A mixture of 61 mmole of 3,4-ethylenedioxybenzaldehyde and 97 mmole of p-(n-butyl)aniline was dissolved in 65 ml of anhydrous toluene, 9.7 mmole of boron trifluoride etherate was added, and the mixture was refluxed for 25 h with a Dean–Stark trap. The mixture was then worked up as described above, and the reaction product obtained after chromatography and removal of the solvent by distillation was vacuum dried at 70-80 °C to give 10 g (50%) of a viscous liquid with $n_\text{D}^2$ 1.1620. UV spectrum, $\lambda_{\text{max}}$, nm (log e): 232 (4.32), 283 (3.96), and 317 (3.85) in alcohol. Found: C 77.3; H 7.2; N 4.4%. C$_{18}$H$_{21}$NO. Calculated: C 77.2; H 7.2; N 4.7%.

2-[p-(n-Amyl)phenyl]-6-formylquinoline. A 0.3-g sample of Raney nickel was added to a solution of 1.3 g of IId in 25 ml of moist toluene, after which the mixture was hydrogenated in a long-necked hydrogenation flask. The catalyst was then removed by filtration, and the solvent was evaporated to give 0.35 g (65%) of a product with mp 71-72 °C (from hexane). IR spectrum: 1710 cm$^{-1}$ (CO). PMR spectrum (CCl$_4$), $\delta$, ppm: 1.20 t (3H) for CH$_3$, 1.48-2.17 m (6H) for the CH$_2$ groups, 2.97 t (2H) for the aromatic ring CH$_2$ groups, 7.52 d (J = 8 Hz, 2H) for the aromatic protons adjacent to the C$_5$H$_{11}$ group, 8.05-8.55 m (7H) for the aromatic protons, and 10.35 s (1H) for the CHO groups. Found: C 83.0; H 6.9; N 4.7%. C$_{21}$H$_{21}$NO. Calculated: C 83.1; H 7.0; N 4.6%.

2-[p-(n-Amylphenyl]quinoline-6-carboxylic Acid. A mixture of 1 g of IId and 50 ml of hydrochloric acid (1:1) was refluxed for 30 h, after which it was cooled, and the resulting precipitate was recrystallized from alcohol to give 0.8 g (80%) of a product with mp 245-247 °C. IR spectrum (in mineral oil): 1700 cm$^{-1}$ (CO). PMR spectrum (CF$_3$COOH), $\delta$, ppm: 0.77 t (3H) for the CH$_3$ group, 1.0-1.75 m (6H) for the CH$_2$ groups, 2.68 t (2H) for the aromatic ring CH$_2$ groups, and 7.45-9.03 m (9H) for the aromatic protons. Found: C 78.6; H 6.3; N 4.5%. C$_{21}$H$_{21}$NO$_2$. Calculated: C 79.0; H 6.6; N 4.4%.

LITERATURE CITED

HETARYLATION OF CYCLOPENTADIENE, INDENE, AND AZULENE

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The direct hetarylation of cyclopentadiene, indene, and azulene with several benzopyridines in the presence of acyl halides was studied. It is shown that the most electrophilic N-benzoyl-isoquinolinium salt is capable of hetarylating CH acids with $\text{pK}_a < 21$.


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N-Heteroaromatic systems with free $\alpha$ or $\gamma$ positions in the presence of acyl halides hetarylinate such weak CH acids as acetophenone ($pK_a$ 19) and acetone ($pK_a$ 20) without catalysts [1]. It seemed of interest to ascertain the limiting $pK_a$ values of CH acids that are still able to undergo this reaction. For this, we studied the possibility of hetarylation of cyclopentadiene (CPD, $pK_a$ 15), indene ($pK_a$ 18.5), azulene and guaiazulene ($pK_a$ 20-21), and fluorene ($pK_a$ 22.9)* with pyridine, quinoline, and isoquinoline in the presence of acyl halides.

The reactions of quaternary pyridinium and benzopyridinium salts with similar CH acids in the presence of alkali metals, which lead to the formation of heterocyclic analogs of sesquifulvalene, are known [3-5]. In these cases, either organometallic compounds with a polar $\delta^{\text{C-Me}}$ bond or carbanions, either free or in the ion-pair state, essentially undergo hetarylation. However, insofar as we know, the hetarylation of cyclopentadiene, indene, fluorene, or azulene in the absence of catalysts has not been studied.†

It was found that in the reaction with cyclopentadiene and indene, N-acylpyridinium and benzopyridinium salts behave differently as a function of the electrophilicity of the N-acylheteroaromatic cation and the acidity of the substrate.

Specifically, none of the investigated N-acylpyridinium salts hetarylated cyclopentadiene, indene, and fluorene under various conditions: Only the starting reagents of their polymerization products were isolated in all cases.

Hetarylation also did not take place in the reaction of N-acetyl salts of isoquinoline and quinoline with cyclopentadiene. In all cases we obtained the same compounds, regardless of the CH acids used in the reaction.

Similar compounds were also obtained by heating N-acetyl salts in the absence of a hetarylateable component. We found that the compounds obtained are 1,1'-diacetyl-1,2,1',2'-tetrahydro-2,2'-difluorenyl (I) and 2,2'-diacetyl-1,2,1',2'-tetrahydro-1,1'-dilisoquinolyl, which were subsequently separated to give their stereoisomers, which proved to be identical to the compounds that we obtained by reduction of fluorene and isoquinoline with zinc dust in acetic anhydride.

Under the hetarylation conditions, the N-acylcylammonium cations evidently react with the anions to give a charge-transfer complex (CTC), which then undergoes decomposition to radicals, which dimerize via the following scheme:

\[
\begin{align*}
\text{CH}_2-C=O & \quad \text{CH}_2-C=O \\
\text{CH}_2-C=O & \quad \text{CH}_2-C=O \\
\text{CH}_2-C=O & \quad \text{CH}_2-C=O
\end{align*}
\]

Under standard conditions, the more electrophilic N-benzylioisoquinolinium chloride hetarylated CPD and indene to give adducts II and III (Table 1), but the reaction with fluorene also gave dimer IV, from which we obtained a disoquinolyl by alkaline hydrolysis, which confirms its structure.

\[
\begin{align*}
\text{II} & \quad \text{III} \\
\text{IV} & \quad \text{V}
\end{align*}
\]

Oxidation of colorless II and III with nitrobenzene gives colored heterocyclic analogs of sesquifulvalene of the V type. These same compounds are formed in the reaction of indenylsodium (cyclopentadienylsodium also reacts similarly) with the appropriate salts, for example:

\[
\begin{align*}
\text{III} & \quad \text{C}_6\text{H}_5\text{NO}_2 \\
\text{IV} & \quad \text{V}
\end{align*}
\]

*The $pK_a$ values are presented on the McEwen-Streitwieser-Applequist-Dessy scale (the MSAD scale) [2].
†See [6] for our preliminary communication in this regard.