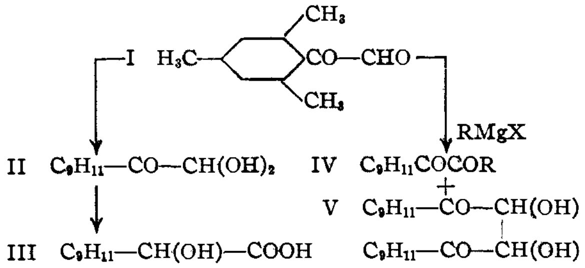
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Highly Activated Carbonyl Group: Mesitylglyoxal

BY ARZY R. GRAY AND REYNOLD C. FUSON

Highly activated carbonyl groups have not been extensively investigated because of the difficulty of finding an activating group which will not interfere with the reactions to be studied. Perhaps the most effective of these activating functions is a second carbonyl group as in compounds containing twinned carbonyl groups. By the introduction of steric hindrance it has now been found possible to diminish the reactivity of one of the twinned carbonyl groups without losing its activating effect upon the other. This objective has been realized in mesitylglyoxal (I), an α-keto-aldehyde which is unique in having two adjacent carbonyl groups one of which is extremely reactive and the other relatively inert.

Mesitylglyoxal (I) was obtained in good yields from acetomesitylene by oxidation with selenium dioxide by a modification of the general method of Riley, Morley and Friend[1] for preparing phenylglyoxal. The principal change in the method was the use of dioxane as solvent. That the keto-aldehyde contains a highly activated carbonyl group is demonstrated by the fact that it readily forms a stable hydrate (II). On the other hand, the ketone group shows no tendency to react with hydroxylamine, phenylhydrazine, the Grignard reagent and other reagents ordinarily used to detect carbonyl groups. The aldehyde reduced Tollens' reagent but not Fehling's solution.



The Benzilic Acid Rearrangement.—In contact with alkali mesitylglyoxal or its hydrate rapidly rearranges to mesitylglycolic acid (III). This result is similar to that observed in the case of unhindered α-keto-aldehydes, which indicates that the mechanism of the benzilic acid rearrangement is independent of the influence of the two ortho methyl groups. This result also means that the ketone group *does not react additively* during the rearrangement and provides a new type of evidence in favor of the currently accepted theory that the driving force of the rearrangement is to be sought in an intermediate in which one of the carbonyl groups remains unaltered.

Reaction with the Grignard Reagent.—It is in its behavior toward the Grignard reagent that mesitylglyoxal shows the most radical variation from the normal. The benzoin which was to be expected in the case of arylmagnesium halides could not be prepared; the product actually formed was the corresponding benzil. Thus with phenylmagnesium bromide the product was the trimethylbenzil (IV, R = C_6H_5). This diketone was distinctly yellow; it formed a monosemicarbazone but could not be caused to undergo the benzilic acid rearrangement. Its formation would appear to involve oxidation as well as addition; consequently, a search was made for a reduction product. In the case of mesitylmagnesium bromide this search was successful. Two compounds were isolated, one yellow and the other colorless. The former proved to be hexamethylbenzil (IV, R = C_9H_{11}). Its structure was established by an independent synthesis in which magnesium was allowed to act on the acid chloride of 2,4,6-trimethylbenzoic acid. Very recently Kohler and Baltzly[2] synthesized this diketone by the action of mesitylmagnesium bromide on the ester of mesitylglyoxylic acid.

The colorless compound has been shown to be 1,2-di-(β-isoduryloyl)-ethylene glycol (V)—a compound which is a dimolecular reduction product of mesitylglyoxal. The structural proof for this compound rests on the fact that reduction with phosphorus and iodine gave 1,2-di-(β-isoduryloyl)-ethane ($C_9H_{11}COCH_2CH_2COC_9H_{11}$)—a compound which is known.[3] The evidence in support of the structure assigned to the glycol is greatly strengthened by the discovery that it can be made by the reduction of the keto-aldehyde by the method of Gomberg and Bachmann[4] and that the glycol produced a diacetate.

It was shown, furthermore, that the formation of the glycol could also be brought about by use

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(1) Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932).

(2) Kohler and Baltzly, THIS JOURNAL, **54**, 4024 (1932).

(3) Conant and Lutz, *ibid.*, **45**, 1306 (1923).

(4) Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

of isopropylmagnesium bromide. It seems probable, therefore, that the reaction involves the reduction of the keto-aldehyde by the bromomagnesium alcoholate which is the preliminary addition product formed by the condensation of the aldehyde with the Grignard reagent. The oxidation of the alcoholate would account for the formation of the α-diketone.

