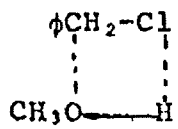
EXPLORATORY ORGANIC CHEMISTRY

I. PHOTOCHEMICAL REACTIONS

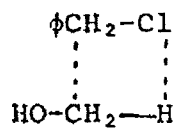
A) Reactions of activated halides

The photolysis of organohalogen compounds has continued. The emphasis has been on benzyl chloride, which has been found to give only three major products; benzyl methyl ether, 2-phenylethanol and bibenzyl plus a small amount of toluene when photolysis is conducted in methanol. The amount of the "photo solvolysis" product, benzyl methyl ether, is not greatly changed by running the reaction at -70° rather than 10°C. Originally it was felt that the reactions not involving ether formation followed a radical pathway. The lack of any large temperature effect has led to the idea that the results so far obtained could be explained on the basis of a four-center mechanism.



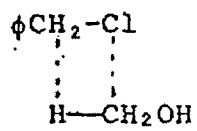
$\longrightarrow$ $\phi CH_2OCH_3 + HCl$

or



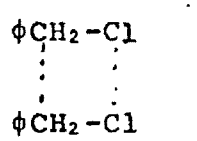
$\longrightarrow$ $\phi CH_2CH_2OH + HCl$

or



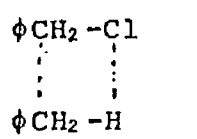
$\longrightarrow$ $\phi CH_3 + ClCH_2OH$

or



$\longrightarrow$ $(\phi CH_2)_2 + Cl_2$ (goes on to react with solvent)

or



$\longrightarrow$ $(\phi CH_2)_2 + HCl$

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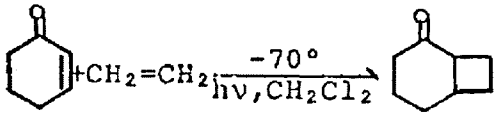
An Arochlor solution (dilute in isooctane) photolyzed very rapidly. When a 15 ml sample was irradiated for 10 min. by a 450 watt Hanovia lamp the Arochlor completely disappeared (analysis by Scott Tucker, Org. Div). We hope that this reaction can be used to create new products with no environmental problems.

One of the most interesting results so far is the observation that even allyl chloride undergoes ready photolysis to a number of, as yet, unidentified products. This experiment has caused us to consider that almost any activated or perhaps even vinylic halide is capable of undergoing fairly facile halide replacement leading to ethers, dimers and insertion products.

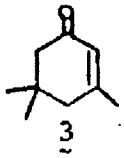
B) Cycloadditions

The cycloaddition of ethylene to 2-cyclohexene-1-one (1) was found to give bicyclo [4.2.0] octane-2-one, 2, in 53% yield (eq. 1). Compound 2 has been obtainable previously only by multistep reaction sequences. In contrast to the smooth



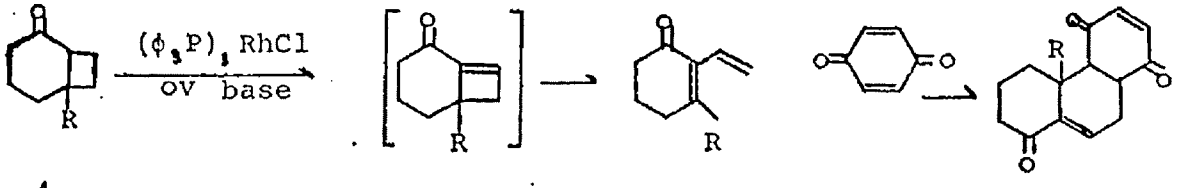
1 2, 53% (1)

addition of ethylene to 1, it was found that acetylene did not react under any conditions with either 1 or isophorone (3), eq.(2).



1 or 3 + HC ≡ CH $\xrightarrow[h\nu,\ >=O]{-70°}$ N.R.. (2)

These attempted cycloadditions with acetylene were undertaken in order to explore a possible new route into steroid or terpenoid ring systems. Thus, if structure 4 can be arrived at either by a direct addition of acetylene or by an addition of dichloroethylene and subsequent dehalogenation, technology developed in CRD should allow the proposed sequence to occur to rapidly build up precursors for steroids.



