was carried out in a Burgess–Parr low pressure apparatus using 0.8 g. of palladium–charcoal as the catalyst. A pressure drop of 4.9 p.s.i.g. from the initial 40 p.s.i.g. was measured (theoretical 4.85 p.s.i.g.). The product was recrystallized from 95 ml. of acetone at −25° to yield 9.7 g. of colorless liquid (65% yield from mixed olefins). The melting point, −3.0°, and $n^{20}D$, 1.4810, agreed well with those reported by Cheltsova and Petrov.[9]

A 5-ml. cylindrical, fused-quartz test-tube was equipped with a capillary tube and vent tube extending through a two-hole cork. This was mounted at the geometric center of an ultraviolet exposure apparatus. The latter consisted of three General Electric germicidal lamps symmetrically located 4 inches apart and mounted in a cylinder of polished sheet aluminum. The quartz test-tube was filled with 2.83 g. of 2-phenyltetradecane. Pure O_2, at a flow rate of 4 to 5 ml. per minute, was passed into the hydrocarbon. The heat from the lamps maintained an air temperature of 50–55° throughout the oxidation. Extent of oxidation was determined periodically by infrared analysis and iodometric titration. The autoxidized hydrocarbon was removed after 17 days of continuous oxidation. A sample of this material titrated 1.4% peroxide calculated as 2-phenyl-2-tetradecyl hydroperoxide. Chromatographing of a 2-g. sample on alumina gave 0.27 g. titrating 6.4% hydroperoxide. The infrared spectrum of the peroxide fraction was determined. The most significant feature is an 11.84 μ absorption band. This is characteristic of tertiary hydroperoxides and is found at the same wave length in 2-phenyl-2-tetradecyl hydroperoxide. The presence of extensive oxygenated hydrocarbons other than the hydroperoxide is evidenced by strong —OH and C=O absorptions at 3.0 and 5.8–5.9 μ, respectively, and a strong 8–11 μ absorption. Retention of the long chain and phenyl groups is shown by a 13.89 and 13.15 plus 14.33 μ absorptions, respectively.

CLEVELAND 6, OHIO

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[9] M. A. Cheltsova and A. D. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **12**, 87 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MAINE]

The Failure of the Darzens Reaction to Produce α-Aryl-Substituted Glycidic Esters[1]

BY HORTON H. MORRIS, RAYMOND H. YOUNG, JR., CAROL HESS AND THEODORE SOTTERY

RECEIVED JULY 18, 1956

The preparation of glycidic esters containing a phenyl group in the α-position cannot be accomplished by means of the Darzens reaction if the carbonyl component of the reaction mixture contains an α-hydrogen atom. The products formed when an ethyl α-halophenylacetate and a carbonyl component containing an α-hydrogen atom are treated with potassium *t*-butoxide are ethyl phenylacetate, diethyl 2,3-diphenylsuccinate and diethyl 2,3-diphenylmaleate.

Previous reports[2] from this Laboratory have been concerned with the production of a number of α-aliphatic-substituted glycidic esters and with the nature of the decarboxylation products obtained from the corresponding glycidic acids. It seemed of interest to extend the work to include glycidic esters containing aryl groups as the α-substituent and to determine whether decarboxylation of the corresponding glycidic acids might cause migration of the α-substituent to yield aldehydes—a result not found when the α-substituent is aliphatic in nature.[2]

All but one attempt to prepare glycidic esters containing an aromatic group as α-substituent have failed. The failure seems to be related to the presence of an α-hydrogen atom in the carbonyl component of the reaction mixture, since only the use of benzaldehyde allowed the formation of a glycidic ester. The carbonyl compounds which have failed to yield a glycidic ester when allowed to react with ethyl α-bromophenylacetate or with ethyl α-chlorophenylacetate in the presence of potassium *t*-butoxide are acetone, cyclohexanone, pinacolone, acetophenone and isobutyrophenone.

In every case the products isolated were derived from the halo ester component of the reaction mixture and were ethyl phenylacetate, diethyl 2,3-diphenylsuccinate and diethyl 2,3-diphenylmaleate (isolated as 2,3-diphenylmaleic anhydride).

