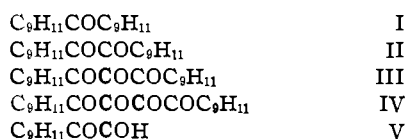


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

**The Highly Activated Carbonyl Group: Dimesityl Triketone**

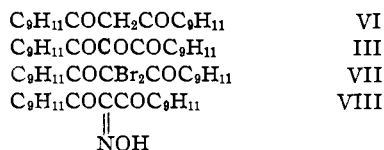
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Highly activated carbonyl groups in linear polycarbonyl compounds can be singled out for study by suppressing the reactivity of adjacent carbonyl groups through the introduction of steric hindrance. Thus the relative inertness of a ketone group attached to a mesityl radical as in dimesityl ketone (I), dimesityl diketone (II)<sup>1</sup> and mesityl-glyoxal (V)<sup>2</sup> appears to be equally marked in dimesityl tetraketone (IV).<sup>3</sup>



That such hindered carbonyl groups retain their activating influence upon adjoining groups is evident from the highly active character of the aldehyde group in V and of the intermediate ketone groups in IV. These considerations lead to the prediction that the medial carbonyl group in dimesityl triketone (III) would exhibit enhanced activity whereas the terminal ketone groups would show little tendency to participate directly in the reactions of the molecule.

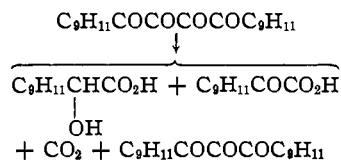
The synthesis of the triketone has been accomplished by oxidation of di-( $\beta$ -isoduryloyl)-methane (VI). Indirect methods proved unavailing. The dibromide (VII) when heated with potassium acetate gave the monobromide; with nitrous acid the methane gave a compound whose analysis corresponded to that of the expected oxime (VIII), but this compound resisted hydrolysis. Direct oxidation with lead tetraacetate gave no crystalline products. The triketone was finally obtained by oxidation of the methane with selenium dioxide.



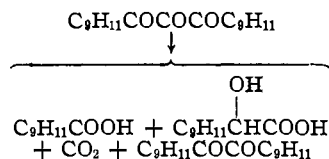
The triketone, prepared in this way, was a bright orange solid melting at 111–112.5°; it proved to be identical with the compound, mentioned earlier,<sup>3</sup> resulting from the action of alkali on the

tetraketone (IV). Investigation showed that the triketone was also a by-product in the oxidation of the formoin ( $C_9H_{11}COCOCH(OH)COC_9H_{11}$ ) by nitric acid. This suggested that the transformation of the tetraketone into the triketone was independent of the reagent. Accordingly, the tetraketone was subjected to heat in a neutral solvent, ethanol; similarly, it was heated with glacial acetic acid. In both cases the triketone was produced. Indeed, the latter method proved to be the most suitable one for preparing the compound.

**The Action of Alkali.**—The triketone is rapidly decomposed by the action of sodium hydroxide; the decomposition presents an almost complete analogy to that of the tetraketone. In the light of the present work, the latter process may be summarized as follows



The triketone gives rise to carbon dioxide,  $\beta$ -isodurylic acid, mesitylglycolic acid and dimesityl diketone



The analogy is incomplete with respect to the point in the process at which the ketone appears. In the decomposition of the tetraketone, the triketone is not formed until the reaction mixture is acidified. The diketone, on the other hand, forms from the triketone in the alkaline solution.

**The Action of Semicarbazide.**—It has not been possible to form a normal semicarbazone from either the tetraketone or the triketone; in the latter case the product obtained is the semicarbazone of mesitylglyoxal ( $C_9H_{11}COCH=NNHCONH_2$ ). Thus it would appear that mesitylglyoxal is a primary cleavage product not only in the case of decomposition with alkali but also in the presence of semicarbazide. This appears to be true for both the tri- and the tetraketone.

(1) Kohler and Baltzly, *THIS JOURNAL*, **54**, 4024 (1932).(2) Gray and Fuson, *ibid.*, **56**, 739 (1934).(3) Gray and Fuson, *ibid.*, **56**, 1367 (1934).

### Experimental

**The Action of Sodium Acetate on Di-( $\beta$ -isoduryloyl)-dibromomethane (VII).**—A mixture of 0.9 g. of VII, 0.4 g. of fused sodium acetate and 30 cc. of glacial acetic acid was refluxed for ten hours; dilution of the resulting solution with water gave a product which, after three recrystallizations from alcohol, melted at 164–165°. A mixture of this compound with the monobromide of VI showed no depression of the melting point.

### The Action of Various Reagents on Di-( $\beta$ -isoduryloyl)-methane (VI)

(a) *p*-Chlorobenzaldehyde.—A solution of VI and the aldehyde in aqueous alcohol, containing sodium hydroxide, was heated to boiling and allowed to stand overnight; the methane (VI) was recovered unchanged.

(b) Lead Tetraacetate.—A sample of VI was added to a suspension of lead tetraacetate in glacial acetic acid and the mixture was heated for two hours and allowed to stand for two days. No solid product could be obtained.

