

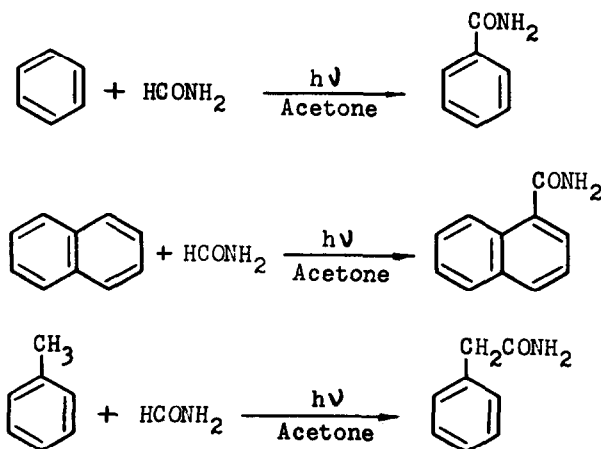
THE PHOTSENSITIZED AMIDATION OF
AROMATIC HYDROCARBONS¹

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RECENT reports from our laboratory show that amidation of ethylenic and acetylenic bonds with formamide can be induced by light.^{1b,c} We wish to report now the amidation of aromatic hydrocarbons with formamide in the presence of acetone as a photosensitizer.



^{1a} Photochemical Studies, Part III.

^{1b} D. Elad, Chem. & Ind. 362 (1962) is regarded as Part I.

^{1c} D. Elad, Proc. Chem. Soc. 225 (1962) is regarded as Part II.

Irradiations,² carried out at room temperature in acetone, gave mixtures from which the tabulated compounds were isolated.

TABLE 1

Hydrocarbon	Product ^a
Benzene	Benzamide (15%)
Naphthalene	1-Naphthamide (20%)
Toluene	Phenylacetamide (23%)
<u>o</u> -Xylene	<u>o</u> -Tolylacetamide (28%)
<u>m</u> -Xylene	<u>m</u> -Tolylacetamide (26%)
<u>p</u> -Xylene	<u>p</u> -Tolylacetamide (32%)

^a Yields of the products isolated are based on the hydrocarbons consumed.

When t-butanol was used as solvent traces only of the amides could be isolated from the irradiated mixtures.

Similarly, exposure of solutions of benzene or naphthalene in formamide-acetone to sunlight for 6-8 weeks gave benzamide and 1-naphthamide, respectively.

It has been noted that irradiated mixtures of formamide and acetone gave considerable amounts of oxamide, which is also formed in all the present reactions. In addition, traces of bibenzyl, 2,2'-dimethylbibenzyl and 4,4'-dimethylbibenzyl are formed in the reactions of toluene, o-xylene and p-xylene, respectively. These results are consistent with a mechanism involving free radicals (carbamoyl $\cdot\text{CONH}_2$ and benzyl) as intermediates. On the other hand, the results do not exclude the possibility that reactions may proceed by way of reactive triplet states produced

² Hanau Q 81 high pressure mercury vapour lamps were used as the radiation source.

through energy transfer from the ketonic photosensitizer.³

The amidation of other aromatic systems is in progress.

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^{3a} G.O. Schenck and R. Steinmetz, Tetrahedron Letters
No. 21, 1 (1960).

^b N.J. Turro and G.S. Hammond, J. Amer. Chem. Soc. 84, 2841
(1962) and references given therein.