4 5 (3)

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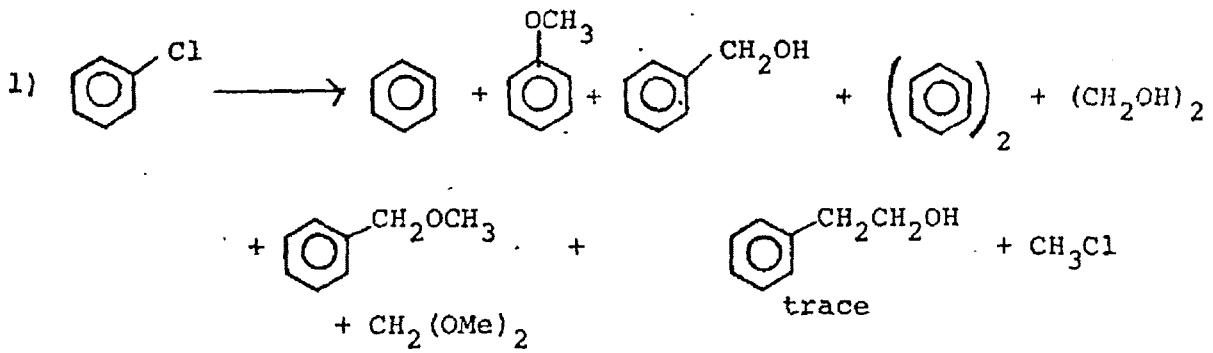
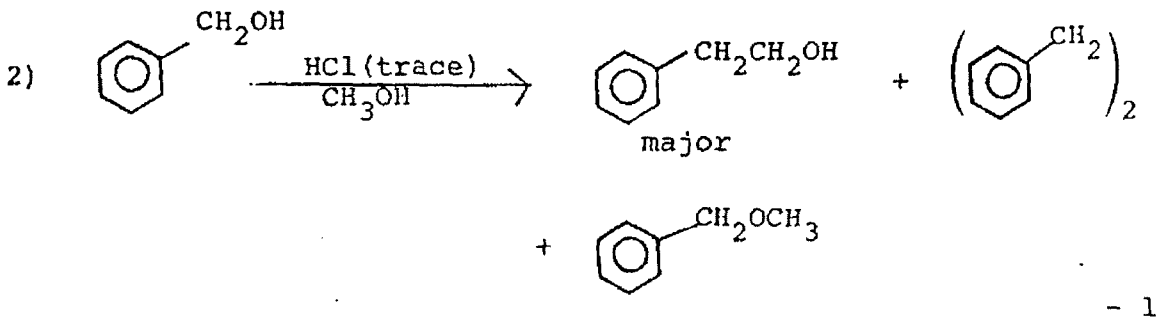
that shows no sharp definition of lines. The emission spectrum of 5 could be due either to a mixing of both $n\pi^*$ and $\pi\pi^*$ excited states or to an excited state which has a number of degrees of freedom, resulting in emissions from a multiplicity of excited states. Emission spectra will be obtained on a number of model compounds.

B. Photochemical Dehalogenation of Aryl Halides (JJB,DCO,JMN)

At the beginning of this quarter we were asked by W. C. Hammann (Organic Division) to examine the photochemical behavior of some chlorocarbanilides in methanol solution. When approximately 1% solutions were exposed to sunlight for three weeks in ordinary glass bottles chloride ion was produced and so was formaldehyde. This apparently novel reaction stimulated the idea that the reaction might be fairly general and perhaps utilitarian. A variety of other compounds was promptly screened. The photolysis (200 or 450 watt unfiltered Hanovia medium pressure lamp) of 1% methanolic solutions was followed by g.l.c.



