

Peninsular Chemicals Co., Gainesville, Fla., and redistilled, Eastman Kodak white label haloacids, highly toxic, center-fraction CH_2FCOOH prepared from $\text{NaOCOCH}_2\text{F}$ and concentrated H_2SO_4 , propenoic acid distilled free of inhibiting hydroquinone, methyl methacrylate with inhibitor left present, and $\text{AgOCOCH}_2\text{OH}$ made from AgNO_3 , $\text{NaOCOCH}_2\text{OH}$, and a little excess HOCH_2COOH in aqueous solution.

Analytical methods included determination of tin as SnO_2 after treatment of the organotin compound with mixed fuming nitric and fuming sulfuric acids, determination of molecular weights in camphor solution when the compound had sufficient thermal stability, and direct determination of the OCOR group through titration with ethanolic sodium hydroxide. This last procedure may be part of a future publication upon analytical methods.

Determination of corrected melting points in Table I employed an Anschutz thermometer with the tiny bulb immersed in the melted compound or more frequently employed the customary capillary method without recovery of the compound. Three to five recrystallizations sufficed to produce a compound of constant melting point.

Reactions with acids. Typically, 2.35 g. (11.0 milliequivalents) of $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2\text{O}$ and 10.0 milliequivalents of the haloacid were combined and heated for 10 min. at 100° if the haloacid decomposed easily, but up to 60 min. at 100° if the haloacids were relatively stable. Some water formed; pipetting separated most of the water and Na_2SO_4 accepted

the rest. The material was crystallized from small volumes of an organic solvent such as $n\text{-C}_4\text{H}_9\text{Cl}$ or petroleum ether ($30\text{--}60^\circ$) until the melting point became constant; often the use of a salt-ice bath was necessary in crystallization. At the melting point or slightly above it $(\text{C}_2\text{H}_5)_3\text{SnOCOCH}=\text{CH}_2$ decomposed somewhat. Formation of two immiscible layers in the preparation of $(\text{C}_2\text{H}_5)_3\text{SnOCOCH}_2\text{F}$ probably was responsible for the low yield of ester.

Reaction with methyl methacrylate. Methacrylic acid alone would probably polymerize too rapidly for use with $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2\text{O}$. Three individual runs consisted of heating 2.60 g. of $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2\text{O}$ and 1.30 g. of inhibited $\text{CH}_3\text{OCOC}(\text{CH}_3)=\text{CH}_2$ for 1.5 hr. at 100° and then crystallizing from CCl_4 at -10° to get 0.6–1.0 g. of $(\text{C}_2\text{H}_5)_3\text{SnOCOC}(\text{CH}_3)=\text{CH}_2$ without isolation of the CH_3OCH_3 . In one run excessive viscous polymeric methyl methacrylate prevented recovery of the organotin ester. Later crystallizations employed mixtures of CCl_4 and petroleum ether ($30\text{--}60^\circ$) first and finally petroleum ether alone.

Reaction with AgOCOCH₂OH. No reaction occurred between $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2\text{O}$ and 70% aqueous HOCH_2COOH . However, 1.8 g. of $\text{AgOCOCH}_2\text{OH}$ and 2.25 g. of $(\text{C}_2\text{H}_5)_3\text{SnI}$ after 15 min. reflux in 15 ml. of CCl_4 and the usual filtration and washing of silver salts^{4,8} finally yielded 0.4 g. of $(\text{C}_2\text{H}_5)_3\text{SnOCOCH}_2\text{OH}$ upon crystallization from mixed CCl_4 and $n\text{-C}_4\text{H}_9\text{Cl}$. Two crystallizations from $n\text{-C}_4\text{H}_9\text{Cl}$ followed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

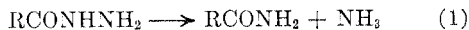
Hydrogenolysis of the Nitrogen—Nitrogen Bond of Acylhydrazines with Raney Nickel

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The scope of the reductive cleavage of mono- and diacylhydrazines by Raney nickel in the absence of added hydrogen has been explored. Alkyl substituted monoacylhydrazines and unsubstituted 1,2-diacylhydrazines are cleaved readily. 1,2-Diacylhydrazines, which bear substituents other than hydrogen on the nitrogens, are generally reduced with difficulty or not at all. The nitrogen—nitrogen bonds of 1-acyl-2-alkylidenehydrazines undergo smooth hydrogenolysis, yielding the corresponding amides.

