benzene separations have been esterified and fractionated and their bromine addition products analyzed.

The ether-insoluble bromine addition products of the unsaturated acids have been debrominated and fractionated and their bromine addition products analyzed.

We believe that we have demonstrated the presence in fish oils of myristic, palmitic, palmitolic (hexadecatrienoic), clupanodonic (octodecatetrenoic), arachidonic, eicosapentenoic, docosapentenoic and docosahexenoic acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A NEW METHOD OF PREPARING DIBENZOYL ETHYLENE AND RELATED COMPOUNDS

BY JAMES B. CONANT AND ROBERT E. LUTZ

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Unsaturated 1,4 diketones are of interest because they contain a very reactive grouping similar in many respects to that which is present in *para* quinones. In connection with our studies of the reversible and irreversible reductions of unsaturated compounds we desired to prepare dibenzoyl ethylene and some of its derivatives. Dibenzoyl ethylene has hitherto been prepared either by heating dibenzoyl malic acid[1] or by condensing benzoylformaldehyde and acetophenone.[2] Both of these methods involve expensive and somewhat difficult preparative steps and are not convenient for preparing such substances as ditoluyl ethylene. We endeavored, therefore, to find a more convenient and general method of preparation.

We were also led to a study of this question by our interest in a convenient method of preparing substituted 1,4 saturated diketones and from them pyrroles and furans. We are now investigating the addition reactions of dibenzoyl ethylene with such substances as acid chlorides and anhydrides and sodium malonic ester, and hope at some future time to report on the synthesis of pyrroles and furans through these reactions.

Dibenzoyl ethane was prepared some years ago by the action of succinyl chloride on benzene in the presence of aluminum chloride. By the use of fumaryl chloride in a similar Friedel and Crafts reaction we have been able to prepare dibenzoyl ethylene with good yields (60–75%).

$$\mathrm{ClOCHC{=}CHCOCl} + 2\mathrm{C_6H_6} \xrightarrow[(\mathrm{AlCl_3})]{} \mathrm{C_6H_5COCH{=}CHCOC_6} + 2\mathrm{HCl}.$$

By replacing benzene by chlorobenzene, toluene and mesitylene we have also prepared the corresponding derivatives of dibenzoyl ethylene. The

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[1] Paal and Schulze, *Ber.*, **33**, 3800 (1900).

[2] Smedley, *J. Chem. Soc.*, **95**, 219 (1909).

preparation of dianisoyl ethylene was found to be unexpectedly difficult and, in spite of many trials, only a very poor yield of the desired product could be obtained; hence, this compound has not yet been studied.

The best method of operating is to add the fumaryl chloride slowly to a mixture of the aluminum chloride and hydrocarbon. In the case of such an expensive material as mesitylene, carbon disulfide was used as a diluent. The product in every case is the colored isomer. A certain amount of red by-product is also formed which, however, is removed by crystallization. The colorless isomer (*cis*) can be prepared by exposing a solution of the yellow isomer to sun light.

The following table gives the properties of the compounds prepared. In every case the yellow isomer was formed as a result of the Friedel and Crafts reaction and could be converted into a colorless isomer by the action of sunlight on the appropriate solution. The reverse transformation was brought about by heating a solution of the colorless isomer with a little hydrochloric acid, or by adding a trace of iodine to the solution and allowing the mixture to stand for some time. It is interesting to note that in the case of dibenzoyl ethylene the colored stable isomer has the lower melting point and greater solubility, while in the case of the other compounds the colorless labile isomer is the more soluble and has the lower melting point. Paal[3] originally assigned the *cis* configuration to the high-melting, colorless form of dibenzoyl ethylene because of the ease of its reaction with hydrazine to form a ring compound. Miss Smedley[2] on the basis of a determination of the refractive indices and because of the higher melting point of the colorless isomer[4] reversed Paal's configurations. This, however, seems hardly warrantable in view of the melting points of the substances we have prepared, and particularly as the colorless isomer[4] in each case is apparently the labile isomer, requiring a definitive absorption of light energy for its formation.[5] We shall, therefore, adopt Paal's configurations and hope shortly to investigate the stereo-isomerism of this series of compounds.

Substance	*Trans* isomer (yellow) M. p. ° C.	*Cis* isomer (colorless) M. p. ° C.
$C_6H_5COCH{=}CHCOC_6H_5$	111	134
$CH_3C_6H_4COCH{=}CHCOC_6H_4CH_3$	148	123
$ClC_6H_4COCH{=}CHCOC_6H_4Cl$	172	102
$(CH_3)_3C_6H_2COCH{=}CHCOC_6H_2(CH_3)_3$	174	120

Both isomers of each of the 4 ketones were rapidly reduced in hot alcoholic solution by the addition of an aqueous solution of sodium hydro-

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[3] Paal and Schulze, *Ber.*, **35**, 168 (1902) and Ref. 1.

[4] Ref. 1, p. 226.