$$C_9H_{11}COCHO + RMgX \longrightarrow C_9H_{11}COCH(OMgX)R$$

$$C_9H_{11}COCH(OMgX)R + 2C_9H_{11}COCHO \longrightarrow$$

$$C_9H_{11}COCOR \ + \ C_9H_{11}COCH(OMgX)CH(OH)COC_9H_{11}$$

Experimental

Dimesityl Diketone.—In the usual Grignard apparatus[5] was placed 7 g. of magnesium turnings. Enough absolute ether was added to cover the magnesium and then an ether solution of 48.5 g. of β-isoduryloyl chloride was added gradually. The mixture was warmed slightly and a few drops of methylmagnesium iodide were added. The solution soon became colorless and began to boil. The remainder of the acid chloride was then added. The mixture boiled quietly for an hour and gradually developed a brown color. After the spontaneous reaction had practically ceased the mixture was boiled on the steam-bath for forty-five minutes. It was then decomposed by the addition of water and hydrochloric acid and the ether layer was washed and dried. The ether was driven off and the residue was recrystallized from alcohol. The diketone formed in long yellow needles melting at 120–121°. The yield was 30% of the theoretical amount.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5; mol. wt., 294. Found: C, 81.5; H, 7.4; mol. wt., 290 (freezing point method).

A second product obtained in the above reaction was a colorless solid melting at 231–232°. It has not been identified.

Anal. Calcd. for $C_{30}H_{33}O_3$: C, 81.6; H, 7.5. Found: C, 81.4; H, 7.5.

Attempts to cause dimesityl diketone to react with alkali, with methylmagnesium iodide or with semicarbazide were unsuccessful. In each case the diketone was recovered unchanged.

Mesitylglyoxal.—A solution of 72.9 g. of selenium dioxide, 10 cc. of water and 107.1 g. of acetomesitylene in 600 cc. of dioxane was refluxed for five hours, with stirring. The solution was decanted from the free selenium and the dioxane was distilled. The crude mesitylglyoxal was collected at 130–134° (20 mm.); the yield was 82.5% of the theoretical amount. The purified aldehyde was a heavy yellow oil with a choking odor when hot. It darkened and became viscous on standing. When treated with concentrated sulfuric acid, sirupy phosphoric acid or phosphorus pentoxide the compound developed a red color. A methyl alcohol solution of the aldehyde was colorless. The pure compound distils at 105–106° (4 mm.); 118–119° (12 mm.); n_D^{19} 1.5520.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found: C, 75.1; H, 6.9.

Hydrate.—The aldehyde was dissolved in hot water from which the hydrate crystallized in long colorless needles. It was recrystallized from chloroform; melting point 100.0–100.5°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3. Found: C, 68.3; H, 7.1, 7.0.

TABLE OF NITROGEN DERIVATIVES OF MESITYLGLYOXAL

Compound	Oxime	Phenylhydrazone	Semicarbazone
Solvent	Dil. alc.	95% alc.	95% alc.
M. p., °C.	138.5–139.0	145.5–146.0	207–208
Color	Colorless	Yellow	Pale yellow
Formula	$C_{11}H_{13}O_2N$	$C_{17}H_{18}ON_2$	$C_{12}H_{15}O_2N_3$
N calcd.	7.3	10.5	18.0
N found	7.4	10.8	18.0

Methone Derivative.—An alcoholic solution of 0.36 g. of mesitylglyoxal hydrate and 0.75 g. of 5,5-dimethyldihydroresorcinol was warmed at 45° for thirty minutes then allowed to stand three hours. The solution was heated, diluted with water and allowed to cool; colorless crystals separated. They were recrystallized from dilute alcohol; melting point 194.5–195.0°.

Anal. Calcd. for $C_{27}H_{24}O_5$: C, 73.9; H, 7.8. Found: C, 73.9; H, 7.9.

Mesitylglycolic Acid.—To a suspension of 0.4 g. of calcium oxide in 100 cc. of water was added 1.0 g. of mesitylglyoxal hydrate. The suspension was warmed for thirty minutes and allowed to stand for eighteen hours. The mixture was then acidified with hydrochloric acid. Extraction with ether and evaporation of this solvent gave 1.0 g. of a light yellow oil which soon crystallized and proved to be relatively pure mesitylglycolic acid. After repeated recrystallizations from water the acid melted at 152.0–153.0°. The value 151–152° is reported by van Scherpenzeel.[6]

Neutral equivalent. Calcd., 194.1. Found: 193.5. The methyl ester of the above acid was prepared by the use of a solution of dry hydrogen chloride in dry methyl alcohol. It was recrystallized from petroleum ether; melting point 88–89°. The ester according to van Scherpenzeel melts at 90–91°.

The rearrangement was also carried out in the presence of potassium hydroxide with results which were similar to those obtained with calcium oxide.

Phenyl Mesityl Diketone.—Seventeen and six-tenths grams of mesitylglyoxal in ether was added dropwise to an ether solution of phenylmagnesium bromide prepared from 31.4 g. of bromobenzene and 4.8 g. of magnesium. A vigorous reaction occurred and the solution turned bright yellow. After being heated three and a half hours under reflux the mixture was hydrolyzed by pouring into water. A brilliant red resulted which changed to a pale yellow on acidifying with hydrochloric acid. The product was extracted with ether and the ether solution was washed with sodium carbonate solution and water and dried over calcium chloride. The solid which remained after evaporation of the ether was recrystallized from alcohol. The phenyl mesityl diketone formed pale greenish-yellow crystals which melted at 136–137°. The yield was 6.43 g.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.3. Found: C, 80.8; H, 6.4.

