The Synthesis of Some N-*Hydroxyimides.*

By D. E. Ames and T. F. Grey.

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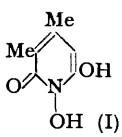
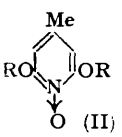
N-Benzyloxyimides, prepared by heating benzyloxyamine with succinic, glutaric, αβ-dimethylglutaconic, and other dibasic acids, have been catalytically hydrogenated to give *N*-hydroxyimides, the structures of which have been examined by measurements of infra-red and ultra-violet spectra and of pK_a values.

The antibiotic aspergillic acid is a pyrazine cyclic hydroxamic acid (Dutcher, *J. Biol. Chem.*, 1947, **171**, 321) and more recent work has shown that analogous pyridine and quinoline derivatives also possess antibacterial properties (Newbold and Spring, *J.*, 1948, 1864; Cunningham, Newbold, Spring, and Stark, *J.*, 1949, 2091; Shaw, *J. Amer. Chem. Soc.*, 1949, **71**, 67; Lott and Shaw, *ibid.*, p. 70). We have now synthesised the related hydroxamic acid (I).

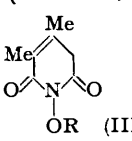
Newbold and Spring (*loc. cit.*) prepared 1-hydroxypyrid-2-one by hydrolysis of 2-methoxypyridine *N*-oxide, and an analogous method employing a dimethoxypyridine *N*-oxide was therefore first examined. 2 : 6-Dimethoxy-4-methylpyridine (Ames, Bowman, and Grey, *J.*, 1953, 3008) with perbenzoic acid gave a small yield of the *N*-oxide (II; R = Me) but attempts to demethylate the latter resulted in decomposition. We next attempted to prepare the dibenzyloxypyridine *N*-oxide (II; R = CH_2Ph), catalytic debenzylation of which should be possible (cf. Shaw, *loc. cit.*). 2 : 6-Dibenzyloxy- and



(I)



(II)



(III)

$HO_2C{\cdot}[CH_2]_n{\cdot}CO{\cdot}NH{\cdot}OR$ (IV)

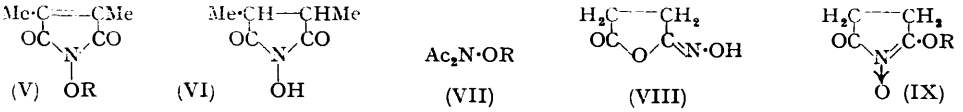
2 : 6-dibromo-4-methylpyridine could not be converted into the *N*-oxides, however, although in both cases more than 1 mol. of perbenzoic acid was consumed. The difficulty of preparing *N*-oxides from 2 : 6-disubstituted pyridines has been indicated by Gilman and Edward (*Canad. J. Chem.*, 1953, **31**, 457). The high consumption of perbenzoic acid in the present case may be analogous to the behaviour of alkoxybenzenes (Friess, Soloway, Morse, and Ingersoll, *J. Amer. Chem. Soc.*, 1952, **74**, 1305).

The compound (I) was synthesised by condensation of αβ-dimethylglutaconic acid with benzyloxyamine followed by catalytic hydrogenation of the resulting *N*-benzyloxyimide (III; R = CH_2Ph). The rearrangement of the intermediate (III; R = H) is shown by physical measurements (see below).

Similar use of benzyloxyamine has also provided convenient syntheses of other *N*-benzyloxy- and *N*-hydroxy-imides. Succinic, glutaric, α-dodecylglutaric, and αβ-dimethylmaleic anhydride in benzene give *N*-benzyloxy-succinamic and -glutaramic acids (IV; R = CH_2Ph, $n = 2$ and 3 respectively) and thence the corresponding hydroxamic acids (IV; R = H). Similarly, the benzyloxyimides furnished the corresponding *N*-hydroxyimides; in the case of (V; R = CH_2Ph), complete hydrogenation gave the compound (VI) but, under different conditions, the semihydrogenation product (V; R = H) could be isolated.