In 1954, Ainsworth¹ showed that the nitrogen—nitrogen bond of simple carboxylic acid hydrazides can be reductively cleaved by refluxing an ethanolic solution of the hydrazide with a large quantity of Raney nickel (Equation 1). More recently this



reaction has been extended to a variety of other compounds, including 1,2-diacylhydrazines and some heterocycles which contain a nitrogen—nitrogen bond.²

The purpose of the present work was to explore more completely the scope and limitations of this useful reaction, as it applies to acylhydrazines bearing various substituent groups on the nitrogens. A number of the acylhydrazines were those prepared in connection with other recently re-

ported work.³ Raney nickel W-2⁴ was used in most of the experiments. However, a commercial catalyst⁵ was used in a few of the experiments for comparison purposes. No significant differences in activity were observed. The results are summarized in Table 1.

Although 1,2-dibenzoylhydrazine was cleaved to benzamide in 3 hr., as reported by Ainsworth,² only a trace of acetamide was isolated from the reaction of 1,2-diacetylhydrazine which was recovered largely unchanged after 3 hr. Since acetamide was isolated in good yield from the latter reaction after a 15-hr. reaction period, the longer time was used with all 1,2-diacylhydrazines.

As examples 1 to 3 show, the accumulation of

(3a) R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

(3b) R. L. Hinman, *J. Am. Chem. Soc.* **79**, 414 (1957).

(4) R. Mazingo, *Org. Syntheses, Coll. Vol. III*, 181 (1955).

(5) "Raney Catalyst in Water," Raney Catalyst Co., Chattanooga, Tennessee.

(1) C. Ainsworth, *J. Am. Chem. Soc.*, **76**, 5774 (1954).

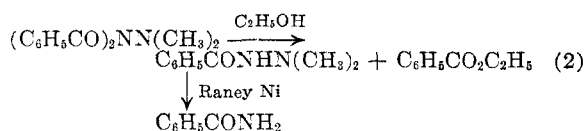
(2) C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 1636 (1956).

TABLE I
 SUMMARY OF REDUCTIVE CLEAVAGES OF ACYLHYDRAZINES WITH RANEY NICKEL

Example No.	Compound Reduced	Reference to Preparation	Product Isolated ^a	Reaction Time, Hr.	Yield, %
1	C ₃ H ₇ CONHNHCH ₂ C ₆ H ₅	^b	B	4	45
2	C ₆ H ₅ CONHNHC ₂ H ₅	^b	A	4	40
3	C ₆ H ₅ CONHN(CH ₃) ₂	^c	A	4	45
4	(CH ₃ CONH—) ₂	^d	C	15	50
5	(C ₆ H ₅ CONH—) ₂	^e	A	15	60
6	$\begin{array}{c} \text{CH}_2 \\ \\ \text{C}_6\text{H}_5\text{CONNHCOC}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array}$	^f	A	18	12
7	$\begin{array}{c} \text{CH}_3\text{CONNHCOC}_6\text{H}_5 \\ \\ \text{CH}_3 \end{array}$	^g	C + D	20	30
8	(CH ₃ CONCH ₃) ₂	^c	^h	15	—
9	(C ₆ H ₅ CONCH ₃) ₂	^e	ⁱ	20	—
10	(C ₆ H ₅ CO) ₂ NN(CH ₃) ₂	^c	A ^j	15	5
11	N,N'-Dimethylphthalhydrazide	^h	E	15	35
12	Phthalhydrazide	ⁱ	^l	20	—
13	C ₃ H ₇ CONHN=CHC ₆ H ₅	^j	B	4	50
14	C ₆ H ₅ CONHN=CHCH ₃	^k	A	4	40

