# Enol Esters. II.[1a] N-Acylation of Amides and Imides

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An improved method for N-acylation of certain amides and imides has been developed. Brief fusion of a mixture of isopropenyl stearate and acid catalyst with cyclic imides (succinimide, maleimide, phthalimide, barbituric acids), cyclic imide-amides (spirohydantoins), N-alkyl amides, or N-aryl amides causes elimination of acetone as the temperature exceeds 150–175° and gives high yields of N-acylated products. N-Stearoylsuccinimide (I) undergoes ring opening on refluxing with methanol to form methyl ester Ia of the aliphatic imide, N-succinoylstearamide, whereas mild hydrogenation yields stearaldehyde, octadecanol, octadecyl ether, and succinimide.

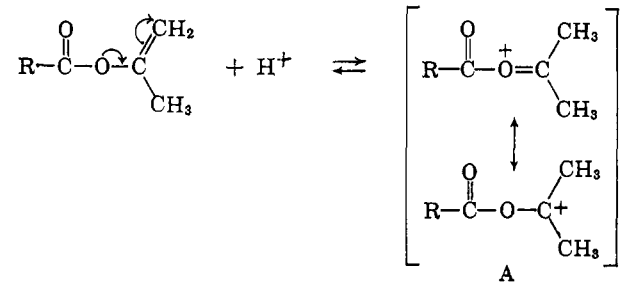
Acylation of amides to form diacyl or triacyl amides is a reaction rarely encountered in the modern chemical literature. The situation has not altered significantly from that in 1904 when Titherley,[3] after listing half a dozen methods, noted that "no single method has even approximately the character of a general reaction, but by selecting one of the foregoing processes, an acyl group may he introduced into practically any primary or secondary amide or cyclic amide."

Recent contributions include (1) the work of Davidson and Skovronek[4] who showed that acid-catalyzed amide–anhydride systems at reflux form an equilibrium mixture containing acylamide, nitrile, and carboxylic acid; (2) the finding of Thompson[5] that aroyl chloride–pyridine mixture (1:1) at an optimum temperature of −60° aroylates amides directly to tertiary amides under conditions where the secondary amide cannot be an intermediate since it is inert to the aroylation mixture; (3) the use of ketene[6]; and (4) Hagemeyer's[7] use of refluxing isopropenyl acetate to form diacetamide and N-acetylsuccinimide from acetamide and succinimide, respectively.

Hagemeyer's work, which is most pertinent to the present study, was re-examined in some detail. In our hands, conversion of succinimide to N-acetylsuccinimide by refluxing (98°) isopropenyl acetate was extremely low. The "product," although exhibiting a boiling point of 168° (10 mm.), in accordance with that reported in Hagemeyer's patent, consisted mainly of unchanged succinimide codistilling with tiny amounts of N-acetylsuccinimide, recovered from recrystallization mother liquors. We have confirmed the fact that succinimide and N-acetylsuccinimide have identical boiling points at 10-mm. pressure. Since Hagemeyer[7] identifies his N-acetylsuccinimide product only by boiling point, his identification must be held tentatively in question. In connection with Hagemeyer's patent, we also call attention to the coincidence of boiling points and melting points of acetamide and diacetamide, *viz.*, 222° *vs.* 223.5° and 81° *vs.* 78°, respectively. In any case, none of these previously reported methods is general.

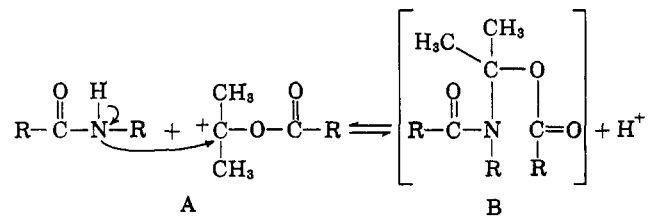
The present paper describes a convenient high-yield procedure for the N-acylation of cyclic imides (succinimide, maleimide, phthalimide, barbituric acids) cyclic imide-amides (spirohydantoins), N-alkyl amides, and N-aryl amides with long-chain acyl groups using enol esters as acylating agents. The enol ester, isopropenyl stearate, was taken as the standard reagent for introduction of the long-chain acyl group. This enol ester, on fusion with the amide or imide in the presence of a trace of *p*-toluenesulfonic acid, reacts readily as the temperature of the melt exceeds 150–175° forming N-acylated products and acetone.

The reaction may be reasonably explained by protonation of the enol ester to form a resonance-stabilized carbonium ion A.