Maleic anhydride in benzene reacted with benzyloxyamine giving *N*-benzyloxymaleinamic acid but repeated attempts to obtain the *N*-benzyloxyimide by thermal dehydration failed. Treatment of *N*-benzyloxymaleinamic acid with thionyl chloride and then pyridine, however, gave a crystalline product which appeared to be the benzyloxyimide, although the light-absorption properties were rather anomalous (see below). Attempts to debenzylate this product by catalytic hydrogenation and by sodium and liquid ammonia were unsuccessful. The dehydration of *N*-benzyloxymaleinamic acid by boiling acetic anhydride was also attempted, but the product was *NN*-diacetyl-*O*-benzylhydroxylamine (VII; R = CH_2Ph) which was also prepared directly from benzyloxyamine. Catalytic

debenzylation of this material yielded the hitherto unknown *NN*-diacetylhydroxylamine (VII; R = H).



(V) (VI) (VII) (VIII) (IX)

The *N*-benzyloxy- and *N*-hydroxy-amides show the expected infra-red absorption bands (Table 1). The imides have infra-red spectra (Table 2) similar to those of unsubstituted and *N*-alkyl-imides with bands at *ca.* 1700 and 1760 cm.$^{-1}$. The former is always the more intense; in several cases the latter band occurs at unusually high frequency (above 1780 cm.$^{-1}$; cf. Randall, Fowler, Fuson, and Dangl, *op. cit.*, p. 20). The close similarity between the spectra of *N*-benzyloxy- and *N*-hydroxy-succinimide and

TABLE 1. *Absorption spectra in region* 1450—1900 *cm.*$^{-1}$.

Bands	Amide	Phenyl	Carboxy	Other bands
N-Benzyloxybenzamide †	1653, 1511	1580, 1484	—	—
NN'-Dibenzyloxy-α-dodecylglutaramide	1656, 1515	*	—	—
N-Benzyloxysuccinamic acid	1653, 1536	1499	1727	1553, 1517
N-Benzyloxyglutaramic acid	1658, 1522	*	1694	—
N-Benzyloxymaleinamic acid	1639, 1534	—	1709	1567
N-Hydroxysuccinamic acid	1664, 1567	—	1709	1621
N-Hydroxyglutaramic acid	1634, 1541	—	1718	—

* No bands detected. All in Nujol. † Beckmann, *Ber.*, 1893, **26**, 2633.

TABLE 2. *Absorption spectra in region* 1450—1900 *cm.*$^{-1}$.

	Imide bands	Other bands
N-Benzyloxysuccinimide	1712, 1779	—
N-Hydroxysuccinimide	1709, 1789	1511, 1692
N-Hydroxy-αβ-dimethylsuccinimide	1695, 1783	1495
N-Pentylsuccinimide [a]	1706, 1770	—
N-Acetoxysuccinimide	—	1754,[b] 1779, 1802, 1832
N-Bromosuccinimide	1718, 1776	1821
N-Benzyloxyglutarimide [c]	1715, 1754	—
N-Hydroxyglutarimide	1672, 1742	—
N-Benzyloxy-α-dodecylglutarimide	1701, 1736	—
α-Dodecyl-*N*-hydroxyglutarimide	1704, 1733	1468
β : β : *N*-Trimethylglutarimide	1672, 1727	—
N-Benzyloxymaleinimide	1721, 1733	—
N-Benzyloxy-αβ-dimethylmaleinimide	1724, 1783	—
N-Hydroxy-αβ-dimethylmaleinimide	1730, 1792	1667
α : β : *N*-Trimethylmaleinimide	1715, 1770	1504, 1536
N-Benzyloxy-αβ-dimethylglutaconimide	1678, 1724	1495
α : β : *N*-Trimethylglutaconimide	1678, 1709	1645
(I) or (X)	—	1466, 1518, 1587, 1637
6-Methoxy-1 : 4-dimethylpyrid-2-one [d]	—	1531, 1580, 1656
2 : 6-Dimethoxy-4-methylpyridine *N*-oxide	—	1585, 1623, 1736,[e] 1779 [e]
NN-Diacetyl-*O*-benzylhydroxylamine	— 1721	1464
NN-Diacetylhydroxylamine	1715, 1799	1608
ON-Diacetylhydroxylamine [f]	—	1534, 1664, 1802