When ethyl α-bromophenylacetate was treated with potassium *t*-butoxide in the absence of a carbonyl compound, only diethyl 2,3-diphenylmaleate was formed. Ethyl α-chlorophenylacetate did not react with cyclohexanone in the absence of a condensing agent.

The amount of ethyl phenylacetate formed is dependent upon the nature of the carbonyl component used in the reaction. The reaction of acetone with ethyl α-bromophenylacetate gave a 35–40% yield of ethyl phenylacetate, acetophenone gave 28–32%, pinacolone gave about 20%, while the use of cyclohexanone gave a 50–65% yield of this ester. The reaction of isobutyrophenone with ethyl α-bromophenylacetate yielded no ethyl phenylacetate.

The use of an α-chloro ester in the reaction gave lower yields of ethyl phenylacetate than when an α-bromo ester was used. Thus, the reaction of acetone with ethyl α-chloroacetate gave ethyl phenylacetate in 29% yield while use of the α-bromo ester gave a 35–40% yield. The reaction of the α-chloro ester with cyclohexanone gave a 20–23% yield of ethyl phenylacetate while the α-bromo ester gave a 50–65% yield.

Diethyl 2,3-diphenylsuccinate and diethyl 2,3-diphenylmaleate were isolated in varying amounts from some of the runs.

Large amounts (30–80%) of unreacted ketone were recovered from every run. The unrecovered portion of the ketone had apparently undergone some type of polymerization, since extensive investigations failed to allow the isolation of any materials other than tars, derived from the ketone.

A re-examination of the low-boiling cuts obtained during the preparation of an α-decyl-substituted glycidic ester[3] showed the presence of ethyl laurate, which was formed in 17% yield from the reaction

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[1] Presented before the Division of Organic Chemistry at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956.

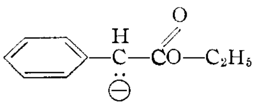
[2] H. H. Morris and Raymond H. Young, Jr., THIS JOURNAL, **77**, 6678 (1955), and previous papers.

[3] H. H. Morris and C. J. St. Lawrence, *ibid.*, **77**, 1692 (1955).

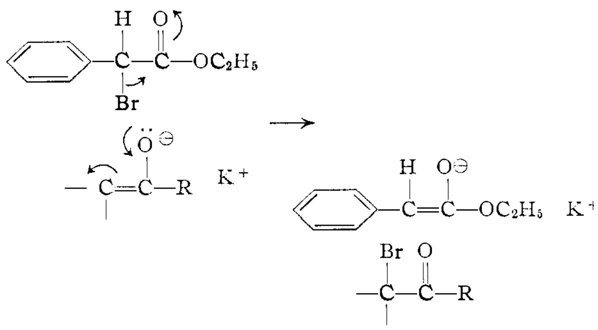
of acetone and ethyl α-bromolaurate under the influence of potassium *t*-butoxide.

It is of interest to note that Newman, *et al.*,[4] have reported the formation of reduced ester and unreacted ketone from Reformatsky reactions.

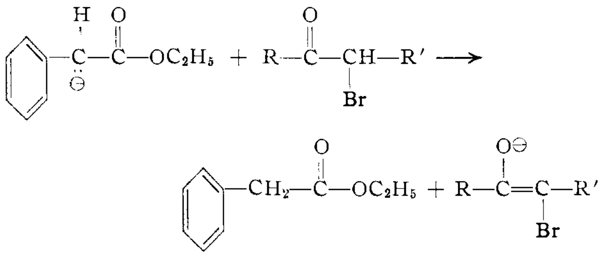
The formation of the "abnormal" products might be accounted for by assuming the intermediate formation of a resonance stabilized carbanion



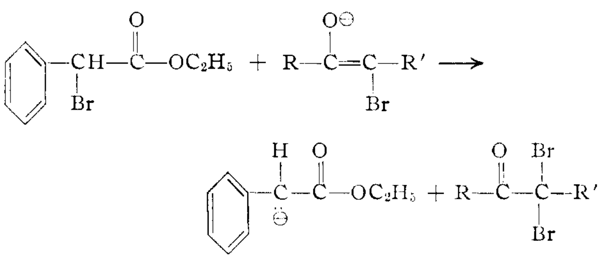
formed by a metal–halogen interchange between the ketone enolate and the halo ester