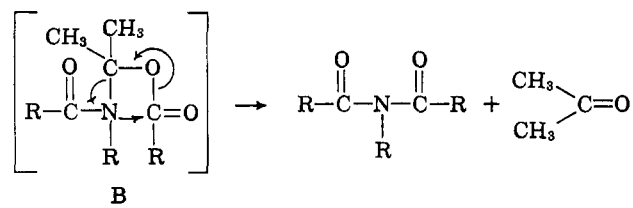
A

Ion A may react with the amide to form the adduct B regenerating the proton catalyst.



A B

Adduct B then undergoes thermally induced collapse to the observed products, acetone and acylamide.



B

An alternative pathway involves preliminary protonation of the carbonyl, rather than of the vinyl ether system, to form carbonium ion C.

(1) (a) For the previous paper in this series, see E. S. Rothman, S. Serota, T. Perlstein, and D. Swern, *J. Org. Chem.*, **27**, 3123 (1962); (b) presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., January 19, 1964.

(2) One of the laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

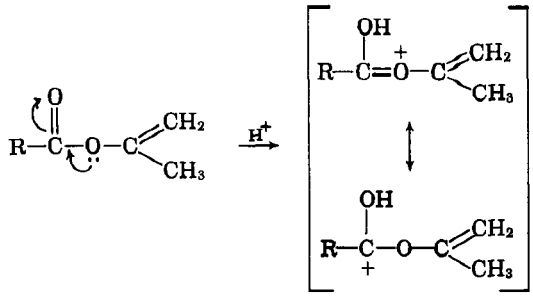
(3) A. W. Titherley, *J. Chem. Soc.* (London), **85**, 1684 (1904).

(4) D. Davidson and H. Skovronek, *J. Am. Chem. Soc.*, **80**, 376 (1958).

(5) Q. E. Thompson, *ibid.*, **73**, 5841 (1951).

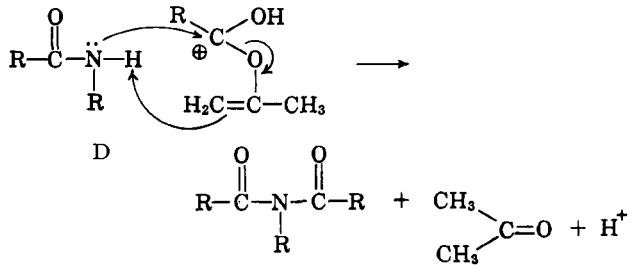
(6) R. E. Dunbar and W. M. Swenson, *J. Org. Chem.*, **23**, 1793 (1958).

(7) H. J. Hagemeyer, Jr., U. S. Patent 2,656,360 (October 20, 1953).



Carbonium Ion C

This carbonium ion is then coordinated by the amide, as shown in D, the intermediate collapsing to the observed products.



D

The proposed reaction paths may not proceed in the discrete steps shown, but carbonium ion formation may be followed by concerted addition and collapse to products.

The course of the reaction is observed by noting acetone evolution (bubbling) as the temperature reaches the optimum range of approximately 150–175° followed by cessation of bubbling signalling reaction completion. The reaction time required is short, typically 10–20 min. The yields are high, and the "crude" products are often in a high state of purity, requiring only removal of catalyst which can be carried out simultaneously with a decolorization with carbon.

The compounds (R = *n*-heptadecyl) in Chart I indicate the range of compounds attainable by the fusion procedure, and Table I summarizes yields and reaction conditions.

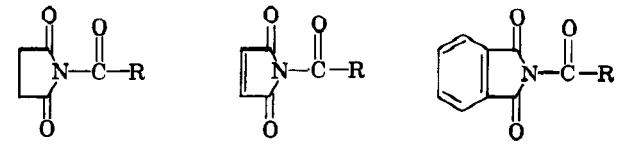
The products are crystalline solids, stable to storage for long periods of time, but are labile to chromatography on Florisil to a varying degree, depending on the compound in question. N-Lauroylsuccinimide (I) is rapidly cleaved by adsorption on Florisil, presumably by hydrolysis, since elution even with relatively polar solvents dislodges no material from the column. N-Stearoylsuccinimide (I) is also reactive toward Florisil chromatography but at a much slower rate.

In cases where a compound has two acylatable nitrogen atoms there is apparently little specificity or preference by the reagent. In the stearoylation of pentamethylene spirohydantoin both the imide and amide nitrogen atoms are attacked even with a 1:1 molar ratio of reactants. The two isomers, m.p. 92° and 107°, resulting from monostearoylation of pentamethylene spirohydantoin, differ in that one (VII) has a remaining *imide* hydrogen atom, while the other (VI) has a remaining *amide* hydrogen atom. These protons were examined by 60-Mc. n.m.r. The isomer, m.p. 92°, showed a $\delta$ value of 8.3 p.p.m. and is, therefore, tentatively assigned the free amide structure VI. The isomer, m.p. 107°, showed a $\delta$ value of 9.1 p.p.m. and is assigned the free imide structure VII, correlating with the higher acidity of the imide hydrogen expected to appear at lower field.[8] Both NH groups are stearoylated when a 2:1 molar ratio of isopropenyl stearate to pentamethylene spirohydantoin is used to form 1,3-diacylated VIII.