The presence of methyl chloride and dimethylformal was determined by repetitive mass spectrometer scans of the solvent peak. The benzyl alcohol disappears as the methylbenzylether forms. The formation of 2-phenylethanol puzzled us until we found that



and that

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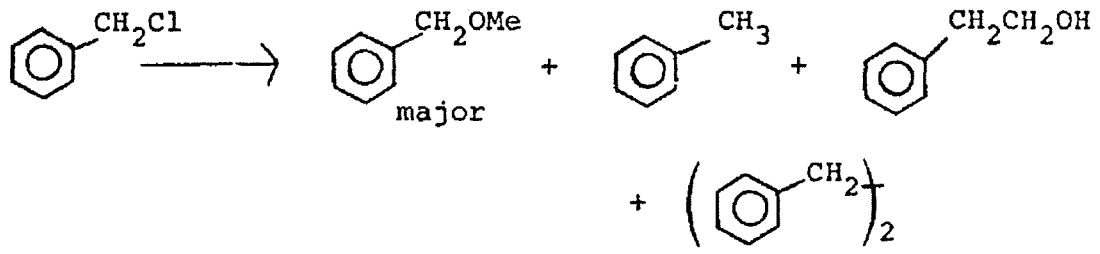
3) 

The formation of methyl benzyl ether (eqs. 2 & 3) is truly a photochemical reaction. Neither benzyl alcohol plus HCl nor benzyl chloride in methanolic solutions produce the ether in dark reactions at any appreciable rate. Clearly, there are two reaction pathways. Products like biphenyl, ethylene glycol, benzyl alcohol and phenyl ethanol are formed by radical coupling reactions. The ethers are formed by photo-nucleophilic displacements.

Thus $ArCl \xrightarrow{h\nu} Ar\cdot + Cl\cdot$

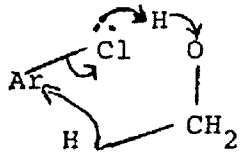
4) $Cl\cdot + CH_3OH \longrightarrow \cdot CH_2OH$

$Ar\cdot + CH_3OH \longrightarrow ArH + \cdot CH_2OH$

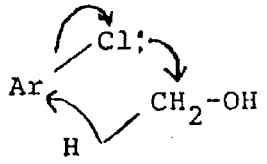
$2\ Ar\cdot \longrightarrow Ar_2$

$2\ \cdot CH_2OH \longrightarrow (CH_2OH)_2$

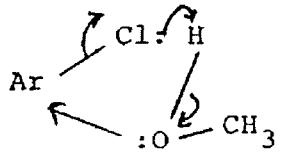
$Ar\cdot + \cdot CH_2OH \longrightarrow Ar\ CH_2OH$

and 

$\longrightarrow ArH + HCl + CH_2O$

or 

$\longrightarrow ArH + (ClCH_2OH) \longrightarrow HCl + CH_2O$

or 

$\longrightarrow ArOCH_3 + HCl$

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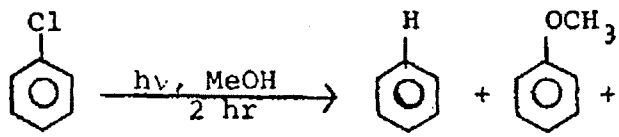
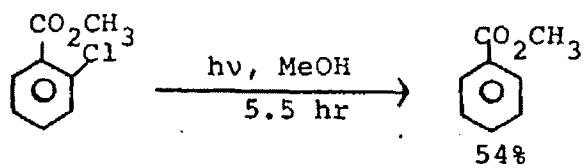
There is precedent for all these reactions although formaldehyde does not appear to have been previously observed in aryl halide photochemical reduction. The three monochloro anilines were also photolyzed in methanol (1% solutions). While the solutions all ultimately turned very dark only the para isomer reacted rapidly, to give aniline as the only volatile product. (When i-PrOH was the solvent several other g.l.c. peaks were observed). The ortho isomer was slow and the meta isomer produced no detectable aniline even after several days.

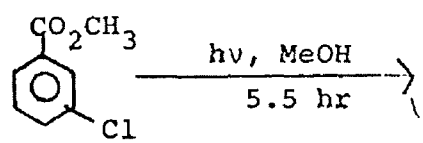
Experiments were also run on 0.1% solutions of several compounds in the presence of an internal standard in order to determine relative yields.