[5] Maleic acid is formed by the action of ultraviolet light on fumaric acid [Stoermer, *Ber.*, **42**, 4870 (1909)] and is easily converted into fumaric acid again by the action of hydrochloric acid, halogens, etc.

sulfite. The corresponding ethane derivative was obtained in each case. In a typical experiment 2 g. of *trans* dibenzoyl ethylene yielded 2 g. of crude product which melted at 139–142°, and after recrystallization at 144–145°. Very little if any substance other than the ethane is formed in the reduction. This ease of reduction with sodium hydrosulfite is of interest because it is so similar to the behavior of all quinones. Maleic acid on the other hand and benzal-acetophenone, $C_6H_5CH=CHCOC_6H_5$, are not reduced by this reagent under similar conditions. The presence of a conjugated system of 2 ketone groups and an ethylene linkage is particularly favorable for reduction.[6]

Experimental Part

Preparation of *trans* Dibenzoyl Ethylene.—The Friedel and Crafts reaction can be carried out either by adding the powdered catalyst to a well-stirred mixture of the reactants, or by adding the fumaryl chloride to a suspension of aluminum chloride in the hydrocarbon. The latter procedure is preferable, and is illustrated below.

A mixture of 31 g. of finely powdered aluminum chloride and 250 cc. of benzene was stirred mechanically under a return condenser and 18 g. of fumaryl chloride slowly added to the mixture. The stirring was continued for 1 hour at room temperature. The mixture was then decomposed in the usual manner by pouring it upon ice; the benzene layer was washed with sodium carbonate solution, dried and evaporated. The dibenzoyl ethylene separated from the conc. benzene solution in pale yellow needles; further evaporation yielded more material somewhat colored by a reddish impurity. This residue was recrystallized from alcohol after the solution had been boiled with bone black. The total yield of pure material was 20.5 g., or 74%.

Ditoluyl Ethylene (*trans*), $CH_3C_6H_4COCH=CHCOC_6H_4CH_3$.—The same procedure can be employed as for the preparation of dibenzoyl ethylene, a large excess of toluene serving as the diluent. In a typical experiment 300 cc. of toluene, 55 g. of aluminum chloride and 31 g. of fumaryl chloride were allowed to interact. After the reaction mixture was decomposed in the usual manner, 34 g. of a somewhat colored product was obtained (75% of the calculated amount). It was further purified by recrystallization from alcohol; it separates as pale yellow needles which melt at 148°. It is soluble in benzene, chloroform, carbon disulfide or acetone in the cold, but is only slightly soluble in cold alcohol. It was reduced by sodium hydrosulfite in hot alcohol, and by zinc and acetic acid to give the known ditoluyl ethane, which melted at 159°.

Analyses. Calc. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.5; H, 6.1.

Cis **Isomer.**—One g. of the *trans* isomer was dissolved in 50 cc. of acetone and the solution placed in bright sunlight for 6 hours. The product was recrystallized from alcohol and obtained as colorless needles which melted at 123°. The conversion is nearly quantitative. A chloroform solution of the compound containing a little iodine yielded the *trans* isomer on standing. Reduction with sodium hydrosulfite or zinc and acetic acid yielded the ditoluyl ethane melting at 159°.

Analyses. Calc. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.6; H, 6.3.

Di-(4-Chlorobenzoyl) Ethylene (*trans*), $ClC_6H_4COCH=CHCOC_6H_4Cl$.—A mixture of 50 g. of fumaryl chloride, 300 g. of carbon disulfide and 125 g. of chlorobenzene was placed in a flask and well stirred. The aluminum chloride (125 g.) as a fine powder was added during 15 minutes and the mixture then heated to 45–50° for 2.5 hours. The

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[6] Compare Conant and Lutz, THIS JOURNAL, **45,** 1047 (1923).

reaction mixture was decomposed in the usual manner, the carbon disulfide layer extracted with sodium carbonate solution and then evaporated to dryness. The product was recrystallized from hot acetone; it weighed 51 g., equivalent to 51% of the calculated amount. It formed pale yellow crystals which melted at 172°, and which were only slightly soluble in hot alcohol.

Analysis. Calc. for $C_{16}H_{10}Cl_2O_2$: Cl, 23.2. Found: 23.4.

Cis **Isomer.**—A solution of 1 g. of the *trans* isomer in 50 cc. of chloroform was exposed to bright sunlight for 6 hours. By crystallizing the product from alcohol, fine white needles were obtained which melted at 102°. A chloroform solution of the compound containing a trace of iodine yielded the *trans* isomer on standing.

Analysis. Calc. for $C_{16}H_{10}Cl_2O_2$: Cl, 23.2. Found: 23.5.

Di-(4-chlorobenzoyl Ethane), $ClC_6H_4COCH_2CH_2COC_6H_4Cl$.—This compound was obtained by reducing either the *trans* or *cis* isomer of dichlorobenzoyl ethylene with sodium hydrosulfite in hot alcoholic solution or by the action of zinc dust and acetic acid. It crystallized from alcohol as colorless crystals melting at 151°.

Analysis. Calc. for $C_{16}H_{12}Cl_2O_2$: Cl, 23.1. Found: 23.3.