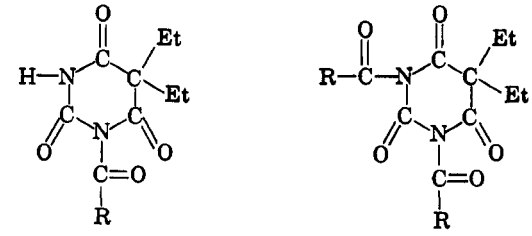
Similarly, 5,5-diethylbarbituric acid may be monostearoylated or distearoylated to IV or V. The possibility of O-acylation of tautomeric forms is excluded by the ultraviolet transparency of the products.

CHART I

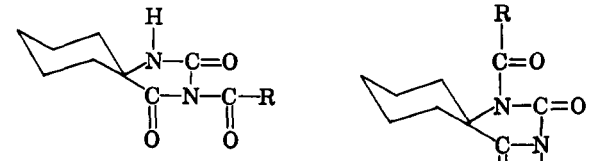
Cyclic N-acylimides



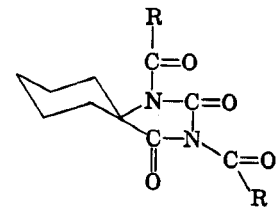
I (R = *n*-heptadecyl, or *n*-hendecyl) II III



IV V

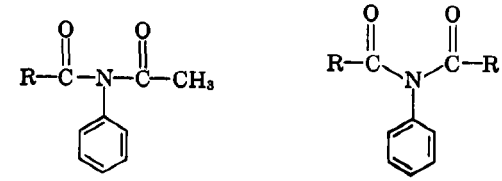


VI VII



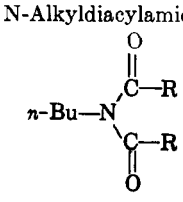
VIII

N-Aryl-N-Diacylamides



IX X

N-Alkyldiacylamides



XI

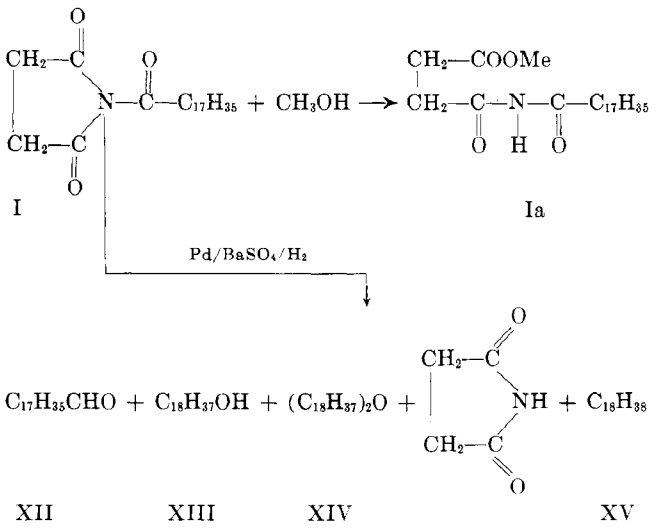
(8) Compare G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962).

TABLE I

ACYLATION BY FUSION WITH ENOL ESTERS

| Starting material | Product | Time, min. | Temp., °C. | Yield, % |
|---|---|---|---|---|
| Succinimide | N-Stearoylsuccinimide I | 20 | 190 | 87 |
| Succinimide | N-Lauroylsuccinimide I | 17 | 165 | 64 |
| Maleimide | N-Stearoylmaleimide II | 10 | 185 | 81 |
| Phthalimide | N-Stearoylphthalimide III | 30 | 230–250 | 80 |
| 5,5-Diethylbarbituric acid | 1-Stearoyl-5,5-diethylbarbituric acid IV | 15 | 200 | 35 |
| 5,5-Diethylbarbituric acid | 1,3-Distearoyl-5,5-diethylbarbituric acid V | 9 | 170–190 | 53 |
| Pentamethylene-spirohydantoin, procedure A, 1:1 molar ratio (see Experimental) | 3-Stearoyl-1,3-diazaspirodecane[4.5]-2,4-dione VI | 13 | 220 | 39 |
| | 1-Stearoylated isomer VII | | | 32 |
| Pentamethylene-spirohydantoin, procedure B, 2:1 molar ratio (see Experimental) | 3-Stearoylated product | 10 | 200 | .. |
| | 1-Stearoylated product | | | 87 |
| | 1,3-Distearoylated product | | | .. |

Reactions of N-stearoylsuccinimide (I) are interesting. Refluxing in methanol opens the ring to form a crystalline methyl ester which separates in large platelets from the cooled reaction mixture. Evidence that ring opening occurred includes the elementary analysis indicating retention of nitrogen and addition of the elements of methanol, and the infrared spectrum which clearly shows the NH and ester bands of the product. This product is evidently the methyl ester of N-succinoylstearamide (Ia).




