[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

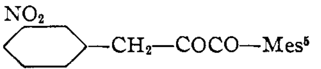
Quinoxaline Formation in Certain Alpha Diketones with a Nitromesityl Group Adjacent to a Carbonyl

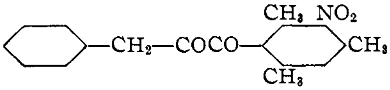
BY R. PERCY BARNES AND LEWIS A. GIST, JR.[1]

It has been found[2] that quinoxaline formation is made possible by introducing bromine atoms or nitro groups on the mesityl ring of mesityl glyoxal or mesityl phenyl diketone, and that the effect persists even when the substituent is on the phenyl ring. This work shows that other factors than possible hydrogen bonding[3] are involved.

Since the alpha diketone, $C_6H_5CH_2$–COCOMes, does not form a quinoxaline,[4] the authors were interested in determining the effect of substitutions in this substance.

Accordingly we prepared several alpha diketones and subjected them to treatment with *o*-phenylenediamine


I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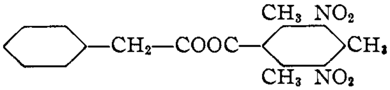
III

These diketones are enolic as indicated by the production of color in the presence of alcoholic ferric chloride.

The diketone (I) did not form a quinoxaline, but instead yielded a Schiff base. The diketones (II) and (III) formed quinoxalines. These experiments show that substitution in the phenyl ring in these compounds has no appreciable activating effect upon the highly hindered carbonyl, whereas substitution in the mesityl nucleus does activate the highly hindered carbonyl to the extent that the ortho effect is nullified.

Experimental

Condensation Reaction Producing Chalcones.—Both benzal-3-nitroacetomesitylene and benzal-3,5-dinitroacetomesitylene were prepared according to the typical alkaline condensation reaction.

To alcoholic solutions of equimolecular quantities of (1) benzaldehyde and 3-nitroacetomesitylene,[6] and (2) benzaldehyde and 3,5-dinitroacetomesitylene[7] was added, with stirring, equimolecular quantities of 0.6 *N* aqueous sodium hydroxide. The temperature of the solutions was maintained at 25°, and stirring was continued for five hours. In each case a cream-colored solid was formed which was recrystallized from ethanol.

Chalcone			$C_6H_5CH{=}CHCOC_6H$-$(CH_3)_3NO_2$	$C_6H_5CH{=}CHCOC_6$-$(CH_3)_3(NO_2)_2$
M. p., °C.			104.5	131
Yield, %			91	88
Mol. formula			$C_{18}H_{17}NO_3$	$C_{18}H_{16}N_2O_5$
Analyses, %	C	Calcd.	73.2	63.4
		Found	73.1	63.3
	H	Calcd.	5.8	4.7
		Found	6.0	4.7

Oxidation of the Chalcones to Ethylene Oxides.—Benzal-3-nitroacetomesitylene and benzal-3,5-dinitroacetomesitylene were oxidized to the corresponding 1-(3-nitromesitoyl)-2-phenylethylene oxide as follows: To alcoholic solutions of the chalcones was added equivalent amounts of 6 *N* potassium hydroxide. The solutions were stirred continuously and alcohol added gradually until at 20° there was complete solution. Then an excess of 15% hydrogen peroxide was added, the temperature maintained at 20°, and stirring continued for one and one-half hours. The alkaline solutions which were yellow gradually faded to almost colorless, and colorless solids began to separate. The solutions were diluted largely with water, chilled and filtered. The crystalline solids were recrystallized from alcohol.

Ethylene oxide			$C_6H_5\overbrace{CH—CH}^{O}COC_6H$-$(CH_3)_3NO_2$	$C_6H_5\overbrace{CH—CH}^{O}COC_6$-$(CH_3)_3(NO_2)_2$
M. p., °C.			70	139
Yield, %			86	73
Mol. formula			$C_{18}H_{17}NO_4$	$C_{18}H_{16}N_2O_6$
Analyses, %	C	Calcd.	69.5	60.7
		Found	69.2	60.4
	H	Calcd.	5.5	4.5
		Found	5.5	4.4

Isomerization of the Ethylene Oxides to the Alpha Diketones.—Hot alcoholic solutions of the ethylene oxides were treated with one and one-half molar quantities of *N* potassium hydroxide. The solutions were boiled for one-half hour, during which time they turned dark red. They were then chilled and acidified with dilute hydrochloric acid. The resulting crystalline masses were recrystallized from methanol.

Diketone			$C_6H_5CH_2COCOC_4H$-$(CH_3)_3NO_2$	$C_6H_5CH_2COCOC_6$-$(CH_3)_3(NO_2)_2$
M. p., °C.			119.5–120.5	163–164
Yield, %			75	75
Color			Yellow	Cream
Mol. formula			$C_{18}H_{17}NO_4$	$C_{18}H_{16}N_2O_4$
Analyses, %	C	Calcd.	69.5	60.7
		Found	69.5	60.4
	H	Calcd.	5.5	4.5
		Found	5.5	4.4

Reaction with *o*-Phenylenediamine.—The procedure adopted by Fuson and co-workers[2] for the conversion of 1,2-dicarbonyl compounds into quinoxalines was employed here with the following modification, since quantitative transformations did not result. The solutions were refluxed for three hours and then diluted with five times their volume of water, chilled, and the resulting solid material filtered and washed with water. The solid was then dissolved in ether and washed with dilute hydrochloric acid until the washings were colorless. The

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[1] In partial fulfillment of the requirements for the Master's Degree.