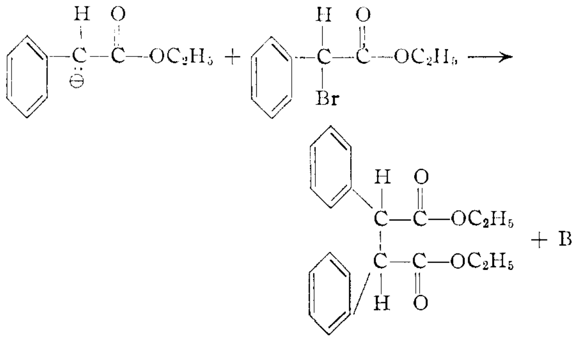
Such an intermediate could yield the reduced ester by combining with a proton. An assumption that a mono-brominated ketone must serve as the proton donor would explain the failure to isolate reduced ester from the isobutyrophenone run.



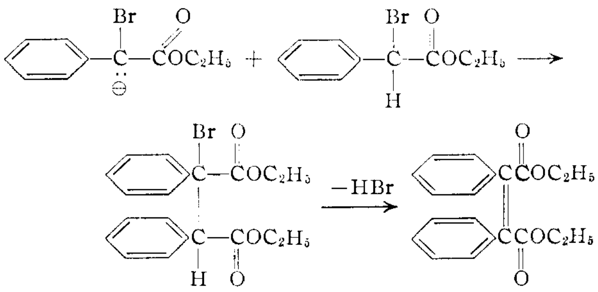
The enolate of the bromo ketone might then react to allow the formation of more of the carbanion.



The carbanion also could conceivably combine with a molecule of halo ester by a displacement reaction to yield the diethyl 2,3-diphenylsuccinate.



Diethyl 2,3-diphenylmaleate may be formed by reaction of the halo ester with halo ester enolate



Experimental

The following reactions were performed according to a previously reported procedure[2,5] which involves the slow addition of a *t*-butyl alcohol solution of potassium *t*-butoxide to a cooled, well-stirred mixture of an α-halo ester and a ketone or aldehyde, the reaction being conducted under anhydrous conditions in a nitrogen atmosphere.

The Reaction with Acetone and Ethyl α-Bromophenylacetate.—Three runs were made using this combination of reactants and good agreement was found in the amount of ethyl phenylacetate obtained (43, 38 and 37%).

In a typical run, a mixture of 0.5 mole of acetone and 0.5 mole of ethyl α-bromophenylacetate was treated with potassium *t*-butoxide (0.5 mole) dissolved in 500 ml. of *t*-butyl alcohol and the reaction mixture worked up in the usual way. Distillation of the water-insoluble material gave 30.9 g. (37.8%) of a material (b.p. 103° (5 mm.), n^{20}_D 1.4964, d^{20}_4 1.0314; *MR* found 46.46, *MR* calcd. for ethyl phenylacetate, 46.51) which was identified as ethyl phenylacetate[6] by its constants and by saponification of a sample of the material and isolation of an acid which melted at 76–76.5° after recrystallization from petroleum ether. A mixed melting point determination with an authentic sample of phenylacetic acid showed no depression.

Anal. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.88; neut. equiv., 136. Found: C, 70.34; H, 5.85; neut. equiv., 134 ± 3.

The Reaction with Acetone and Ethyl α-Chlorophenylacetate.—The use of the α-chloro ester gave a lower yield of ethyl phenylacetate (28.8%), identified as before. Acetone was recovered from the reaction mixture in an amount corresponding to 80% of the amount added. The residue from the distillation was not examined.

The Reaction with Cyclohexanone and Ethyl α-Bromophenylacetate.—A 50% yield of ethyl phenylacetate, identified as indicated previously, was obtained from the reaction of 0.5-mole quantities of cyclohexanone, ethyl α-bromophenylacetate and potassium *t*-butoxide. Unreacted cyclohexanone was recovered in 66% of the amount originally added.