(c) Nitrous Acid.—Gradual and simultaneous introduction of hydrogen chloride and *n*-butyl nitrite to an ether solution of 5 g. of VI gave a colored solution which was allowed to stand overnight and was then repeatedly extracted with aqueous sodium hydroxide solution. Addition of the resulting deeply colored solution to a mixture of concentrated hydrochloric acid and ice gave a white flocculent precipitate which when dried weighed 4 g. After recrystallization from alcohol the compound melted at 153–154°.

*Anal.* Calcd. for  $C_{21}H_{33}NO_3$ : C, 74.7; H, 6.8. Found: C, 74.4; H, 6.9.

The compound was not affected by long treatment with alcoholic solutions of sulfuric and hydrochloric acids.

(d) Selenium Dioxide.—A mixture of 5 g. of VI, 2 g. of selenium dioxide and 75 cc. of dioxane was refluxed for five and one-half hours. Removal of selenium and dioxane in the usual way left an oil which crystallized difficultly from an ether-petroleum ether solution. Fractional crystallization from petroleum ether gave some unchanged VI and two yellow products, melting at 201–202° and 111–112°. The high-melting compound was insoluble in alkali; it was not investigated further.

The low-melting solid, when mixed with the bright yellow solid previously obtained by Gray and Fuson by the action of alkali on dimesityl tetraketone,<sup>3</sup> showed no lowering of the melting point. This compound, evidently dimesityl triketone, was also identified as a by-product in the oxidation of the formoin,  $C_9H_{11}COCOCH(OH)CO-C_9H_{11}$ , by nitric acid.

*Anal.* Calcd. for  $C_{21}H_{22}O_3$ : C, 78.3; H, 6.8. Found: C, 78.3; H, 6.9.

### Conversion of Dimesityl Tetraketone (IV) into Dimesityl Triketone (III)

(a) **In Alcohol.**—One gram of IV was dissolved in a mixture of 50 cc. of alcohol and 20 cc. of water, and the solution was boiled for sixty-six hours. After removal of the solvent the residue was crystallized from petroleum ether; it melted at 111–112.5° and when mixed with the specimen of III obtained above by selenium dioxide oxidation did not depress the melting point.

(b) **In Glacial Acetic Acid.**—A solution of 30 g. of IV in 250 cc. of glacial acetic acid was refluxed for sixty-seven hours. The acetic acid was then removed by steam distillation. The oil remaining was taken up in ether and the solution was dried over sodium sulfate. The oil which remained after the ether was removed was dissolved in alcohol, and this solution was seeded with crystals of III. About 9 g. of impure III was obtained accompanied by a small amount of unidentified colorless solid. The residual oil could not be induced to solidify.

### Reactions of Dimesityl Triketone (III)

(a) **Hydroxylamine.**—By the usual procedure a compound was isolated which was soluble in alkali and melted at 180–181°. It appeared to be isomeric with the oxime of mesitylglyoxal (m. p. 138.5–139°).<sup>2</sup>

*Anal.* Calcd. for  $C_{11}H_{13}O_2N$ : N, 7.3. Found: N 7.5.

(b) **Phenylhydrazine and 2,4-dinitrophenylhydrazine** in acidic media failed to react with III; in all cases the latter was recovered.

(c) **Semicarbazide.**—The semicarbazone melted at 207°. A mixed melting point with a sample of the semicarbazone of mesitylglyoxal showed no depression.

(d) **Alkali.**—Ten per cent. sodium hydroxide solution was used in the reaction. A sample of 1.085 g. of dimesityl triketone was added to 20 cc. of the alkali and heated to boiling. The solution was then allowed to stand for two and one-half hours. It was then filtered; a yellow precipitate separated. This was washed several times with distilled water; yield of the yellow compound when dried, 0.043 g.; m. p. 117–119°. A mixed melting point with an authentic sample of dimesityl diketone showed no depression.

The filtrate from the above was placed in a closed system which was so arranged that any gas generated would be bubbled through a calcium hydroxide solution. The filtrate was acidified with concentrated sulfuric acid. No gas was generated. When the acidified solution was heated almost to boiling, the lime water turned milky and a precipitate separated. It is probable that the small amount of carbon dioxide which formed during the reaction was held in solution until it was driven out by heating.

The acidified solution of the products of decomposition was then transferred to a beaker, made alkaline with solid sodium hydroxide, and extracted with ether. Very little residue was left when the ether in these extracts was evaporated.

The solution was then acidified with hydrochloric acid and extracted several times with ether. The product obtained from the ether extracts weighed 0.974 g. when it was dried, and melted at 110–115°. Fractional recrystallization in petroleum ether (mixtures of high- and low-boiling petroleum ether) revealed two compounds, one melting at 152–153°, the other at 151–152°. Separation was possible since the compound melting at 151–152° was much less soluble than the other.

A mixed melting point with an authentic sample identified the compound melting at 151–152° as mesitylglycolic acid (m. p. 152–153°). Similarly, that which melted at 152–153° was shown to be  $\beta$ -isodurylic acid.