Di(2,4,6-trimethylbenzoyl) Ethylene (*trans*), $(CH_3)_3C_6H_2COCH{=}CHCOC_6H_2(CH_3)_3$.—This compound could be obtained only by the procedure in which the fumaryl chloride was added to the mixture of aluminum chloride, mesitylene and carbon disulfide. A mixture of 9 g. of mesitylene, 50 cc. of carbon disulfide and 10 g. of finely ground aluminum chloride was well stirred and 5 g. of fumaryl chloride slowly added. After standing for 0.5 hour at room temperature, the mixture was decomposed and treated in the usual manner. The product was recrystallized from alcohol; 7.8 g. was obtained which melted at 174°; yield, 75%. The substance forms light yellow crystals.

Analyses. Calc. for $C_{22}H_{24}O_2$: C, 82.5; H, 7.6. Found: C, 82.2; H, 7.8.

Cis **Isomer.**—Some difficulty was experienced in obtaining this isomer. It formed in only very small amounts when a chloroform solution of the *trans* isomer was exposed to sunlight. It was best obtained by allowing an alcoholic solution of the *trans* isomer containing a slight amount of undissolved substance to stand in quartz vessels in the sunlight. It formed colorless needles and melted at 120° when pure.

Analyses. Calc. for $C_{22}H_{24}O_2$: C, 82.5; H, 7.6. Found: C, 81.8; H, 7.6.

Di-(2,4,6-trimethylbenzoyl) Ethane, $(CH_3)_3C_6H_2COCH_2CH_2COC_6H_2(CH_3)_3$.—This substance was obtained by reducing both the *trans* and *cis* isomers in the usual way. It was recrystallized from alcohol and obtained as colorless crystals melting at 138.5°.

Analysis. Calc. for $C_{22}H_{26}O_2$: C, 82.0; H, 8.1. Found: C, 81.8; H, 8.1.

Di-(4-methoxybenzoyl) Ethylene, $CH_3OC_6H_4COCH{=}CHCOC_6H_4OCH_3$.—The best yield of this compound was obtained by using exactly the same procedure as that used for preparing the corresponding ketone from mesitylene; 1.5 g. of product was obtained from 10 g. of fumaryl chloride. Variations in the procedure were unsuccessful in increasing the yield. Lack of material prevented the thorough study of this compound. The product, after several recrystallizations from acetone, was vermilion. This color was bleached on exposing a solution of the material in chloroform to sunlight, and a pale yellow solid melting at 165.5° was obtained. It was insoluble in hot alcohol. Apparently no conversion to a colorless isomer took place by the action of sunlight, as the melting point was essentially unchanged. This matter, however, should be investigated further.

Analyses. Calc. for $C_{18}H_{16}O_4$: C, 72.7; H, 5.5. Found: C, 72.5; H, 5.4.

Summary

1. Dibenzoyl ethylene has been prepared by the action of fumaryl chloride on benzene in the presence of aluminum chloride. Derivatives of dibenzoyl ethylene have been prepared by the use of toluene, chlorobenzene, mesitylene and anisole.

2. The product of the reaction is the colored *trans* isomer which is converted to the colorless *cis* isomer by the action of sunlight; the reverse transformation is caused by acid or a trace of iodine. With the exception of dibenzoyl ethylene, the *trans* isomer has the higher melting point and the lower solubility.

3. Both the *cis* and *trans* isomers of each compound are easily reduced to the corresponding saturated 1,4 diketone by sodium hydrosulfite.

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ARSENATED DERIVATIVES OF PHENYLDIKETO-PYRROLIDINE[1]

BY JOHN R. JOHNSON[2] WITH ROGER ADAMS

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Trypanocidal compounds of practical importance containing an arsonic acid grouping and not containing other unstable groupings have been sought by many investigators, but none has been discovered which combines the properties found in the arsphenamines. Previous observations have shown that the most valuable arsenic-containing trypanocidal substances must contain nitrogen in some form. Since numerous drugs of various types and pharmacological properties have been discovered which contain nitrogen in a heterocyclic ring, this research was undertaken with the preparation of substances containing the arsonic acid group and a nitrogen atom in a heterocyclic ring as its object. Of the many arsenicals which have been described since the first work of Ehrlich and Bertheim, very few compounds of this type have been made.

Direct arsenation of indole and certain of its derivatives[3] introduces the arsonic acid group into the 2-position of the pyrrole ring. An unsuccessful attempt to arsenate quinoline and tetrahydroquinoline in a similar way, is reported by Fränkel and Löwy.[4]

A substance described as quinaldine-6-arsonic acid was obtained by Fränkel and Löwy[4] in poor yields, by the condensation of acetaldehyde with arsanilic acid in the presence of hydrobromic acid, but no evidence was presented to prove the quinaldine structure in this compound.

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[2] This communication is an abstract of a thesis submitted by John R. Johnson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Ger. pat., 240,793; *Friedländer*, **10,** 1252 (1910–12).

[4] Fränkel and Löwy, *Ber.*, **46,** 2546 (1913).