

TABLE I  
 KETENE ACETYLATION PRODUCTS OF AMIDES

Amide	Solvent	Catalyst	M.P., °C.		Mol. Wt.		N %		Recryst. Solvent
			Obs.	Lit.	Found	Calcd.	Found	Calcd.	
Acetamide	Ligroin	H <sub>2</sub> SO <sub>4</sub>	79	78-79 <sup>a</sup>	100	101	...	...	Acetone
Acrylamide	Ether	CuSO <sub>4</sub>	200	...	...	...	12.3	12.4	Insol.
Benzamide	Benzene	H <sub>2</sub> SO <sub>4</sub>	114	115 <sup>b</sup>	162	163	...	...	Ethanol
Formamide <sup>c</sup>	Ether + ethanol	H <sub>2</sub> SO <sub>4</sub>	107	...	130	129	10.5	10.8	Water
Methacrylamide	Ether	None	Dec. at 300	...	...	...	11.1	11.0	Ether
<i>p</i> -Toluamide	Benzene	H <sub>2</sub> SO <sub>4</sub>	145	147 <sup>d</sup>	179	177	...	...	Acetone-H <sub>2</sub> O
Cyanoacetamide	Benzene	H <sub>2</sub> SO <sub>4</sub>	115	...	126	126	22.0	22.2	Acetone

<sup>a</sup> W. Hentschel, *Ber.*, **23**, 2394 (1890). <sup>b</sup> C. E. Colby and F. D. Dodge, *Am. Chem. J.*, **13**, 1 (1891). <sup>c</sup> Product isolated was diacetyl formamide. *Anal.* Calcd. for C<sub>6</sub>H<sub>7</sub>NO<sub>3</sub>: C, 46.5; H, 5.42. Found: C, 47.2% and H 5.50%. <sup>d</sup> G. Glock, *Ber.*, **21**, 2650 (1888).

by Bolstad and Dunbar,<sup>5</sup> together with a suitable solvent, and an acetylation catalyst<sup>8</sup> or a polymerization<sup>6</sup> inhibitor in one instance.

A typical acetylation is that of benzamide, which is described in detail. Exceptions to this procedure for other amides will be noted. A suspension of 3.6 g. (0.03 mole) benzamide and two drops of concentrated sulfuric acid in 70 ml. of benzene was agitated with a magnetic stirrer at room temperature while 0.03 mole of ketene was passed through the suspension. Care was taken to avoid any appreciable excess of ketene. The resulting product was soluble in the solvent. At the end of the run the solution was washed with 25-ml. portions of water until the washings were neutral to litmus, and the solvent was then allowed to evaporate at room temperature. The resulting product was recrystallized from a minimum amount of 95% ethanol. Yields were essentially quantitative except for mechanical loss in handling and recrystallizing the product. The molecular weights were determined by the Rast method<sup>7</sup> using camphor as the solvent. The nitrogen content was determined by the micro-Kjeldahl method.<sup>8</sup> Physical constants and other significant data are recorded in Table I.

Concentrated sulfuric acid proved to be a satisfactory catalyst for most of these acetylations. The unsaturated amides, however, when acetylated in the presence of sulfuric acid, formed gelatinous polymeric products. Methacrylamide was acetylated satisfactorily without any catalyst, but acrylamide had to be stabilized with copper sulfate. When acetamide was acetylated in hot ligroin it formed an oily insoluble product that was isolated with a separatory funnel, solidified at -5°, and was recrystallized from acetone. The diacetamide, contrary to most of the reaction products, was relatively stable at elevated temperatures.