The residue from distillation of the reaction mixture was exhaustively extracted with petroleum ether (30–60°).

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[4] M. S. Newman, THIS JOURNAL, **64**, 2131 (1942); A. S. Hussey and M. S. Newman, *ibid.*, **70**, 3024 (1948).

[5] W. S. Johnson, J. Belew, L. Chinn and R. Hunt, *ibid.*, **75**, 4995 (1953).

[6] R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 270; "Handbook of Chemistry and Physics," 35th Ed., Chem. Rubber Publ. Co., Cleveland, Ohio.

Evaporation of the petroleum ether left a clear yellow oil from which diethyl 2,3-diphenylsuccinate, m.p. 138–139°, lit.[7] m.p. 140–141° (corrected, *meso* form), was obtained.

A mixed melting point determination with the product identified as diethyl 2,3-diphenylsuccinate from the isobutyrophenone–ethyl α-bromophenylacetate reaction (see later) showed no depression.

The Reaction with Cyclohexanone and Ethyl α-Chlorophenylacetate.—The reaction of the α-chloro ester with cyclohexanone gave lower yields of ethyl phenylacetate than when the α-bromo ester was used.

Distillation of the reaction mixture allowed a 76% recovery of cyclohexanone and gave a 23% yield of ethyl phenylacetate. The possible presence of diethyl diphenylsuccinate and diethyl diphenylmaleate was unsuspected at the time this run was made and the residue was not examined.

The use of a weaker base did not cause the formation of the type of product obtained when potassium *t*-butoxide was used as the condensing agent. A mixture of cyclohexanone and ethyl α-chlorophenylacetate, treated with potassium hydroxide in absolute methanol, yielded mandelic acid and ethyl mandelate in about 49% yield. No ethyl phenylacetate was formed.

In order to establish the need of a basic condensing agent, a mixture of cyclohexanone, ethyl α-chlorophenylacetate and *t*-butyl alcohol were refluxed for 1 hr. in a nitrogen atmosphere and then distilled. The unchanged ketone and α-chloro ester were recovered in virtually quantitative yield.

The Reaction with Isobutyrophenone and Ethyl α-Bromophenylacetate.—In an orienting run, a mixture of 0.3 mole of isobutyrophenone and 0.3 mole of ethyl α-bromophenylacetate was treated with 0.3 mole of potassium *t*-butoxide in *t*-butyl alcohol. After the usual water wash and the removal of the *t*-butyl alcohol on the steam-bath, a solid (I) precipitated. This solid was recrystallized from methanol and identified as diethyl 2,3-diphenylsuccinate on the basis of the following data. The solid (I) melted at 138.5–139°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80; sapn. equiv., 163.2. Found: C, 73.37; H, 7.05; sapn. equiv., 163 ± 6.

A solid acid was obtained from the saponification of I which melted at 229–232° and which gave a neutralization equivalent of 138 ± 6 as compared to a calculated value of 135.1 for 2,3-diphenylsuccinic acid. Transesterification of the solid I with sodium and methanol produced a solid (II) which melted at 218.5–219.5°. Wren and Still report[7] that diethyl 2,3-diphenylsuccinate melts at 140–141°, that 2,3-diphenylsuccinic acid melts at 229° and that dimethyl 2,3-diphenylsuccinate[8] melts at 219–220°.

The liquid residue, after removal of the diethyl diphenylsuccinate, was distilled at reduced pressure and yielded 13 g. of isobutyrophenone (29% of the amount originally added) and 24 g. of a viscous yellow liquid which boiled at 200–208° (7 mm.). No trace of ethyl phenylacetate could be detected. Much work with the high boiling fraction from the distillation allowed the isolation of additional diethyl 2,3-diphenylsuccinate and a viscous yellow oil (presumably diethyl diphenylmaleate) which could not be induced to crystallize and so was saponified (sapn. equiv., 154 ± 6; calcd. for diethyl 2,3-diphenylmaleate, 162). Acidification of the saponification mixture gave a yellow solid which melted at 159–160° after recrystallization from methanol and which gave a neutralization equivalent of 133 ± 6 (the mixture must be warmed after each addition of base). The calculated neutralization equivalent for 2,3-diphenylmaleic anhydride is 125.

