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# USE OF THE ZINC CHLORIDE COMPLEX IN THE 1,2-PHOTOADDITION OF ACRYLONITRILE TO BENZENE

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Maleic anhydride and some maleinimides are well known to form 2:1 photoadducts with benzene.[1] However, acrylonitrile, less reactive dienophile, forms a 1:1 1,2-photoadduct with benzene in a poor yield(0.25%).[2] We now report that irradiation of an acrylonitrile-benzene-$ZnCl_2$ complex[$(AN)_2Bz\text{-}ZnCl_2$] and its analogues in place of a simple mixture of the olefin and the benzenoid remarkably increased the 1:1 1,2-adduct formation.

The 2:1 complex[3] of AN and $ZnCl_2$ was added to an excess amount of benzene or toluene to yield a viscous liquid of $(AN)_2Bz\text{-}ZnCl_2$ or $(AN)_2Tol\text{-}ZnCl_2$.[3] Irradiation of a solution of $(AN)_2Bz\text{-}ZnCl_2$ in ethyl acetate (0.1 M) with a low pressure mercury arc under nitrogen at 10-15° for 33 h gave a colorless liquid in 10% yield. This liquid(b.p. 55°/3 mmHg) showed a single peak on vpc, and the elemental analysis (C, 82.5; H, 7.08) and spectral properties agree with those reported for I.[2]

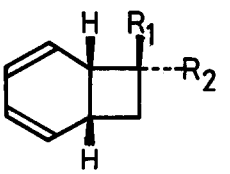
Irradiation of $(AN)_2Tol\text{-}ZnCl_2$ under similar conditions gave a liquid(b.p. 57°/2 mmHg). Vpc analysis showed that it is a mixture of four components in nearly equal amounts. GC-MS technic revealed that the mass spectrum of each component exhibited a base peak at m/e 92 and a molecular ion peak at m/e 145, indicating that they are the 1:1 photoadducts(II) of acrylonitrile with toluene.

A methacrylonitrile-benzene-$ZnCl_2$ complex[$(MAN)_2Bz\text{-}ZnCl_2$] behaved similarly upon irradiation, and yielded a colorless liquid, b.p. 47°/1 mmHg. Although the elemental analysis(C, 82.44; H, 7.52) and spectral properties[$\lambda$max 275 nm($\varepsilon$2230), IR 2215 and 1590 $cm^{-1}$, and $M^+$ 145] agree with a structure of the 1:1 photoadduct, the NMR spectrum exhibited two methyl signals at $\delta$ 1.65 and 1.58 ppm(intensity ratio 1:2) suggesting that it is a mixture of IIIa and IIIb. Referring to the anisotropy effect of the ring double bonds on the chemical shift of methyl signals we concluded that the major compornent must be IIIb. Irradiation of the simple mixture of MAN and benzene also gave IIIa and IIIb in the same ratio as above but in a lower yield.

The table summarizes these results comparing with those obtained by irradiation of mixtures(1:1) of the olefins and the benzenoids without $ZnCl_2$. The trend appeared in the table is likely to be ascribed to the increased electron acceptability of the acrylonitriles by the complex formation with $ZnCl_2$.

Table

| Reactant | Light source* | Irradiation time | Product | Yield |
|---|---|---|---|---|
| AN, Bz | H | 30 h | I | 0.14, 0.25%[2] |
| AN, Bz | L | 34 | I | 1.8 |
| $(AN)_2Bz\text{-}ZnCl_2$ | L | 33 | I | 10.7 |
| AN, Tol | H | 41 | II | 0.23 |
| AN, Tol | L | 44 | II | 1.5 |
| $(AN)_2Tol\text{-}ZnCl_2$ | L | 45 | II | 15.7 |
| MAN, Bz | L | 41 | III | 1.5 |
| $(MAN)_2Bz\text{-}ZnCl_2$ | L | 46 | III | 10.1 |




I $R_1, R_2$=CN,H

IIIa $R_1$=$CH_3$, $R_2$=CN

IIIb $R_1$=CN, $R_2$=$CH_3$

*) H; a 200W medium pressure mercury lamp.
L; a 10W low pressure mercury lamp.

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