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(5) The experimental work on dimesityl diketone was carried out by Messrs. M. C. Vaughan and T. S. Oakwood.

(6) Van Scherpenzeel, *Rec. trav. chim.*, **19**, 381 (1900).

The mono-semicarbazone formed long colorless needles (from dilute alcohol) melting at 203–204°.

Anal. Calcd. for $C_{18}H_{19}O_2N_3$: C, 69.9; H, 6.2; N, 13.6. Found: C, 69.9; H, 6.4; N, 13.6.

The Action of Mesitylmagnesium Bromide on Mesitylglyoxal.—Seventeen and six-tenths grams (0.1 mole) of mesitylglyoxal was added, over a period of six hours, to a solution of mesitylmagnesium bromide containing approximately 0.1 mole of reagent and no unchanged magnesium metal. The reaction mixture was decomposed with ice and hydrochloric acid and extracted with ether. Evaporation of the ether solution left an oil from which, on cooling, colorless crystals separated. Further cooling of the mother liquor gave a small amount of bright yellow crystals. The yellow solid was shown by the method of mixed melting points to be dimesityl diketone.

1,2-Di-(β-isoduryloyl)-ethylene Glycol.—The colorless product obtained from the above procedure melted at 160.5–161.5° (from alcohol).

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.4; mol. wt., 354. Found: C, 74.7; H, 7.7; mol. wt., 368.

The glycol was also prepared by the method of Gomberg and Bachmann.[4] To the reducing mixture prepared from 2.5 g. of magnesium and 7 g. of iodine in 17 cc. of dry ether and 25 cc. of dry benzene was added 8.8 g. of mesitylglyoxal dissolved in 8 cc. of benzene. The mixture was shaken and cooled frequently under the tap. At the end of forty-five minutes it was poured into water. By this method 39% of the theoretical amount of glycol was obtained.

Attempts to oxidize the glycol with nitric acid were unsuccessful. Also, the cömpound did not rearrange when treated according to the method of Gomberg and Bachmann.[4]

Diacetate of 1,2-Di-(β-isoduryloyl)-ethylene Glycol.—Two-tenths of a gram of the glycol was boiled with acetyl chloride for one hour. A colorless solid separated when water was added. The compound was recrystallized from alcohol; melting point 185.0–185.5°. The yield was nearly quantitative.

Anal. Calcd. for $C_{26}H_{30}O_6$: C, 71.2; H, 6.9. Found: C, 71.2; H, 7.0.

1,2-Di-(β-isoduryloyl)-ethane.—A mixture of 25 cc. of glacial acetic acid, 0.5 g. of red phosphorus, 0.5 g. of iodine and 0.5 cc. of water was heated for a few minutes and to the resulting solution was added 1.5 g. of the 1,2-di-(β-isoduryloyl)-ethylene glycol. The solution was boiled for two hours, filtered while hot and poured into 250 cc. of water containing 2 g. of sodium bisulfite. The reduction product when recrystallized from alcohol melted at 138–139°. According to Conant and Lutz[3] 1,2-di-(β-isoduryloyl)-ethane melts at 138.5°.

Summary

Mesitylglyoxal has been prepared by the oxidation of acetomesitylene with selenium dioxide.

In contact with alkalies mesitylglyoxal rearranges to mesitylglycolic acid.

Grignard reagents reduce the keto-aldehyde to the 1,2-di-(β-isoduryloyl)-ethylene glycol. It seems probable that the reducing agent is the bromomagnesium alcoholate. This suggestion is supported by the fact that an α-diketone is formed in the reaction.

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The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VII. The Ethylidene Radical

BY F. O. RICE AND A. L. GLASEBROOK(1)

Staudinger and Kupfer(2) have shown that when carbon monoxide is passed through an ethereal solution of diazomethane, $CH_2{=}N{\equiv}N$, and the resulting gaseous mixture is led through a quartz tube heated in the range 400–500°, ketene $CH_2{=}CO$, which may easily be identified either by its odor or by combining it with aniline, is formed. They concluded that the CO combines directly with the nascent CH_2. It occurred to us therefore that a repetition of this experiment using diazoethane $CH_3CH{=}N{\equiv}N$ instead of diazomethane should give us some evidence concerning the existence of the ethylidene radical CH_3CH. When we repeated the original experiment we confirmed Staudinger's results, obtaining more than a gram of acetanilide from 0.8 g. of diazomethane; however, a second run, using diazoethane, yielded not a trace of methylketene, $CH_3CH{=}CO$; the gases leaving the hot tube had no characteristic odor, and a small quantity of aniline through which the gases were passed was recovered unchanged.

We next determined to test for the Paneth effect(3) with metallic mirrors during the decomposition of diazoethane. To this end we purified some diazoethane by distilling it at diminished pressure through a vacuum jacketed column, since our crude material contained some lower

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(1) General Motors Co. Fellow, 1930–1934.

(2) Staudinger and Kupfer, *Ber.*, **45**, 508 (1912).

(3) Paneth and Hofeditz, *ibid.*, **62**, 1335 (1929).