Tetrahedron Letters No. 35, pp 3271 - 3274.
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0040-4039/78/0822-3271$02.00/0

# USE OF PHASE TRANSFER AGENTS FOR PHOTOCYANATION OF AROMATIC HYDROCARBONS

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The photocyanation of aromatic hydrocarbons is usually a sluggish reaction [1,2] due to the fact that the leaving group is an hydrogen atom which moreover is not activated. We report here new results which make this reaction useful for synthesis.

## PHOTOCYANATION IN HOMOGENEOUS SOLUTION :

### Solvents :

i) Acetonitrile is commonly used for phase transfer catalyzed aliphatic nitrile synthesis in the ground state [4a,b,c]. The experiments A and C (Table 1) show clearly that this solvent, in which $CN^-$ is present as a weakly solvated species, and therefore a strong nucleophile, is also efficient in photochemical nucleophilic substitutions.

The solvation, provided it remains weak enough, does not affect much the course of the photoreaction. Thus, experiment B ($CN^-$ produced as a "naked" anion [5]) is almost similar to experiment A ($CN^-$ solvated by $CH_3OH$ which was used to prepare the solution (KCN + 18-C-6) and carefully removed before adding $CH_3CN$).

We have checked that if the solvation by an hydroxylic solvent (EtOH) becomes strong, no photocyanation will take place (experiment H).

TABLE 1 : Photocyanation in homogeneous solution[a,b]

| | | | Naphthalene<br>1 + 2 cyano | 1/2 | Biphenyl<br>2 + 4 cyano | 2/4 | Phenanthrene<br>cyano[c] |
|---|---|---|---|---|---|---|---|
| A | $CH_3CN$ | 18-C-6[d] | 8h ; 15% | | 20h ; 50% | | 3h ; 25% |
| B | $CH_3CN$ | 18-C-6[e] | 18h ; 30% | 7 | | | |
| C | $CH_3CN$ | TBACN | 8h ; 30% | | 18h ; 7% | | 18h ; 20% |
| D | $CH_3CN$ | TBACN | 18h ; 70% | 3 | 18h ; 72% | 0.6 | 4h ; 23% |
| E | $CH_3CN$ | TEACN | 18h ; 70% | 5 | 18h ; 97% | 0.5 | 18h ; 9% |
| F | $CH_2Cl_2$ | 18-C-6 | 18h ; 0% | | | | |
| G | $CH_2Cl_2$ | TBACN | 18h ; 0% | | 18h ; 0% | | 18h ; 0% |
| H | EtOH | TBACN | 3h ; 0% | | 3h ; 0% | | |

18-C-6 : 18-6 Crown Ether ; TBACN : Tetra-Butyl Ammonium Cyanide ; TEACN : Tetra-Ethyl-Ammonium Cyanide.

a) 10 ml of a 0.01 M solution of hydrocarbon containing the Phase Transfer Agent in a quartz tube were irradiated by a 450 W HP Lamp. All runs contained 0.4 mMol of the P.T.A. except A, B (1 mMol) and C (0.15 mMol); b) yields and ratio of photoproducts measured by glc ; c) Mixture of two monocyano compounds with 9-cyano phenanthrene predominant ; d) prepared according C.J. Pedersen [6] ; e) according C.L. Liotta's procedure [5].

The concentration of the nucleophile exerts some effect as shown by comparing the experiments C ($CN^-$ molar excess = 1,5) and D ($CN^-$ molar excess = 4). In the second one the yield of 4-cyano biphenyl is dramatically enhanced, while almost no variation is observed in the yields of either 1-cyano naphthalene or 9-cyano phenanthrene.

ii) Methylene chloride allowed no photocyanation to occur either using 18-6 Crown Ether (experiment F) or TBACN (experiment G) in contrast with experiments A and D which were in all respects identical except for the solvent.

The nature of the cation is an important feature as shown by experiment E. No difference occurred in naphthalene photocyanation when TBACN was replaced by TEACN, but an increased yield of cyano biphenyl and a strong decrease in phenanthrene reactivity were observed.

