about two weeks 620 cc. of ethylene had been introduced. When an attempt was made to recover the ethylene, only 120 cc. of gas could be recovered on heating the solution to 100°. This gas was not pure ethylene but contained some inert material, probably air, which must have been present in the commercial gas. The ethylene did not remain in the oil as such because a similar experiment without the lithium alkyl showed that all of the gas could be recovered.

A similar experiment was tried with lithium ethyl instead of lithium *n*-butyl. The results were essentially the same. Only a small amount of gaseous hydrocarbons could be recovered by heating the paraffin oil solution.

Another experiment was made using a solution of 0.031 mole of lithium *n*-butyl in 50 cc. of petroleum ether (40–45°). Ethylene was absorbed readily and within two weeks a white solid began to appear on the surface of the solution. This solid has not been studied further.

The authors desire to express their thanks to Dr. G. F. Smith for help in some of the analytical problems met in this work.

Summary

1. Lithium alkyls have been found to react readily with tetra-alkyl arsonium bromides to give trialkylarsines and hydrocarbons which come from disproportionation of the alkyl groups. No evidence of the formation of a stable penta-alkyl arsenic compound was obtained.

2. Lithium alkyls have been found to cause polymerization of ethylene to give non-gaseous products.

3. It has been observed that trialkylarsines are oxidized by air to give dialkylarsinic acids.

4. Improved methods for the preparation of some trialkylarsines and tetra-alkyl arsonium salts have been reported.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

DIACYLSTYRENES. II

BY CHARLES F. H. ALLEN AND J. ROCKWELL HUBBARD

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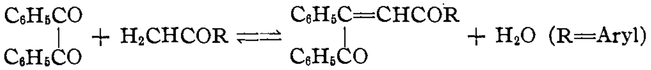
In an earlier paper[1] it was shown that benzil easily condensed with acetophenones that did not have a substituent in the position ortho to the carbonyl group.



$$\begin{array}{l} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + H_2CHCOR \rightleftharpoons \begin{array}{l} C_6H_5C{=}CHCOR \\ | \\ C_6H_5CO \end{array} + H_2O \quad (R{=}Aryl)$$

We have extended this investigation to include methyl ketones having different types of rings and found that diacylstyrenes are always formed under the conditions previously described. Methyl α-thienyl (I) and methyl α-furyl (II) ketones were selected as examples of heterocyclic compounds.

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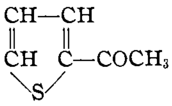
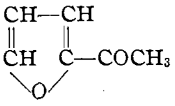
[1] Allen and Rosener, THIS JOURNAL, 49, 2110 (1927).



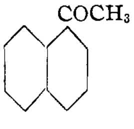
I



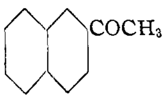
II

III

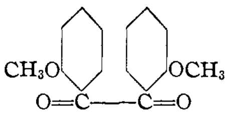
Since the acetophenones used in the earlier paper had only alkyl substituents, the *p*-phenyl compound (III) was taken, to show that an aryl group would not prevent the reaction.



IV



V



VI

We then examined the naphthyl methyl ketones for two reasons: (1) x-ray data indicate that one ring is bent over on the other, so that it might possibly exert a hindrance because of spatial relations; (2) in methyl α-naphthyl ketone (IV) there is an ortho substituent, that is, the second ring is fused on in an ortho position. It was found that while methyl β-naphthyl ketone (V) readily formed a diacylstyrene, the α-compound did not react. Thus rings in the ortho position offer the same kind of hindrance as other groups in the ortho position; elsewhere they have no effect.

The following acetophenones, which have become available since our earlier paper, were also investigated—*p*-ethyl, 3,4-dichloro, 3-nitro[2] and 2,4-dihydroxy. The first two formed diacylstyrenes, as expected. The last one, having an ortho substituent, did not react. With the third compound, the nitro group was attacked by alkali, and a mixture of high melting substances formed which it was not thought worth while to identify. Japp and Maitland[3] have previously examined pinacolone and found that it formed trimethacetylstyrene.