[a] Randall, Fowler, Fuson, and Dangl, "Infra-red Determination of Organic Structures," Van Nostrand, New York, 1949, p. 172. [b] Acetate band. [c] In $CHCl_3$ (others in Nujol). [d] Ames, Bowman, and Grey, *loc. cit.* [e] Very weak bands which may be due to some impurity. [f] Prepared by Hantzsch's method (*Ber.*, 1892, **25**, 701).

of the *N*-pentyl compound confirms these structures and excludes the alternative (VIII) (cf. Orndorff and Pratt, *Amer. Chem. J.*, 1912, **47**, 99). The spectrum of *N*-acetoxysuccinimide, however, shows some anomalous features: although the very strong acetate band (1754 cm.$^{-1}$) has some masking effect, the apparent absence of the imide bands is unexpected; the maxima observed at 1779, 1802, and 1832 cm.$^{-1}$ are unexplained. (*N*-Bromosuccinimide similarly shows a band at 1821 cm.$^{-1}$.) Despite these results the acetoxy-imide structure appears to be more satisfactory than the possible alternative (IX; R = Ac) in view of the low-intensity ultra-violet light absorption (Table 3).

In the case of the αβ-dimethylglutaconic acid derivatives, there is a striking difference between the spectra of the *N*-benzyloxy-imide and of the derived debenzylation product.

TABLE 3. *Ultra-violet light absorption data (95% ethanol solutions) and pK_a values.*

	R = CH_2Ph			R = H		
	$\lambda_{max.}$ (Å)	ε	pK_a	$\lambda_{max.}$ (Å)	ε	pK_a
$HO_2C{\cdot}[CH_2]_2{\cdot}CO{\cdot}NH{\cdot}OR$	2520	176	4·6 [a]	—	—	4·5 [a]
	2580	222	10·2	—	—	9·6
	2640	191				
	2680	127				
$HO_2C{\cdot}[CH_2]_3{\cdot}CO{\cdot}NH{\cdot}OR$	2080	10,800	4·7 [a]	<2100	>1400	4·6 [a]
	2520	164	10·2	—	—	9·6
	2580	218				
	2640	182				
	2680	120				
$HO_2C{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}OR$	2100	18,000	3·8 [a]	—	—	—
	2750	5400	10·0			
$CH_2{\cdot}CO$ >N·OR, $CH_2{\cdot}CO$	2060	22,700	—	<2050	>7900	6·0 [a]
	2460	512	—	2655	625	
	2520	336				
	2575	342				
	2630	299				
	2690	208				
$CH_3{\cdot}CH{\cdot}CO$ >N·OR, $CH_3{\cdot}CH{\cdot}CO$	—	—	—	2650	1670	7·2 [b]
$CH_2(CH_2{\cdot}CO)_2$ >N·OR	2090	19,000	—	2160	9700	7·6 [a]
	2520	298				
	2580	319				
	2630	280				
	2690	171				
$CH_2(CH_2{\cdot}CO)_2$ >N·OR, n-$C_{12}H_{25}{\cdot}CH{\cdot}CO$	2110	15,800	—	2170	9000	10·5 [b]
	2550 *	278				
$CH{\cdot}CO$ >N·OR, $CH{\cdot}CO$	2880	14,000	—	—	—	—
$MeC{\cdot}CO$ >N·OR, $MeC{\cdot}CO$	2175	16,700	—	2270	16,800	8·5 [b]
	2250 *	14,500	—	2300	17,000	
$Ac_2N{\cdot}OR$	2130	15,200	—	2220	5400	—
Benzyloxyamine	2090	7200	—	—	—	—
	2580	203				
	2640	162				
N-Benzyloxybenzamide	<2050	>18,000	—	—	—	—
	2160 *	13,500				
NN'-Dibenzyloxy-α-dodecylglutaramide	2070	22,000	—	—	—	—
	2520	393				
	2580	507				
	2640	430				
	2680	283				
α : β : *N*-Trimethylmaleinimide	2230	16,600	—	—	—	—
	2280	16,700				

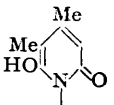
* Inflexion.

