Experimental. Melting points were obtained on a Kofer micro hot stage. IR-spectra were recorded on a Perkin-Elmer No. 257 instrument. UV-spectra were measured with a Beckman DK 2 spectrophotometer. The NMR spectra were obtained on a Varian A-60 spectrometer. All reactions were followed by TLC on silica gel HF (Merck) plates with carbon tetrachloride-methanol (9:1) as solvent. The spots were detected by examining the plates under UV. The presence of unreacted starting material was also revealed by spraying with a solution of iron(III) hexacyanoferrate(III) reagent.7

General procedure for dehydration of 2,2'-alkylidene-bis-dimethones. The 2,2'-alkylidenebis-dimethone (100 mg) was treated with formic acid (98—100 %, Merck, 1—2 ml) at 90—100°C for 5 min. Water was added dropwise until the mixture became cloudy. After cooling the crystals which formed were collected by filtration and washed with aqueous ethanol. Alternatively the formic acid was removed under reduced pressure and the residue recrystallised from aqueous ethanol.

The same result was obtained upon treatment with formic acid at room temperature for 90 min.

Dehydration of methylene-bis-dimethone. Methylenedioxybis-dimethone (1.17 g, 4 mmole) was stirred with formic acid (98—100 %, 10 ml) and a catalytic amount of p-toluene sulfonic acid at 90—100°C for 2 h. Cooling, addition of water (10 ml) and filtration gave Ia (97 %). Recrystallisation from 80 % ethanol gave the pure substance, m.p. 172—173°C (lit.5 171°C).

Treatment with formic acid for 6 h at 90—100°C without catalyst gave the same result.

Dehydration of methylene-bis-1,3-cyclohexandione. Methylene-bis-1,3-cyclohexanandione (0.95 g, 4 mmole) was stirred with formic acid (98—100 %, 18 ml) and a small amount of an acetic acid exchange resin (Dowex 50) at 90—100°C for 3 h. The solution was filtered and evaporated to dryness in vacuo. The residue was crystallised from methanol-isopropyl ether (2:3) to give 3,4,5,6-tetrahydro-1,8(2H,7H)-xanthenedione (0.81 g, 70 %). Recrystallisation from methanol gave the pure substance, m.p. 166—168°C (lit.6 163°C). NMR (CDCl3) δ 1.7—2.7 (m, 12H), δ 2.85 (quintet, J~1.5 cps, 2H).

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The Reaction of o-Chlorobenzylidenemalononitrile with Substituted N-Arylbenzimidoyl Chlorides

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Meerwein et al.1 have shown that N-substituted benzimidoyl chlorides react with aliphatic as well as aromatic mononitriles in the presence of a Lewis acid to give 2,4-disubstituted quinazolines. In our search for a reaction which can be used analytically to detect o-chlorobenzylidenemalononitrile (III) we have investigated the reaction between III and a series of N-arylenzimidoyl chlorides (II) substituted with auxochromic as well as chromophoric groups.

It was our hope by extending the conjugated system of o-chlorobenzylidenemalononitrile to that of IV to produce a bathochromic shift of the absorption band into the visible region of the spectrum. Despite that IV was formed we did not obtain any significant colour shift.

However, it seems to be of value to report the results of the investigation. As far as we know from the literature the reaction between II and \( R\)-unsaturated nitriles has not been described previously. It is also noteworthy that in the reaction investigated leading to 2,4-disubstituted quinazolines only one of the nitrile groups in III is involved. Furthermore most of the imidoyl chlorides and all the quinazolines in this paper are new.

The compounds II have been prepared from the corresponding benzanilides (I) by refluxing with phosphorus pentachloride\(^2\) (Method a) in dry benzene. This method is of general use while refluxing with thionyl chloride\(^3\) or heating with finely powdered phosphorus pentachloride\(^4\) (Method b) only led to II in a few cases. The following imidoyl chlorides were prepared but not isolated in analytically pure form: (R, R', melting point in parenthesis) 3,5-(NO\(_2\))\(_2\)H (120–130\(^\circ\))È, 3,5-(NO\(_2\))\(_2\)H, 4-NO\(_2\) (148–150\(^\circ\)); 4-NO\(_2\), 2,4-(NO\(_2\))\(_2\) (160\(^\circ\)); 4-NO\(_2\), 2-CH\(_2\), 4-CH\(_2\) (128–130\(^\circ\)); 4-NO\(_2\), 2,5-(CH\(_2\))\(_2\), (83–85\(^\circ\)); 4-NO\(_2\), 2-CH\(_2\)-4-NO\(_2\), (160–170\(^\circ\)); 4-N=C=N-C\(_6\)H\(_5\), (113–118\(^\circ\)); 4-NO\(_2\), 4-N=N-C\(_6\)H\(_5\), 4-OCH\(_3\), (135–140\(^\circ\)); 4-Cl, 4-Cl, (73\(^\circ\)). I containing R=3,5-(NO\(_2\))\(_2\) and R'=H could only be prepared by Method b. The reaction time varied from 1 to 24 h and the yields ranged from 50 to 80\% of the theoretical. The IR spectra showed a strong absorption band in the region 1650–1689 cm\(^{-1}\).

All attempts to prepare II substituted with the auxochromes (CH\(_3\))\(_2\)N- and -OH were unsuccessful.

