation of the corresponding 9-anthrylidene nitroaniline, of the type (VIII). 9-Anthrylidene-*p*-nitroaniline (VIII, R = *p*-$C_6H_4NO_2$ orange-red crystals from alcohol, mp 186° (Found: C, 76.9; H, 4.2; N, 8.4. $C_{21}H_{14}N_2O_2$ requires C, 77.3; H, 4.3; N, 8.6%), 9-anthrylidene-*m*-nitroaniline forms golden-yellow crystals from benzene, mp 176° (Found: C, 77.1; H, 4.2; N, 8.5. $C_{21}H_{14}N_2O_2$ requires C, 77.3; H, 4.3; N, 8.6%), and 9-anthrylidene-*o*-nitroaniline forms yellow crystals from benzene, mp 210° (Found: C, 77.0; H, 4.1; N, 8.4. $C_{21}H_{14}N_2O_2$ requires C, 77.3; H, 4.3; N, 8.6%).



(R′ = anthryl, $C_{14}H_9$)

$C_{33}H_{22}O$ requires C, 91.2; H, 5.1%; M, 434) are formed. Similarly, 9-anthraldehyde condenses with pinacolone, to give 9-anthrylidenepinacolone (1,R = – $C(CH_3)_3$). Fluorene gave 9-(9′-anthrylidene)-fluorene (III), yellow crystals, mp, 230° from xylene (Found: C, 94.8; H. 5.2. $C_{28}H_{18}$ requires C, 94.9; H, 5.1%). α-(9-Anthrylidene)-β-(2′-pyridyl)-ethylene (IV), light-yellow crystals from petroleum ether (bp 60°–80°), mp 106° (Found: C, 89.3; H, 5.1; N, 4.7. $C_{21}H_{15}N$ requires C, 89.7; H, 5.3; N, 5.0%) has been obtained either by the condensation of the aldehyde with α-picoline or by the condensation of the aldehyde with α-picoline methiodide (*3*), forming α-(9-anthrylidene)-β-(2′-pyridyl)-ethylene methiodide, followed by thermal decomposition.

9-Anthraldehyde also condenses with indane-1: 3-dione (*4*), by direct fusion of the two components to give 9-anthrylidene-indane-1: 3-dione (V), dark-red crystals, from xylene, mp 228° (Found: C, 85.7; H, 4.1, M (micro-Rast), 326. $C_{24}H_{14}O_2$ requires C, 86.2; H, 4.2% M, 334).



(VIII, R′ = anthryl, $C_{14}H_9$)

References

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