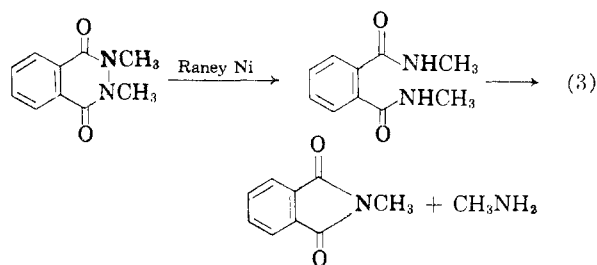
^a A = benzamide, B = *n*-butyramide, C = acetamide, D = acetanilide, E = N-methylphthalimide. ^b From reduction of the corresponding 1-acyl-2-alkylidenehydrazine with lithium aluminum hydride Ref. 3b. ^c Ref. 3a. ^d R. Stollé, *Ber.*, **32**, 796 (1899). ^e H. H. Hatt, *Org. Syntheses*, Coll. Vol. II, 208 (1943). ^f G. von Brüning, *Ann.*, **253**, 5 (1889). ^g A. Michaelis and F. Schmidt, *Ann.*, **252**, 300 (1888). ^h H. D. K. Drew, H. H. Hatt, and F. A. Hobart, *J. Chem. Soc.*, 33 (1937). ⁱ H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937). ^j R. Stollé and G. Zinsser, *J. prakt. Chem.*, [2] **69**, 486 (1904). ^k R. Stollé and E. Münch, *J. prakt. Chem.*, [2] **70**, 393 (1904). ^l More than 50% of starting material recovered.

alkyl groups on the nitrogens of a monoacylhydrazine does not hinder the cleavage. Cleavage of a 1,2-diacylhydrazine can be effected if only one nitrogen is substituted by an additional group (Examples 6 and 7). The lower yields, however, seem to be indicative of diminished reactivity. When both nitrogens bear methyl groups, cleavage does not take place (Examples 8 and 9), and most of the starting material is recovered. A similar result was obtained with the tetrasubstituted 1,1-dibenzoyl-2,2-dimethylhydrazine (Example 10). The formation of a small amount of benzamide in this case may be ascribed to the known reaction of dibenzamide, one of the possible cleavage products, with boiling ethanol to produce ethyl benzoate and benzamide.⁶ It also seemed possible that 1,1-dibenzoyl-2,2-dimethylhydrazine like dibenzamide might benzoylate ethanol under the conditions of the experiment. Although over 80% of the starting material was recovered from refluxing a solution of 1,1-dibenzoyl-2,2-dimethylhydrazine in ethanol for 15 hr., the wintergreen-like odor of ethyl benzoate was quite strong. If acylation occurred to even a slight extent, the resulting 1-benzoyl-2,2-dimethylhydrazine could give rise to benzamide, as shown in Equation 2.



(6) F. Krafft, *Ber.*, **23**, 2389 (1890).

Although 1,2-diacetyl-1,2-dimethylhydrazine, 1,2-dibenzoyl-1,2-dimethylhydrazine, and 1,1-dibenzoyl-2,2-dimethylhydrazine are quite unreactive, a related compound, 2,3-dimethylphthalazine-1,4-dione, yields N-methylphthalimide when refluxed with Raney nickel (Example 11). The product is probably formed by hydrogenolysis of the nitrogen—nitrogen bond, followed by ring closure of the resulting N,N'-dimethylphthalamide, as shown in Equation 3. This ring closure has been effected by merely shaking the diamide in water at 25° for 1 hr.⁷



Since the cleavage reaction undoubtedly occurs at the surface of the nickel catalyst, the failure of the diacylhydrazines 8, 9 and 10 to react may be caused by the bulky groups shielding the nitrogen—nitrogen bond from the surface of the catalyst. The cleavage of 2,3-dimethylphthalazine-1,4-dione is probably made possible by its cyclic form, which would reduce the shielding effect and facilitate the ap-

(7) F. S. Spring and J. C. Woods, *J. Chem. Soc.*, 625 (1945).

proach of the functional group to the surface of the catalyst.

In contrast to 2,4-dimethylphthalazine-1,4-dione, phthalhydrazide was not attacked during a 20-hr. reaction (*cf.* Ref. 2). This is in accord with the observation that the former compound resembles a simple diacylhydrazine (*e.g.*, it undergoes hydrolysis easily⁸), whereas the latter seems to be a more highly stabilized aromatic ring system.