Hydrogenation, under mild conditions, is equally selective but the group attacked is the side chain carbonyl rather than either of the ring carbonyls. Recovery of pure recrystallized succinimide amounted to 93% of the expected value. The side-chain fragment could be accounted for as stearaldehyde (XII), octadecanol (XIII), and dioctadecyl ether (XIV). Small amounts of a solid hydrocarbon, m.p. *ca.* 20° (octadecane?), were also detectable by chromatography.

Side reactions rarely occur during the formation of N-acyl compounds by the enol ester fusion procedure, except that amide exchange[9] takes place in mixed systems. Thus, stearoylation of acetanilide gave both the expected N-stearoylacetanilide (IX) and the amide exchange product, distearoylaniline (X). The enol ester failed to acylate the aliphatic imides, distearamide, and N-succinoylstearamide methyl ester (Ia); starting materials were recovered unchanged. N-Acylated products were not formed from the mono-N-tertiary butyl derivatives of acrylamide, -propionamide, and -stearamide. The primary amides, stearamide and benzamide, suffer extensive dehydration under the described reaction conditions.

Interestingly, the homologous enol ester, vinyl stearate, is not a stearoylating agent in a procedure analogous to the one already described. On fusion with succinimide, for example, starting material is recovered unchanged and no evolution of acetaldehyde occurs. If mercuric acetate is added to the fusion mixture, a vigorous evolution of acetaldehyde does occur, but N-acylation still does not occur. The major product is apparently ethylene glycol distearate, and not ethylidene distearate.

(9) L. F. Beste and R. C. Hovtz, *J. Polymer Sci.*, **8**, 395 (1952).

## Experimental

**N-Stearoylsuccinimide (I).**—Succinimide (11.9 g., 0.12 mole), isopropenyl stearate (38.9 g., 0.12 mole), and *p*-toluenesulfonic acid monohydrate (100 mg.) were heated for 20 min. at 190° in a flask immersed in a heating bath, using electromagnetic stirring as soon as the mixture became fluid. During the reaction, 5.9 g. of acetone (calcd. 7.0 g.) was collected and identified as the 2,4-dinitrophenylhydrazone, m.p. 126–127°. The infrared spectrum of the cooled solidified reaction melt showed no unchanged isopropenyl stearate (1672- and 870-cm.$^{-1}$ bands absent) and was very similar to that of the analytically pure product. Recrystallization from pentane, after decolorization with active carbon, gave 38 g. (87% yield) of N-stearoylsuccinimide as fibrous silky needles, m.p. 95–96°. The infrared spectrum showed three maxima at 1727, 1756, and 1801 cm.$^{-1}$ in the carbonyl region and characteristic maxima at 1085, 1165, 1250, and 1305 cm.$^{-1}$ in the fingerprint region.

*Anal.* Calcd. for $C_{22}H_{39}O_3N$: C, 72.28; H, 10.75; N, 3.83; mol. wt., 365 g./mole. Found: C, 72.19; H, 10.71; N, 4.07; mol. wt., 344 g./mole.

**Monomethyl Ester of N-Stearoylsuccinimide (Ia).**—One sample of N-stearoylsuccinimide was recrystallized from methanol in the usual manner without alteration, but a repetition of the operation gave a new product, m.p. 103–105°. This product could be obtained reproducibly in nearly theoretical yield by refluxing 300 mg. of N-stearoylsuccinimide with 40 ml. of methanol for 1.5 hr., then cooling to deposit large, scaly platelets, m.p. 105–106°. Because of hydrogen bonding, the infrared spectrum is dependent to an unusual degree upon solvent and concentra-

tion, the carbonyl and NH regions appearing as single, double, or tripled bands: $\nu_{max}^{Nujol}$ 1730 (weak shoulder at 1692) (CO), 3180, 3275 (NH); $\nu_{max}^{CHCl_3 \text{ or } CH_2Cl_2}$ 1736, 1704 (CO), 3390 (NH) (weak bands also at 3049, 3230, and 3280); $\nu_{max}^{CS_2}$ 1740, 1710, 1694 (w) (CO), 3150, 3250, and 3380 cm.$^{-1}$ (NH).

*Anal.* Calcd. for $C_{23}H_{43}O_4N$: C, 69.48; H, 10.90; N, 3.52. Found: C, 69.69; H, 11.25; N, 3.48.