The solid was refluxed with concentrated ammonium hydroxide and the bright yellow solid, 2,3-diphenylmaleimide, m.p. 213–214° after recrystallization from methanol, was obtained.

Wren and Still[9] report a melting point of 158–158.5° for 2,3-diphenylmaleic anhydride. Reimer[10] reports that 2,3-diphenylmaleimide has a melting point of 213°.

The reaction was repeated, using 0.15 mole of each reactant. The reaction mixture was washed with water, filtered to remove 6.4 g. of a solid (later shown to consist of 1.1 g. of diethyl diphenylsuccinate, a trace of potassium diphenylmaleate and 5.0 g. of potassium bromide) and then distilled at atmospheric pressure to remove excess *t*-butyl alcohol. A 4.95-g. quantity of solid precipitated and was filtered off and shown to contain 2.4 g. of potassium bromide and potassium diphenylmaleate from which 1.4 g. of diphenylmaleic anhydride was isolated by acidification. Distillation of the filtrate at reduced pressure gave 17.4 g. (78% recovery) of isobutyrophenone and 17.3 g. of a viscous yellow oil, b.p. 185–202° (3 mm.). No trace of ethyl phenylacetate could be isolated. The residue weighed 3.1 g.

The high-boiling yellow oil was washed with warm sodium hydroxide solution to dissolve diphenylmaleic anhydride and the mixture extracted with ether. Acidification of the water layer yielded 4.2 g. of diphenylmaleic anhydride. The material from the ether layer yielded 2.4 g. of diethyl 2,3-diphenylsuccinate and a yellow oil. Saponification of the yellow oil gave 2.4 g. of diphenylmaleic anhydride and 0.2 g. of diphenylsuccinic acid, m.p. 229–232° (two recrystallizations from methanol). An additional 3.9 g. of material that saponified appeared to be a mixture of diphenylmaleic anhydride and diphenylsuccinic acid, but the mixture could not be satisfactorily separated into its components.

The wash water was distilled and 8.7 g. of potassium bromide and 0.7 g. of diphenylmaleic anhydride was recovered from the residue.

In summary, isobutyrophenone was recovered in 78% of the amount added, diethyl 2,3-diphenylsuccinate was formed in 13.5% of the amount expected if the bromo ester was completely converted to this product and diphenylmaleic anhydride was obtained in 57% of theory, based on bromo ester. Approximately 7 g. of tar-like material was formed.

The diethyl diphenylsuccinate and diphenylmaleic anhydride obtained during this run were identified by their melting points and by mixed melting point determinations with the corresponding material from the previous run.

The Reaction of Ethyl α-Bromophenylacetate with Potassium *t*-Butoxide in the Absence of a Carbonyl Component.—In order to establish the involvement of the carbonyl component in the previous reactions, a 0.15-mole run was made following the same reaction procedure but omitting the carbonyl component. The reaction was washed with water and the water layer distilled to recover water-soluble salts. An amount of potassium bromide was recovered (16.2 g.) that corresponded to 91% of theory. Attempted distillation of the reaction mixture gave no distillable material (except *t*-butyl alcohol) below 150° (1 mm.). A 3.4-g. sample of the material was saponified. Acidification of the saponification mixture gave 2.4 g. (91.6%) of diphenylmaleic anhydride, m.p. 159–160° (recrystallized from methanol). A small amount of the material (0.1 g.) did not undergo saponification. No ethyl phenylacetate was formed and no trace of diethyl diphenylsuccinate could be isolated.

The Reaction with Benzaldehyde and Ethyl α-Bromophenylacetate.—A mixture of 0.1 mole of freshly distilled benzaldehyde and 0.1 mole of ethyl α-bromophenylacetate was treated with 0.1 mole of potassium *t*-butoxide and the reaction mixture worked up in the usual manner. Evaporation of the ether layer and recrystallization of the crude product from ethanol gave a 72.5% yield of the expected ethyl α,β-diphenylglycidate, m.p. 56–57°. Blicke[11] prepared this compound, using sodium ethoxide as the condensing agent, and reported it to melt at 59–60°.