Formamide was so insoluble in most inert organic solvents as to make acetylation nearly impossible even when the suspension was vigorously agitated. However, when the formamide was dissolved in an equal volume of ethanol, the resulting mixture was then found to be soluble in ether and the same could then be successfully acetylated. For this preparation 1.35 g. of formamide was, therefore, dissolved in 3 ml. of 95% ethanol and 70 ml. of anhydrous ether was then added. Ketene was then passed into the solution until two equivalents had been provided on the assumption that the ethanol would react with an equal amount of ketene. However, at the end of this period, the ketene was being ab-

sorbed so completely and readily that a third equivalent was provided. The crystalline product was isolated by permitting the solvent to evaporate at room temperature, and adding water to the remaining liquid. According to Smirnova and co-workers,<sup>3</sup> the literature regarding acetylated amides is "erroneous and contradictory." They report that triacetyl-ammonia is a liquid at room temperature and leave the reader with the impression that this is the case with all similarly trisubstituted ammonias. It has been found, however, that treatment of formamide with excess ketene yielded a solid product with a molecular weight of 130 corresponding to the diacetyl derivative and a nitrogen content of 10.5%, also corresponding to the diacetyl derivative. Their conclusion is supported only by a nitrogen determination while this study reports not only the nitrogen percentage, but percentages of carbon and hydrogen, as well as molecular weight.

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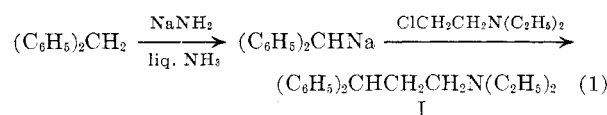
### Alkylations of Alkali Diphenylmethides with $\beta$ -Diethylaminoethyl Chloride and Ethylene Oxide<sup>1</sup>

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Sodium diphenylmethide prepared from diphenylmethane and sodium amide in liquid ammonia has recently<sup>2</sup> been alkylated with alkyl halides in this medium to form hydrocarbons of the type (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CHR, where R is an alkyl group or a phenyl-substituted alkyl group.

This reagent has now been alkylated similarly with  $\beta$ -diethylaminoethyl chloride to form tertiary amine I in 83% yield (Equation 1).



(1) Supported by the Duke University Research Council.

(2) C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79**, 3142 (1957).

(5) L. L. Bolstad and R. E. Dunbar, *Ind. Eng. Chem., Anal. Ed.*, **15**, 498 (1943).

(6) "Technical Bulletin Acrylamide," American Cyanamide Co., Petrochemical Department, New York, N. Y. (1956).

(7) A. Steyermark, *Quantitative Organic Microanalysis*, McGraw-Hill Publishing Co., New York, 1951, p. 82.

(8) T. S. Ma and G. Zuazaga, *Ind. Eng. Chem., Anal. Ed.*, **14**, 280 (1942).



recrystallized from ethanol) prepared from sodium diphenylmethide and ethylene chloride.<sup>5</sup>

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## Fate of Selenium in the Isomerization of Oleic Acid

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Previous work in this laboratory on the selenium-catalyzed isomerization of *cis*-stilbene<sup>2</sup> and of *cis*-9-octadecenoic (oleic) acid<sup>3</sup> at 200° to their respective trans isomers established that the rate of conversion was essentially independent of the concentration of selenium at any particular initial concentration of selenium, despite the fact that the selenium slowly disappeared from the solid phase.

In the present paper, the fate of the selenium during the isomerization of oleic acid is examined and there are presented experimental data, consistent with the requirement that the concentration of the catalytically active species of selenium be essentially constant during the course of the isomerization.

### EXPERIMENTAL

Three forms of the selenium catalyst are present during the isomerization of the oleic to elaidic acid at 200°: the original black, undissolved or bulk selenium; the active form of the selenium in solution, which on cooling, precipitates as the red modification; and the inactive species which remains in "solution" after cooling. In order to determine the approximate quantities of these three forms of selenium, pure oleic acid was heated to 200° for various time intervals using a fixed amount (0.2 weight percent) of black selenium powder.