**N-Dodecanoylsuccinimide** (I, **R** = $C_{11}H_{23}$).—Lauric acid (10 g., 0.05 mole), isopropenyl acetate (27.5 ml., 0.33 mole), and a drop of concentrated sulfuric acid were refluxed for 5 hr. After addition of 200 mg. of potassium acetate, the excess isopropenyl acetate was removed under reduced pressure. On dilution with pentane and cooling to −20°, 1.75 g. of lauric anhydride, m.p. 41.5–42°, separated and was removed by filtration. The filtrate containing the desired isopropenyl laurate was filtered through a column of Florisil which was washed with additional pentane, in the course of which treatment contaminant acid and anhydride were retained by the column. Solvent was removed from the percolate by distillation and the residue was distilled *in vacuo* to yield **isopropenyl laurate,** b.p. 114° (1 mm.), m.p. 6°, $n^{25}D$ 1.4377, $d^{26}_4$ 0.8650.

*Anal.* Calcd. for $C_{15}H_{28}O_2$: C, 74.93; H, 11.74; Found: C, 74.76; H, 11.66.

Isopropenyl laurate (3.46 g., 0.014 mole), succinimide (1.43 g., 0.014 mole), and *p*-toluenesulfonic acid monohydrate (14 mg.) were heated to 165° for 17 min. Infrared examination showed no unreacted isopropenyl laurate or lauric anhydride bands. After decolorization with active carbon in pentane–methylene chloride (2:3 v./v.), the solution was concentrated to deposit 260 mg. of unchanged succinimide. On cooling, 2.5 g. of N-dodecanoylsuccinimide separated as plates, m.p. 76–80.5°. The analytical sample, m.p. 78–81°, was obtained by recrystallization from pentane. The compound was rapidly destroyed by attempted chromatography on Florisil.

*Anal.* Calcd. for $C_{16}H_{27}O_3N$: C, 68.29; H, 9.67; N, 4.98. Found: C, 68.69; H, 9.53; N, 4.79.

**N-Stearoylmaleimide** (II).—Maleimide (1.66 g., 0.017 mole), isopropenyl stearate (6.48 g., 0.02 mole), hydroquinone (100 mg.), and *p*-toluenesulfonic acid monohydrate (12 mg.), were heated to 185° for 10 min. under nitrogen. The cooled mixture was taken nearly into solution with a mixture of 25 ml. of methylene chloride and 100 ml. of pentane, and was filtered to remove 120 mg. of insoluble matter. After decolorization with active carbon, followed by volume reduction, successive crystalline crops of N-stearoylmaleimide were collected, total yield 81%. The analytical sample, recrystallized from hexane, showed double m.p. 73° and 87.5–89.5°; $\nu_{max}^{CS_2}$ 1718, 1755, and 1789 cm.$^{-1}$.

*Anal.* Calcd. for $C_{22}H_{37}NO_3$: C, 72.68; H, 10.26; N, 3.85. Found: C, 72.75; H, 10.33; N, 3.85.

**N-Stearoylphthalimide** (III).—Isopropenyl stearate (3.2 g., 0.01 mole), phthalimide (1.47 g., 0.011 mole), and *p*-toluenesulfonic acid monohydrate (10 mg.) were heated to 230–250° for 30 min. The infrared spectrum of the cooled melt showed substantially complete conversion to the desired product. Anhydride and carboxylic acid bands were absent. The melt was dissolved in hexane containing 10–15% methylene chloride and the solution was decolorized with active carbon. After removal of the lower boiling methylene chloride, cooling of the resultant hexane solution caused crystallization of 4.4 g. (80% yield) of the N-acylated product as felted, transparent filaments, m.p. 93–94.5°. The infrared spectrum showed three carbonyl bands at $\nu_{max}^{CS_2}$ 1805, 1755 (broad), and 1722 cm.$^{-1}$, and strong bands at 1287 and 714 cm.$^{-1}$.

*Anal.* Calcd. for $C_{26}H_{39}O_3N$: C, 75.50; H, 9.51; N, 3.39. Found: C, 75.39; H, 9.51; N, 3.34.

**1-Stearoyl-5,5-diethylbarbituric Acid** (IV). **A. 1:1 Molar Ratio.**—Diethylbarbituric acid (3.68 g., 0.02 mole), isopropenyl stearate (6.48 g., 0.02 mole), and *p*-toluenesulfonic acid (20 mg.) were melted together at 200° for 15 min. The cooled, solidified melt was extracted with hot pentane and 1.2 g. of insoluble diethylbarbituric acid was filtered off. On cooling to 25° an additional 0.3 g. separated and was discarded. On further cooling to 5°, 1.5 g. of stearic acid, m.p. 70–71°, separated. The mother liquors were decolorized with active carbon and, on cooling to −20°, 3.15 g. of the monostearoylated product IV separated, m.p. 55–56°.