The last two examples show that hydrazones also are easily cleaved by refluxing with Raney nickel. Since phenylhydrazine² and phenylhydrazides⁹ undergo cleavage, there is little question that phenylhydrazones can also be cleaved. This promises to

(8) J. C. E. Simpson, *Condensed Pyridazine and Pyrazine Rings*, Interscience Publishers, Inc., New York, N. Y., 1953, p. 175.

(9) C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 1635 (1956).

be an important application of the method, and is under investigation in this laboratory.

EXPERIMENTAL

The reactions with Raney nickel were carried out by refluxing and stirring vigorously a mixture of 0.5–1.0 g. of the compound to be cleaved with ten times its weight of Raney nickel W-2⁴ in 50 ml. of absolute ethanol. When commercial Raney nickel⁵ was used, it was slurried several times with absolute ethanol before use. At the end of the reaction the catalyst was removed by filtration and the solvent was distilled under reduced pressure. The product was recrystallized from a suitable solvent and identified by mixed m.p. with an authentic specimen.

The reactions of 1,2-diacetylhydrazine, 1,2-dibenzoylhydrazine, and 1,2-dibenzoyl-1,2-dimethylhydrazine were carried out with Raney nickel W-2 and with commercial Raney nickel. No significant differences in yield were observed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANNEX C LABORATORIES, EMORY UNIVERSITY]

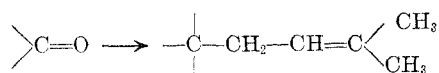
Addition of Isopentenyl¹ Magnesium Chloride to Cyclohexanone

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Isopentenyl magnesium chloride has been prepared and added to cyclohexanone. The alcohol produced, on the basis of its infrared spectrum, its ozonization products, and the ultraviolet absorption spectrum of its dehydration product, has been assigned formula III.

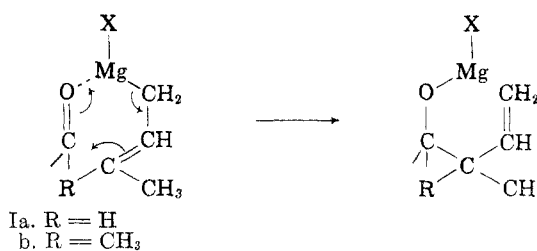
In the course of the syntheses of certain sesquiterpenes, being carried out in these laboratories, it became necessary to add to a ketone group an isopentenyl moiety, that is;



As a possible route for this transformation, the addition of the Grignard reagent of 1-chloro-3-methyl butene-2 to cyclohexanone was studied make clear whether this allylic Grignard reagent adds *via* normal addition or with rearrangement.

The mode of addition of an unsymmetrical allylic Grignard reagent to ketones has been studied by Young and co-workers² who found that butenyl magnesium chloride added to ketones with rear-

angement. Their extensive studies led them to postulate that both 3-chloro butene-1 and crotyl chloride give rise to the same Grignard reagent, namely the primary one, and that due to the favorable cyclic transition state possible, Ia, this primary Grignard adds with rearrangement.



(1) For the sake of simplicity, $\text{—CH}_2\text{—CH=C} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$, is referred to as isopentenyl.

(2) W. G. Young, A. N. Prater, and S. Winstein, *J. Am. Chem. Soc.*, **55**, 4805 (1933); W. G. Young, S. Winstein, and A. N. Prater, *J. Am. Chem. Soc.*, **58**, 289 (1936); J. F. Love, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **66**, 543 (1944); J. D. Roberts and W. G. Young, *J. Am. Chem. Soc.*, **67**, 148 (1945); W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **67**, 319 (1945); W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **66**, 1472 (1946).

This situation may also obtain with isopentenyl magnesium chloride, the only difference being an extra methyl group substituted at the end of the allylic system. However, one could not predict *a priori* whether the analogy would here be valid, for the extra methyl group could so hinder the formation of the cyclic system, Ib, as to raise its energy over that of the transition state needed for normal addition.

The carbonation of the Grignard reagent of isoprene hydrobromide and hydrochloride has been in-