The Reaction with Acetone and Ethyl α-Bromolaurate.—A 70% yield of the expected glycidic ester was obtained when a mixture of 0.5 mole of acetone and 0.5 mole of ethyl α-bromolaurate was treated with 0.5 mole of potassium *t*-butoxide.[3] A lower-boiling material was obtained and has been identified as impure ethyl laurate by its constants (b.p. 153° (4 mm.), $n^{20}\text{D}$ 1.4391; lit.[12] b.p. 269 (760 mm.), $n^{20}\text{D}$ 1.4321) and by saponification to yield an acid, m.p. 43–44°.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.94; H, 12.07; neut. equiv., 200. Found: C, 71.72; H, 12.06; neut. equiv., 198 ± 3.

Lauric acid is reported[12] to melt at 44°. The amount of ethyl laurate produced corresponded to a 17% yield, based on bromo ester.

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[7] H. Wren and C. J. Still, *J. Chem. Soc.*, **107**, 444 (1915).

[8] H. Wren and C. J. Still, *ibid.*, **111**, 1019 (1917).

[9] H. Wren and C. J. Still, *ibid.*, **111**, 513 (1917).

[10] C. L. Reimer, *Ber.*, **13**, 742 (1880).

[11] F. Blicke, J. Foust and H. Raffelson, THIS JOURNAL, **67**, 3161 (1945).

[12] A. W. Ralston, "Fatty Acids and their Derivatives," John Wiley and Sons, Inc., New York, N. Y.

The Reaction with Pinacolone and Ethyl α-Bromophenylacetate.—A 20% yield of ethyl phenylacetate, identified as indicated previously, was obtained from the reaction of 0.15 molar quantities of pinacolone, ethyl α-bromophenylacetate and potassium *t*-butoxide. Unreacted pinacolone was recovered in 32% of the amount originally added. A 33% yield of diethyl 2,3-diphenylsuccinate, identified by a mixed melting point determination with the product previously identified as diethyl 2,3-diphenylsuccinate from the isobutyrophenone—ethyl α-bromo phenylacetate reaction, was also obtained. The presence of diethyl diphenylmaleate in the reaction mixture was shown by the isolation of diphenylmaleic anhydride from the saponified distillation residue.

The Reaction with Acetophenone and Ethyl α-Bromophenylacetate.—A 28.2% yield of ethyl phenylacetate was obtained from the reaction of 0.15 molar quantities of acetophenone, ethyl α-bromophenylacetate and potassium *t*-butoxide. Unreacted acetophenone was recovered in 45% of the amount originally added. Diethyl diphenylsuccinate and diethyl diphenylmaleate were identified in the tarry distillation residue, but the amounts present could not be accurately determined.

Acknowledgment.—We wish to express our appreciation for the financial aid given us through a Cottrell grant from Research Corporation.

ORONO, MAINE

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

The Synthesis of Alkylhydrazines. II. The Reduction of 1-Acyl-2-alkylidenehydrazines with Lithium Aluminum Hydride

BY RICHARD L. HINMAN

RECEIVED AUGUST 3, 1956

Several 1-acyl-2-alkylidenehydrazines have been reduced with lithium aluminum hydride in refluxing tetrahydrofuran. In every case two products were obtained: a 1,2-dialkylhydrazine and a 1-acyl-2-alkylhydrazine. The 1,2-dialkylhydrazines were easily oxidized in air to hydrazones which were identified by their ultraviolet absorption spectra.

Only a few examples have been reported of 1,2-dialkylhydrazines in which the alkyl groups are not identical. Of the few synthetic routes which have been employed only two are at all general in application. One method involves the reaction of an alkylhydrazine with an aldehyde or ketone and reduction of the resulting hydrazone by catalytic or chemical methods.[1] When an *unsym*-dialkylhydrazine is used, this method is useful for the preparation of trialkylhydrazines.[2]