Recrystallization from pentane gave the analytical sample, m.p. 55–56:2°, $\nu_{max}^{CS_2}$ 3390, 3210, 3100 (NH), 1800, 1725, 1700, small shoulder at 1747 cm.$^{-1}$ (CO).

*Anal.* Calcd. for $C_{26}H_{46}O_4N_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.42; H, 10.43; N, 5.97.

**B. 1:2 Molar Ratio.**—Diethylbarbituric acid (1.84 g., 0.01 mole), isopropenyl stearate (6.48 g., 0.02 mole), and *p*-toluenesulfonic acid (120 mg.) were heated together at 170–190° for 9-min. The melt was easily soluble in petroleum ether except for 0.25 g. of recovered diethylbarbituric acid. After decolorization with active carbon the solution was cooled to deposit 0.86 g. of stearic anhydride. The solution was concentrated and cooled, whereupon 3.77 g. of crude distearoylated material separated, m.p. 55–65°. Recrystallization from acetone and from petroleum ether gave the analytical sample of **1,3-distearoyl-5,5-diethylbarbituric acid** (V), m.p. 66.5–68°; $\nu_{max}^{CS_2}$ 1797, 1694 cm.$^{-1}$ (CO); NH bands absent. Other characteristic bands in the fingerprint region occurred at 1391, 1372, 1324, 1220, 1170, 1040, 746, and 715 cm.$^{-1}$.

*Anal.* Calcd. for $C_{44}H_{80}O_5N_2$: C, 73.69; H, 11.25; N, 3.91; mol. wt., 717 g./mole. Found: C, 74.05; H, 11.36; N, 3.85; mol. wt., 689 g./mole (carbon tetrachloride).

**Reaction of Pentamethylene Spirohydantoin**[10] **(1,3-Diazaspirodecane-[4.5]-2,4-dione) with Isopropenyl Stearate. A. 1:1 Molar Ratio.**—The spirohydantoin (3.36 g., 0.02 mole), was heated to 220° for 13 min. with isopropenyl stearate (6.48 g., 0.02 mole), in the presence of *p*-toluenesulfonic acid monohydrate (20 mg.). After trituration of the cooled melt with boiling pentane, 3.35 g. of insoluble **3-stearoyl-1,3-diazaspirodecane[4.5]-2,4-dione** (VI), m.p. 89.5–91°, was removed by filtration. The analytical sample, recrystallized from hexane, gave platelets, m.p. 91–92.5°, and showed no selective ultraviolet maxima in the usable cyclohexane and methanol region. The infrared revealed NH bands at 3135, 3240, and 3460 cm.$^{-1}$ and carbonyl bands at 1717, 1757, and 1805 cm.$^{-1}$ ($CS_2$); n.m.r., $\delta$ = 8.3 p.p.m.

*Anal.* Calcd. for $C_{26}H_{46}O_3N_2$: C, 71.84; H, 10.67; N, 6.45; mol. wt., 435 g./mole. Found: C, 71.70; H, 10.96; N, 6.50; mol. wt., 432 g./mole in methyl ethyl ketone; 708, 722 g./mole in carbon tetrachloride.

Attempted chromatographic separation of the components of the trituration liquors by chromatography on Darco G-60 active carbon gave 1.21 g. of contaminants (mainly stearic acid) on elution with 10–25% methylene chloride in pentane, and 2.78 g. of VII, m.p. 107° (see procedure B below), eluted with 25–100% methylene chloride in pentane. Attempts to dislodge the tenaciously bound residue on the column gave only small amounts of stearic acid tailings.

**Procedure B. 2:1 Molar Ratio.**—Under conditions similar to procedure A, the spirohydantoin (0.84 g., 0.005 mole), isopropenyl stearate (3.24 g., 0.01 mole), and *p*-toluenesulfonic acid monohydrate (10 mg.) were heated to 200° for 10 min. The cooled melt was dissolved in 200 ml. of hexane and decolorized with active carbon. The volume was reduced and successive crystalline crops of VII totaling 1.88 g. (87%), m.p. 101–105° were collected. The analytical sample of **1-stearoyl-1,3-diazaspirodecane[4.5]-2,4-dione** (VII) melted at 106–107°. The infrared spectrum showed NH bands, $\nu_{max}^{CS_2}$ 3080, 3210, and 3410 cm.$^{-1}$, the relative intensity varying with concentration, and four carbonyl bands at 1711, 1725, 1750, and 1788 cm.$^{-1}$ (Beckman IR-7 instrument). The material showed no selective ultraviolet absorption, and thin-layer chromatography on silica gel G, developing with 20% ether in pentane, showed only one spot; n.m.r., $\delta$ = 9.1 p.p.m.