Finally, to see whether the effect of *o*-substituents was confined to the methyl ketone, *o*,*o'*-dimethoxybenzil (VI) in place of benzil was employed with acetophenone. As it was recovered quantitatively, unchanged, it may be concluded that groups in the ortho position of either component prevent the reaction from taking place. Since the effect is independent of the nature of the group, it is evidently due to spacial relations of some sort.

Experimental

Preparation of β-Naphthyl Methyl Ketone.—To the Grignard reagent prepared from 7 g. of magnesium and 40 g. of methyl iodide in 150 cc. of dry ether was added with stirring a warm solution of 14.5 g. of β-naphthonitrile in 50 cc. of the same solvent;

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[2] For this substance we are indebted to Dr. B. B. Corson.

[3] Japp and Maitland, *J. Chem. Soc.*, **85**, 1502 (1904).

the small amount of solid nitrile adhering to the dropping funnel was rinsed in with 30 cc. more ether. There was very little apparent action. After standing overnight, most of the ether was distilled by gradually immersing the flask in boiling water. The viscous residue was decomposed by ice and sulfuric acid in the usual way, the oily layer taken up in ether, dried and fractionally vacuum distilled; 6.5 g. of a yellow oil that readily crystallized was separated. There was considerable gummy residue. We were unable to isolate any of this ketone by the Friedel–Crafts reaction from naphthalene and either acetyl chloride or acetic anhydride. The other ketones were prepared by methods already in the literature.

The condensation with benzil was carried out exactly the same as in the earlier paper, except that ethyl acetate was used as a solvent for recrystallization. The results are summarized in the table.

Derivatives of α,β-Dibenzoylstyrene

No.	Ketone used	M. p., °C.	Formula	Analyses Calcd., % C	H	Found, % C	H
I	Methyl α-thienyl[a]	152	$C_{20}H_{14}O_2S$	75.5	4.4	75.3	4.5
II	Methyl α-furyl[b]	168	$C_{20}H_{14}O_3$	79.5	4.6	79.7	4.6
V	Methyl β-naphthyl	152	$C_{26}H_{18}O_2$	86.2	4.9	86.2	5.0
III	*p*-Phenylacetophenone[c]	132	$C_{28}H_{20}O_2$	86.6	5.2	85.8	5.2
VII	*p*-Ethylacetophenone[c]	117	$C_{24}H_{20}O_2$	84.7	5.9	84.4	6.0
VIII	3,4-Dichloroacetophenone[d,e]	199	$C_{22}H_{14}O_2Cl_2$	69.2	3.7	69.1	3.9

[a] Prepared by excellent directions of Stadnikov and Goldfarb, *Ber.*, **61**, 2341 (1928). [b] Sandelin, *ibid.*, **33**, 493 (1900). [c] Adams and Noller's method, This Journal, **46**, 1889 (1924). [d] Roberts and Turner, *J. Chem. Soc.*, **130**, 1855 (1927). [e] Recrystallized from anisole, insoluble in ethyl acetate and carbon tetrachloride.

o,o'-**Dimethoxybenzil**[2] **(VI) and Acetophenone.**—A methyl alcoholic solution of these two substances was treated in the same manner; as there was no apparent reaction after five minutes the whole was refluxed for eight hours. The dimethoxybenzil was recovered quantitatively.

We were unable to isolate any crystalline material from the reddish gums produced when either methyl β-pyridyl ketone or *p*-amino-acetophenone was used.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. The investigation of the condensation of benzil with derivatives of acetophenone has been extended to include those in which the substituent group is a ring. It has been found that the reaction takes place readily unless the position ortho to the carbonyl group is a part of the ring.

2. Methyl ketones having heterocyclic ring systems can be used equally well in place of acetophenone.

3. The same kind of hindrance is observed whether the *o*-substituent is in the benzil or the ketone.

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