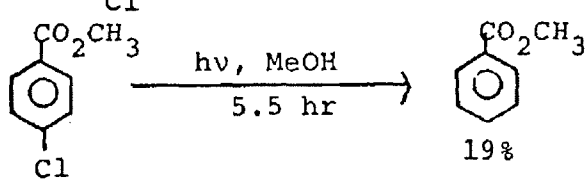
83% 14% + starting material (3%) + trace quantities (< 1%) of ϕCH_2OH, ϕCH_2OCH_3, ϕ-ϕ and $HOCH_2CH_2OH$ (5)



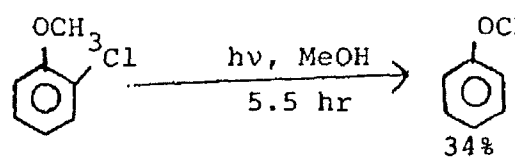
54% + starting material (2%) + unknown products (6)



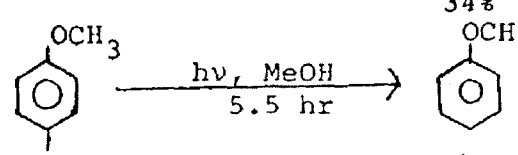
Unknown products (no starting material left) (7)



19% + Starting material (54%) + unknown products (8)



34% + Unknown products (benzene??) (9)



+ Unknown products (benzene??) (10)

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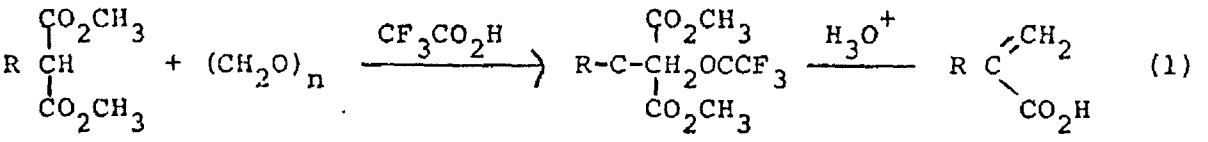
When photolysis of 1% solutions chlorobenzene was carried out in the presence of excess sodium methoxide anisole became the major product. No benzyl alcohol or benzyl methyl ether was detected.

We are planning to photolyze solutions of Aroclors to determine their susceptibility to photoreduction.

Photoreduction and photonucleophilic substitution could have a considerable impact on some of Monsanto's small and medium volume chemical products.

IV. ACID CATALYZED "MANNICH" AND "ALDOL" CONDENSATIONS (DCO)

A new, acid catalyzed "Mannich" reaction of substituted malonic esters with formaldehyde was described in our July 1970 quarterly report (eq. 1). Attempts to extend the synthesis to



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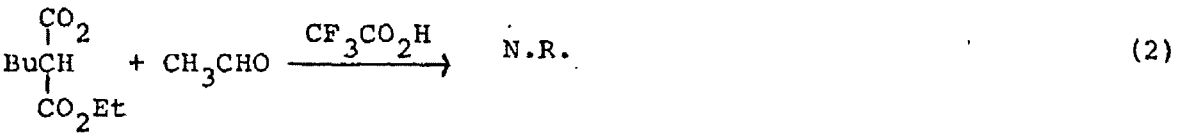
aldehydes other than formaldehyde and esters other than substituted malonic esters failed (eq. 2-4).



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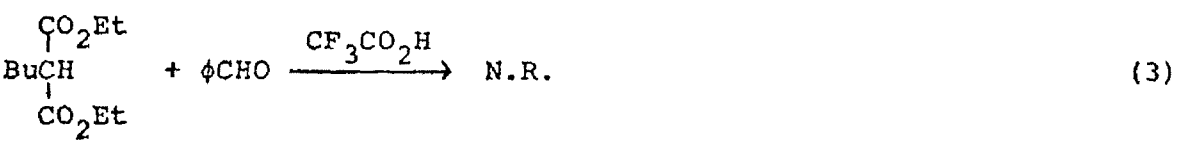

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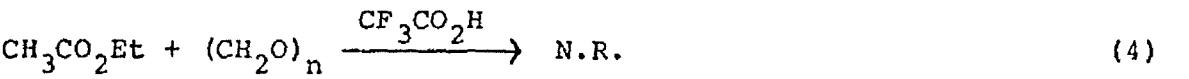

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