*Anal.* Calcd. for $C_{26}H_{46}O_3N_2$: C, 71.84; H, 10.67; N, 6.45; mol. wt., 435 g./mole. Found: C, 71.80; H, 10.86; N, 6.19; mol. wt., 427 g./mole (methyl ethyl ketone).

From the concentrated mother liquors the very soluble distearoylated product, **1,3-distearoyl-1,3-diazaspirodecane[4.5]-2,4-dione** (VIII), was obtained. This material, recrystallized from pentane at −25°, melted at 54.5 to 55.5° and showed no selective ultraviolet maximum. The infrared showed no NH bands; carbonyl bands occurred at 1810, 1760, 1729, and 1711 cm.$^{-1}$ ($CS_2$).

*Anal.* Calcd. for $C_{44}H_{80}O_4N_2$: C, 75.37; H, 11.50; N, 4.00; mol. wt., 701 g./mole. Found: C, 75.52; H, 11.59; N, 3.56; mol. wt., 651 g./mole (carbon tetrachloride).

Attempts at chromatographic separation on active charcoal columns were not successful since only the acylated amide VII is elutable from the column.

(10) H. Bucherer and V. A. Libe, *J. prakt. Chem.* **141**, 5 (1934).

**N-Stearoylacetanilide (IX) and N-Phenylstearimide (X).**—Acetanilide (2.7 g., 0.02 mole), isopropenyl stearate (6.4 g., 0.02 mole), and *p*-toluenesulfonic acid monohydrate (20 mg.) were heated to 165° for 0.5 hr., the cooled melt was dissolved in hot pentane and decolorized with active carbon. On cooling, 320 mg. of unchanged acetanilide separated and was filtered off. On successive volume reductions a series of crops totalling 2 g. of N-phenylstearimide (X) (N,N-distearoylaniline), m.p. 63°, was collected. This substance is distinguishable from the more soluble N-stearoylacetanilide (IX), isolated in later crops, by the occurrence of only a single infrared band near 1200 cm.$^{-1}$. The analytical sample was recrystallized from pentane, m.p. 61–63°, $\tilde{\nu}_{max}^{CS_2}$ 1709 cm.$^{-1}$.

*Anal.* Calcd. for $C_{42}H_{75}NO_2$: C, 80.58; H, 12.08; N, 2.24; mol. wt., 624 g./mole. Found: C, 80.59; H, 12.07; mol. wt., 604 g./mole.

From the mother liquors, successive crops of N-stearoylacetanilide (IX) totalling 4 g., m.p. 60–61°, were collected. This substance showed a characteristic infrared doublet at 1235 and 1205 cm.$^{-1}$ and a weaker doublet at 1040 and 1019 cm.$^{-1}$; $\tilde{\nu}_{max}^{CS_2}$ at 1709 cm.$^{-1}$.

*Anal.* Calcd. for $C_{26}H_{43}NO_2$: C, 77.75; H, 10.79; N, 3.48; mol. wt., 400 g./mole. Found: C, 77.83; H, 11.09; N, 3.48; mol. wt., 374 g./mole.

**N-Butylstearimide (XI).**—N-Butylstearamide (603 mg., 1.78 mmoles), isopropenyl stearate (576 mg., 1.78 mmoles), and *p*-toluenesulfonic acid (8 mg.) were heated to 180–190° for 6 min. after which time no further gas evolution was observable. The cooled melt was dissolved in 30 ml. of hot pentane and cooled to deposit 90 mg. of unidentified, relatively insoluble crystalline material, m.p. 79–82°. The mother liquors were treated with active carbon and gave on volume reduction 820 mg. of crystalline product, m.p. 49.5–50°. Infrared examination in carbon disulfide solution showed the absence of NH bands and a single broad carbonyl band centered at 1700 cm.$^{-1}$, with prominent fingerprint bands at 720, 1105, 1190, 1275, and 1381 cm.$^{-1}$.

*Anal.* Calcd. for $C_{40}H_{79}O_2N$: C, 79.29; H, 13.14; N, 2.31; mol. wt., 606 g./mole. Found: C, 79.45; H, 13.18; N, 2.20; mol. wt., 552 g./mole.