*Apparatus.* The apparatus employed for the determinations consisted of a test tube reactor, equipped with an agitator passing through a glass-tube bearing in a rubber stopper, and having a side tube connected to a helium supply for maintaining an inert atmosphere. The reactor was heated by means of a salt bath controlled at 200° with a heating mantle connected through a variac to a Thermocap relay.

*Procedure.* The determinations were all carried out in the same manner. A typical experiment will be described:

Pure oleic acid, 40.017 g. was placed in the reactor and heated with stirring under a helium atmosphere. After the temperature had become adjusted to 200° ± 2°, the stopper was momentarily removed and 0.0800 g. of black selenium powder on a fragile glass boat was added. After replacing the stopper and starting agitation, the time was noted. After 12 minutes, the heating bath and agitator were

quickly removed and a filter stick inserted. The contents of the reactor were quickly filtered while hot into a tared filter flask. The black selenium remaining in the reaction vessel was transferred to a weighed, fritted-glass, micro-filter funnel with the aid of petroleum ether. Since the material on the filter contained bits of glass from the weighing boat, it was necessary to dissolve the selenium in the weighed mixture with concentrated nitric acid and wash and dry and reweigh the filter funnel to obtain the true weight. Using this procedure it was determined that 0.0390 g. of black selenium powder was present. On cooling the oleic-elaidic acid mixture in the filter flask, red selenium precipitated. The mixture was diluted with petroleum ether and filtered through a weighed, fritted-glass micro-filter funnel. After washing with petroleum ether and drying, 0.0192 g. of red selenium was secured. The weight of "inactivated" selenium which remained in "solution" was 0.0218 g., by difference. The results are semi-quantitative but sufficiently accurate to allow appropriate conclusions.

### RESULTS AND DISCUSSION

The results of measurements with 0.2 weight percent initial selenium at 200° are shown in Table I.

Disappearance of the solid catalyst is rapid until a certain concentration level of the active form is obtained; solution by complexing occurs thereafter only as it is needed to maintain this concentration level against an inactivation reaction occurring concomitantly.

The selenium which precipitates in the red form on cooling is believed to represent the active species of the catalyst. Table I shows that the concentration of this form at 200° increases rapidly and then remains essentially constant (within the limits of accuracy of the analytical method used) during the reaction or until all the undissolved black form has disappeared. These data are in agreement with the pseudo first-order rate equation found for the reversible selenium-catalyzed interconversion of oleic (*cis*) and elaidic (*trans*) acids:

$$-\frac{d[\text{Oleic}]}{dt} = k_1'[\text{Oleic}] - k_2'[\text{Elaidic}]$$

TABLE I  
RATE OF SOLUTION OF SELENIUM IN PURE OLEIC ACID,  
200°, 0.2% INITIAL SELENIUM

Heating Time, (Min.)	Percent of Total Selenium		
	Undissolved black	Precipitated red	Inactive (by diff.)
3	89.0	8.5	2.5
7	58.7	27.7	13.6
12	48.7	24.0	27.3
15	34.2	30.5	35.3
25	19.0	34.7	46.3
35	0.0	6.0	94.0

where the  $k'$  values include a particular initial concentration of selenium. The rapid attainment of the (theoretically) constant value for the concentration of active selenium corresponds to the rapid equilibrium reaction between oleic acid and its  $\pi$  complex with selenium, according to the mechanism previously advanced.<sup>3</sup>

The concentration of the inactive form of selenium increases at a constant rate giving essentially a straight line. This suggests that the inactivation reaction depends on the active species which is in constant concentration. Such an effect follows from the mechanism advanced previously, in which the inactivation of the catalyst was ascribed to an irreversible rearrangement of the  $\pi$  complex to a new species presumably involving the formation of a carbon-selenium sigma bond.

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(2) J. D. Fitzpatrick and M. Orchin, *J. Org. Chem.*, **22**, 1177 (1957).

(3) J. D. Fitzpatrick and M. Orchin, *J. Am. Chem. Soc.*, **79**, 4765 (1957).