A different approach involves the alkylation of a 1-alkyl-1,2-diacylhydrazine to give a 1,2-dialkyl-1,2-diacylhydrazine from which the acyl groups are then hydrolyzed. Starting with isopropylhydrazine and following this method, Ramsperger prepared 1-isopropyl-2-methylhydrazine.[1b] The direct alkylation of hydrazine is of course not feasible because alkylation generally occurs on the nitrogen which already bears an alkyl group.[2c,3]

In the approach to the problem reported in this paper it was hoped that the two alkyl groups could be introduced by the reduction of a 1-acyl-2-alkylidenehydrazine with lithium aluminum hydride. The requisite hydrazine derivatives are easily obtained, and the over-all reaction sequence is shown in equation 1. Since it is known that the

$$\begin{aligned} &RCO_2R \longrightarrow RCONHNH_2 \longrightarrow \\ &RCONHN{=}CR_1R_2 \xrightarrow{LiAlH_4} \underset{\text{I}}{RCH_2NHNHCHR_1R_2} \quad (1) \\ &\qquad\qquad + \underset{\text{II}}{RCONHNHCHR_1R_2} \end{aligned}$$

carbonyl group of an acylhydrazine containing the group –CONH– is usually reduced with difficulty,[4,5] the isolation of products of type II was also anticipated. However, it was hoped that long periods of reaction would give good yields of I at the expense of II.

The results of the reductions of several 1-acyl-2-alkylidenehydrazines are summarized in Table I.

TABLE I

SUMMARY OF THE REDUCTIONS OF 1-ACYL-2-ALKYLIDENEHYDRAZINES WITH LITHIUM ALUMINUM HYDRIDE

Reactant[a]	Excess of LAH, %	Time of reduction, hr.	Yield of 1,2-dialkylhydrazine, %	Yield of acylhydrazine, %
$C_3H_7CONHN{=}C(CH_3)_2$	100[b]	20	48	13
$C_3H_7CONHN{=}CHC_6H_5$	90[b]	27	12	43
$C_3H_7CONHN{=}CHC_6H_5$	167[b]	48	30	28
$C_6H_5CONHN{=}CHCH_3$	100	90	5	45
$C_6H_5CONHN{=}CHCH_3$	100[c]	30	[e]	65
$C_6H_5CONHN{=}CHC_6H_5$[c,d]	..	8	[e]	70
$C_6H_5CONHN{=}CH_2$	100[f]	24	[g]	..

[a] Solution of reactant added to solution of hydride except where noted otherwise. [b] One mole of $LiAlH_4$ required for reduction of both functional groups. [c] Soxhlet technique. [d] Private communication from Dr. Louis Carpino, University of Massachusetts. [e] Isolation not attempted. [f] Powdered hydrazone added to solution of hydride in tetrahydrofuran. [g] Only starting material recovered.

It will be noted that the yield of dialkylhydrazine is higher when the acyl group is butyryl rather than benzoyl. Even 90 hr. of refluxing 1-benzoyl-2-ethylidenehydrazine with lithium aluminum hydride in tetrahydrofuran produced only 5% of 1-benzyl-2-ethylhydrazine. These results follow the pattern of earlier work[4] in which it was shown that the –CONH– group of an acylhydrazine is more difficult to reduce when the acyl group is benzoyl rather than of the aliphatic type. The failure of

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[1] (a) H. L. Lochte, W. A. Noyes and J. R. Bailey, THIS JOURNAL, **44**, 2556 (1922); (b) H. C. Ramsperger, *ibid.*, **51**, 918 (1929); (c) C. D. Garrick, G. W. Drake and H. L. Lochte, *ibid.*, **58**, 160 (1936).

[2] (a) T. Curtius, *J. prakt. Chem.*, [2] **62**, 84 (1900); (b) H. Franzen and F. Kraft, *ibid.*, **84**, 137 (1911); (c) F. Klages, *Ann.*, **547**, 1 (1941); (d) J. G. Aston, J. B. Class and T. S. Oakwood, THIS JOURNAL, **75**, 2937 (1953).

[3] O. Westphal, *Ber.*, **74**, 759 (1941).

[4] R. L. Hinman, THIS JOURNAL, **78**, 1645, 2463 (1956).

[5] R. Huisgen, F. Jakob, W. Siegel and A. Cadus, *Ann.*, **590**, 1 (1954).