**Hydrogenolysis of N-Stearoylsuccinimide (I).**—N-Stearoylsuccinimide (I) (1.88 g.) in 300 ml. of dry ether was stirred at room temperature with 2 g. of 10% palladium-on-barium sulfate catalyst for 20 hr., under a hydrogen pressure of 1 atm. The catalyst was removed by filtration and the filtrate was evaporated to dryness. Trituration of the residue with carbon disulfide allowed the separation of 500 mg. (93% yield) of insoluble succinimide by filtration. The filtrate, again taken to dryness, was chromatographed on Florisil in pentane to elute successively 80 mg. of a hydrocarbon, m.p. *ca.* 20°, presumed to be octadecane (*Anal.* Calcd. for $C_{18}H_{38}$: C, 84.95; H, 15.05. Found: C, 85.41; H, 14.41.); 650 mg. of stearaldehyde, m.p. 63° (lit.[11] 63.5°); $\tilde{\nu}_{max}^{CS_2}$, 1724 cm.$^{-1}$ (CO), 2703 cm.$^{-1}$ (aldehyde C–H) (2,4-dinitrophenylhydrazone, m.p. 108–109°, lit.[11] 105°); and 210 mg. of dioctadecyl ether (XIV), m.p. 62–63° (lit.[12] 62–63°). Alternatively, the octadecyl ether could be separated from the mixture owing to its relative insolubility in hexane. The nearly featureless infrared spectrum showed no detail except for the usual CH bands and a single characteristic C–O band near 1110 cm.$^{-1}$.

*Anal.* Calcd. for $C_{36}H_{74}O$: C, 82.68; H, 14.26; mol. wt., 523 g./mole. Found: C, 82.47; H, 14.04; mol. wt., 514 g./mole.

On continued slow elution with pentane, or preferably more rapidly with methylene chloride, 360 mg. of *n*-octadecanol (XIII) was obtained, m.p. 58.5–59°. The infrared spectrum was identical with an authentic specimen of *n*-octadecanol.

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(11) H. P. Kaufmann and H, Kirschnek, *Fette, Seifen, Anstrichmittel* **55**, 847, 854 (1953), report that stearaldehyde, m.p. 64.5°, is a trimer (trialkyldioxolane) since it shows no infrared carbonyl band but shows C–O ether bands in the 1100–1200-cm.$^{-1}$ region. Our preparation, having the same melting point, shows the usual aldehyde absorption bands but lacked the ether bands. We also have observed the monomer, m.p. 43–44.2°, mol. wt. 263, 271 g./mole, and the dimer, m.p. 55–56°, mol. wt. 599 g./mole, both showing infrared carbonyl bands.

(12) D. A. Shirley, J. R. Zietz, and W. H. Reedy, *J. Org. Chem.*, **18**, 398 (1953).

# Cyanoguanyl Azide Chemistry[1]

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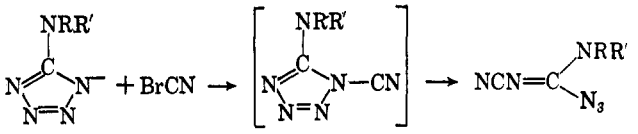
Several cyanoguanyl azides were prepared. Infrared and ultraviolet spectral data indicate that the structure, NC—N=C($N_3$)NHR (where R = H, alkyl, aryl), is the dominant tautomer. The actions of bases on cyanoguanyl azide (1) fall into four categories: (1) cyclization to 5-cyaniminotetrazoline salts, (2) displacement of azide, (3) addition to the cyano group, and (4) simple complex formation. Diazomethane acts as a cyclizing and methylating agent on 1 and N-cyano-N′-methylguanyl azide (2) yielding 1,4-dimethyl-5-cyaniminotetrazoline (7). The role of base in the cyclization of guanyl azides, in general, is discussed. The structures and chemistry of the 5-cyaniminotetrazolines were investigated. Potassium 5-(N-cyano-N-methylamino)tetrazole (4), a member of a new tetrazole series, was isolated, derivatives were prepared, and structures were established.

Cyanoguanyl azide (1) was reported and characterized by Hart[2] in 1928, but the chemistry was not investigated further. This paper deals in more detail with the structure and chemistry of 1 and some of its derivatives.

N-Cyano-N′-methylguanyl azide (2) and N-cyano-N′,N′-dimethylguanyl azide (3) were prepared by Hart's procedure using the potassium salts of 5-methylaminotetrazole and 5-dimethylaminotetrazole, respectively, and cyanogen bromide. One coproduct in the preparation of 2 was potassium 5-(N-cyano-N-methylamino)tetrazole (4); in this case the cyano group attacked the 5-methylamino position. Cyanoguanyl azide formation proceeds through the intermediate formation of a 1-cyano-5-aminotetrazole. Arenesulfonyl halides and 5-aminotetrazole, in the presence of base, proceed similarly to produce arenesulfonylguanyl



**1**, R = R′ = H
**2**, R = $CH_3$; R′ = H
**3**, R = R′ = $CH_3$

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) C. V. Hart, *J. Am. Chem. Soc.*, **50**, 1922 (1928).