[2] Reynold C. Fuson and Quentin F. Soper, *J. Org. Chem.*, **9**, 193 (1944).

[3] Sidgwick and Callow, *J. Chem. Soc.*, **125**, 538 (1924); Dippy and Lewis, *ibid.*, 1426 (1937).

[4] R. P. Barnes, THIS JOURNAL, **57**, 937 (1935).

[5] R. P. Barnes and A. S. Spriggs, *Ibid.*, **67**, 134 (1945).

[6] Fuson and co-workers, *J. Org. Chem.*, **9**, 193 (1944).

[7] Fuson and co-workers, THIS JOURNAL, **52**, 3269 (1930).

ethereal solutions were next extracted with 10% potassium hydroxide until all unreacted diketone had been removed, as indicated by colorless alkaline washings. It was then dried over anhydrous sodium sulfate, filtered and evaporated. The resulting solid material was recrystallized from methanol.

Diketone			I	II	III
Quinoxaline or Schiff base			Schiff	Quinoxaline	Quinoxaline
Color			Yellow	Yellow	Red
M. p., °C.			118	163	214
Molecular formula			$C_{42}H_{38}N_4O_6$	$C_{24}H_{21}N_3O_2$	$C_{24}H_{20}N_4O_4$
Analyses, %	C	Calcd.	72.7	75.0	67.4
		Found	73.0	74.9	67.4
	H	Calcd.	5.5	5.5	4.7
		Found	5.5	5.6	4.7
Mol. wt.		Calcd.	697	384	429
		Found	699	385.5	428.5

The quinoxalines as well as the Schiff base when added to concentrated sulfuric acid produced a dark red coloration.

Summary

1. Herein are reported the preparation and properties of two new chalcones, ethylene oxides and alpha diketones.
2. The introduction of one or two nitro groups into the mesityl nucleus of benzylmesitylglyoxal activates the highly hindered carbonyl or minimizes the ortho effect to the extent that quinoxaline formation occurs.
3. The introduction of a nitro group in the meta position of the phenyl group of benzylmesitylglyoxal does not make possible quinoxaline formation, but leads to the formation of a Schiff base.

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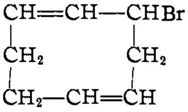
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. V. Preparation of Bromocycloöctadienes and 1,3,5-Cycloöctatriene from 1,5-Cycloöctadiene[1]

BY ARTHUR C. COPE, CALVIN L. STEVENS[2] AND F. A. HOCHSTEIN

This paper reports results obtained in continuing investigation of the preparation of cyclic polyolefins from the eight-membered cyclic dimer of chloroprene (2-chloro-1,3-butadiene).[3] 1,5-Cycloöctadiene was prepared in 69–74% yield by reduction of the dimer with sodium in liquid ammonia.[3] Careful fractionation of the product and determination of the refractive indices and infrared absorption spectra of the fractions indicated that 1,5-cycloöctadiene prepared in this way was a single pure isomer. Its melting point (−70 to −69°) corresponds to the melting point (−70°) reported by Ziegler and Wilms[4] for the 1,5-cycloöctadiene isomer (probably *cis-cis*) obtained by dimerization of 1,3-butadiene.

Reaction of 1,5-cycloöctadiene (I) with N-bromosuccinimide gave a mixture of monobromocycloöctadienes from which one isomer (II) could be obtained in pure form by low-temperature crystallization from ether (freezing point 0°, $n^{25}\mathrm{D}$ 1.5554). Slow fractional distillation converted either the mixture of monobromocyclooctadienes or pure II into a lower boiling liquid isomer, III ($n^{25}\mathrm{D}$ 1.5420). When III was heated it was partially reconverted to II; it is presumed that II and III are allylic rather than stereoisomers. Isomer II reacted with lithium aluminum hydride to give 1,5-cycloöctadiene and accordingly is 3-bromo-1,5-cycloöctadiene, unless an allylic rearrangement occurred during the reaction. Isomer III (6-bromo-1,4-cycloöctadiene) gave a mixture of cycloöctadienes on treatment with lithium aluminum hydride. Both isomers had the reactivity characteristic of allylic halides, and were characterized by catalytic hydrogenation to cycloöctane.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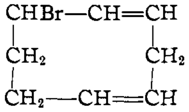
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Infrared absorption spectra indicated that III purified by fractional distillation contained some of the isomer with m. p. 0°, II (the infrared absorption curve of II is shown in Fig. 1). It was possible to determine the approximate amounts of II and III present in a mixture of the two from the refractive index of the mixture. A plot of the refractive indices of samples of II (containing varying amounts of isomer III) against the freezing points of the samples was a straight line (Fig. 2), indicating that the solutions were ideal. A plot of the depression in freezing point of II produced by adding bromobenzene against the composition of the mixtures also was linear (Fig. 3). A plot of the composition of mixtures of II and III (determined from the observed freezing points and calculation of the composition from the freezing point depression interpolated from Fig. 3) against the refractive indices of the mixtures was linear (Fig. 4), and extrapolation of the line showed that the refractive index of pure III should be 1.5400. According to these data the sample of III with $n^{25}\mathrm{D}$ 1.5420 contained 13% of II.

A mixture containing approximately 40% of II and 60% of III (prepared from I and N-bromosuccinimide) reacted with potassium *t*-butoxide

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[1] Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

[2] du Pont Postdoctorate Fellow, 1947–1948.

[3] Cope and Bailey, THIS JOURNAL, **70**, 2305 (1948).

[4] Ziegler and Wilms, *Naturwissenschaften*, **35**, 157 (1948).