The quinazolines IV (Table 1) have been prepared by heating an equimolecular mixture of II, III, and aluminium chloride to 80–210\(^\circ\) in nitrobenzene or o-dichlorobenzene. The products were purified by recrystallization from a suitable solvent or by sublimation under reduced pressure. The reaction products were identified by elemental analysis and IR spectroscopy. The IR spectra show a doublet of medium intensity at 1580 cm\(^{-1}\), a strong band at 1485 cm\(^{-1}\), and a triplet at 1395 cm\(^{-1}\) all of which are ascribed to C=H stretching frequencies.

The yields of IV (see Table 1) lend some support to the mechanism proposed by Meerwein et al.\(^1\) involving as the final step an electrophilic attack of the nitrile carbon atom on the R'-substituted benzene ring. When R' is an electron attracting group the yields are low while electron releasing substituents increase the yields.

Experimental. The benzanilides used were made by known methods. The IR spectra were recorded on a Perkin Elmer 337 spectrophotometer (KBr discs) and the melting points which are all uncorrected were determined with a hot stage microscope (Mikroskop-Heiztisch 350 Ernst Leitz G.m.b.H. Wetzlar). Microanalyses were made by Preben Hansen, Microanalytical Department of Chemical Laboratory II, University of Copenhagen.

General procedures. Imidoyl chlorides. Method a: Equimolecular amounts of I and phosphorus pentachloride are refluxed in dry benzene until a clear solution is obtained and the evolution of hydrogen chloride has ceased. Benzene is then evaporated and a crystalline compound can be obtained by recrystallization from either tetrachloromethane or cyclohexane. Method b: I and phosphorus pentachloride are thoroughly mixed in accordance to Ref. 4 and the mixture heated to melting until the gas evolution has ceased. II is isolated from the mixture by crystallization from a suitable solvent.

Quinazolines. After dissolving equimolecular amounts of II and III in nitrobenzene or o-dichlorobenzene, an equimolecular amount of aluminium chloride is added and the mixture is heated. While the mixture is still warm,
## Table 1. New quinazolines (IV)

<table>
<thead>
<tr>
<th>R'</th>
<th>Reaction conditions</th>
<th>Yield</th>
<th>M.p.</th>
<th>Recryst. from</th>
<th>Analysis (C,H,N,Cl)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>100° in nitrobenzene for 2 min</td>
<td>60</td>
<td>170°</td>
<td>benzene + ethanol</td>
<td>Found: 75.3; C, 82.8; H, 3.6; N, 11.4; Cl, 9.6; Calcd.: 75.1; C, 82.2; H, 3.9; N, 11.4; Cl, 9.6</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>60</td>
<td>170°</td>
<td>DMF</td>
<td>Found: 63.2; C, 3.3; H, 3.8; Cl, 3.8; N, 13.6; Calcd.: 63.5; C, 3.3; H, 3.8; Cl, 3.8; N, 13.6</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>60</td>
<td>230°</td>
<td>acetone</td>
<td>Found: 66.7; C, 3.3; H, 3.3; Cl, 3.3; N, 13.5; Calcd.: 66.7; C, 3.3; H, 3.3; Cl, 3.3; N, 13.5</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>228°—132°</td>
<td>DMF</td>
<td>Found: 60.3; C, 2.7; H, 2.7; Cl, 2.7; N, 13.1; Calcd.: 60.3; C, 2.7; H, 2.7; Cl, 2.7; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>306°—309°</td>
<td>DMF</td>
<td>Found: 60.3; C, 2.7; H, 2.7; Cl, 2.7; N, 13.1; Calcd.: 60.3; C, 2.7; H, 2.7; Cl, 2.7; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>289°—290°</td>
<td>DMF</td>
<td>Found: 62.2; C, 3.4; H, 3.4; Cl, 3.4; N, 13.2; Calcd.: 62.2; C, 3.4; H, 3.4; Cl, 3.4; N, 13.2</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>286°—287°</td>
<td>acetone</td>
<td>Found: 62.2; C, 3.4; H, 3.4; Cl, 3.4; N, 13.2; Calcd.: 62.2; C, 3.4; H, 3.4; Cl, 3.4; N, 13.2</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>270°—280°</td>
<td>acetone</td>
<td>Found: 62.5; C, 3.4; H, 3.4; Cl, 3.4; N, 13.2; Calcd.: 62.5; C, 3.4; H, 3.4; Cl, 3.4; N, 13.2</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>257°—260°</td>
<td>acetone</td>
<td>Found: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1; Calcd.: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>257°—260°</td>
<td>acetone</td>
<td>Found: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1; Calcd.: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>257°—260°</td>
<td>DMF</td>
<td>Found: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1; Calcd.: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>257°—260°</td>
<td>DMF</td>
<td>Found: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1; Calcd.: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
<tr>
<td>H</td>
<td>120° in nitrobenzene for 10 min</td>
<td>10</td>
<td>257°—260°</td>
<td>DMF</td>
<td>Found: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1; Calcd.: 61.3; C, 3.5; H, 3.5; Cl, 3.5; N, 13.1</td>
<td>C_{12}H_{10}ClN_{3}</td>
</tr>
</tbody>
</table>

**Note:** The table entries include details of reaction conditions, yields, melting points, recrystallization from various solvents, and analysis data. The chemical formulas and structures of the compounds are also provided. The table highlights variations in the conditions and products, indicating the versatility of the synthesis process.
20% aqueous sodium hydroxide is added to make the solution basic. The quinazoline separates from the mixture at cooling and is purified either by recrystallization or by sublimation under reduced pressure. Further details of the syntheses are summarized in Table 1.


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