PHOTOCYANATION UNDER PHASE TRANSFER CONDITIONS :

No reaction took place when either TBACN (experiment I) or 18-6 Crown Ether (experiment J) were used as phase transfer agents, a fact which is in agreement with experiments F and G carried out in homogeneous solution.

We then ran a series of phase transfer photoreactions in which the $Q^+$ $CN^-$ species was formed from $Q^+$ $X^-$ and extracted *in situ* by the organic layer containing the hydrocarbon submitted to the UV irradiation.

TABLE 2 : Photocyanation under Phase Transfer Conditions[a,b]

| | | 1 + 2 cyano Naphthalene | 1/2[b] | 4 + 2 cyano Biphenyl | cyano Phenanthrene[c] |
|---|---|---|---|---|---|
| I | TBA$^+$ CN$^-$ | 0% | | 0% | 0% |
| J | 18-C-6 | 0% | | | |
| K | TBA$^+$ SO$_4$H$^-$ | 40% | 16 | 0% | 12% |
| L | TBA$^+$ Br$^-$ | 0% | | 0% | 0% |
| M | TBA$^+$ F$^-$ | 22% | 10 | | |
| N | TBA$^+$ OH$^-$ | 4% | 18 | | |
| O | Aliquat 336 | 25% | 11 | | |
| P | But Ph$_3$P$^+$Cl$^-$ | 13% | 24 | | |
| Q | But$_3$C$_6$H$_{12}$P$^+$Br$^-$ | 4% | | | |

a) The organic phase made of $CH_2Cl_2$ (25 ml) containing the hydrocarbon (0.25 mMol) is added with KCN (1.25 mMol), PTA (0.25 mMol) dissolved in water (2 ml) and NaOH 2.5 M (2 ml). This heterogeneous system is stirred[7] in a Pyrex flask and irradiated with a 450 W high Pressure Mercury Lamp for 18h ; b) yields and ratio of photoproducts measured by glc ; c) mixture of two monocyano phenanthrenes, with 9-cyano predominant.

Using TBA$^+$ SO$_4$H$^-$ (experiment K) a clean Phase Transfer Photocyanation was induced for naphthalene and phenanthrene, whereas biphenyl which was even more reactive than naphthalene under conditions D and E remained unchanged. A total lack of reactivity was observed in L (TBA$^+$ Br$^-$) showing that the counter ion of the P.T.A. is of importance, a conclusion which stemmed already for experiment I. The "Aliquat 336", one of the cheapest P.T.A., seems to be promising (experiment O).

As far as other "Quats" are concerned, (experiments P and Q), the phosphonium salts seem not to be very useful. Nevertheless, an interesting point from (Q) is that Br$^-$, when associated with a phosphonium salt, does not suppress the photocyanation as it did in Experiment L (ammonium bromide).

Thus, provided that the optimal conditions (solvents, P.T.A., stirring [7]) are determined, the photocyanation of aromatic hydrocarbons can be a useful synthetic method. The large knowledge gained from the Phase Transfer Chemistry in the ground state [8] is helpful, but cannot be the only guideline when the excited state is concerned [9].

## NOTES AND REFERENCES

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7. We have determined optimum stirring conditions using 1-nitro naphthalene as a test. An almost quantitative yield better than the one we have previously reported [3] was obtained by external irradiation of efficiently stirred Phase Transfer System. Conversely, a very strong stirring obtained with an ULTRA TURRAX apparatus (7.000 r.p.m.) produced an $OH_2$-$CH_2Cl_2$ emulsion, which being dark to UV light allowed no photocyanation to take place.

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9. To understand the photocyanation reaction, it would be desirable to know about the interactions of the aromatic excited states with the nucleophile $CN^-$, with the phase transfer agent $Q^+X^-$ in which the nature of both $Q^+$ and $X^-$ are of importance.

(Received in UK 13 June 1978; accepted for publication 3 July 1978)