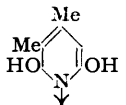
	95% Ethanol		0·1N-HCl		Alkali (pH 8·9)		
	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	pK_a
(III; R = CH_2Ph)	2440	8500	2565	6400	2400	7400	5·8 [c]
	3275	8900	3020	720	3240	12,900	
(I) or (X)	2400	5100	2165	11,400	3050	9100	5·05 [a]
	3130	7600	2600	4400	—	—	10·35
(II; R = Me)	2285	6900	2290	4100	2280	5400	—
	2925	7100	2910	6400	2915	6200	—
α : β : *N*-Trimethylglutaconimide	—	—	—	—	—	—	6·6 [b]

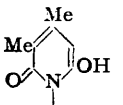
[a] In water. [b] In water–methanol (1 : 1). [c] In water–dimethylacetamide (1 : 1).

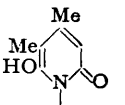
The former shows imide bands very close to those of the *N*-methyl-imide but the latter has no absorption maxima in that region, the spectrum closely resembling that of 6-methoxy-1 : 4-dimethylpyrid-2-one, and it is therefore formulated as (I) or (X). The alternative (XI) is not excluded by the infra-red spectrum but is considered unlikely (see p. 634).

The ultra-violet absorption spectra (Table 3) of most of the *N*-benzyloxy-compounds show the low-intensity absorption band at *ca.* 2600 Å, with fine structure, due to the benzyl group. *N*-Benzyloxymaleinamic acid and *N*-benzyloxymaleinimide, however, unexpectedly exhibit intense maxima at *ca.* 2800 Å, presumably owing to interaction between the two chromophores. *N*-Hydroxyglutaramic acid shows only low-intensity absorption above 2100 Å, but *N*-hydroxyglutarimide and α-dodecyl-*N*-hydroxyglutarimide have absorption maxima of high intensity at *ca.* 2150 Å. *N*-Hydroxysuccinimide and *NN*-diacetylhydroxylamine also absorb fairly strongly at this wave-length. It is suggested that this effect may be due to the presence of hydroxy-*N*-oxide (*e.g.*, IX) in equilibrium with the *N*-hydroxyimide form in solution. The absorption spectra indicate that the compound (III; R = CH_2Ph) is enolised in solution, probably giving an equilibrium mixture of (XII, *a* and *b*).


(X)


(XI)


(XII*a*)


(XII*b*)

The pK_a values (Table 3) show that the *N*-hydroxy- and *N*-benzyloxy-amides are acids of almost equal strength (pK_a *ca.* 10) but, with the exception of α-dodecyl-*N*-hydroxyglutarimide, the *N*-hydroxy-imides are much more strongly acidic (pK_a *ca.* 7); this also may be due to equilibrium with the hydroxy-*N*-oxide form. Of the two pK_a values of (I), the ionisation (pK_a 5·05) is evidently due to the phenolic-type hydroxyl group since the corresponding *N*-benzyloxy- (XII, *a* or *b*) and *N*-methyl compounds are similar; the *N*-hydroxy-group of (I; R = R′ = Me) is therefore only weakly acidic (pK_a 10·35) and of about the same strength as the aliphatic hydroxamic acids. The alternative structure (XI) is improbable as it cannot account for the large difference between the two pK_a values; its exclusion is also supported by analogy with *N*-hydroxypyrid-2-one (Shaw, *loc. cit.*).

Note added, 18.1.55.—Kauffman and Burger (*J. Org. Chem.*, 1954, **19**, 1662) have recently described the synthesis of *N*-nitrosuccinimide and the catalytic hydrogenation of the latter to give succinimide (only 2·01 mols. of hydrogen being absorbed). This result provides a striking contrast with the resistance of the above *N*-hydroxyimides to hydrogenolysis.

Experimental

2 : 6-*Dimethoxy*-4-*methylpyridine* N-*Oxide*.—The dimethoxypyridine (8·5 g.) was treated with perbenzoic acid (25% excess) in chloroform at 0°, almost all the perbenzoic acid being consumed in 18 hr. The mixture was washed with sodium hydrogen carbonate solution and water, and distilled to give some starting material and an oil, b. p. 76—80°/1—1·5 mm., which partly crystallised. Trituration with light petroleum (b. p. 40—60°) and recrystallisation from the same solvent yielded fine needles of the N-*oxide* (0·45 g.), m. p. 68—69° (Found : C, 56·2; H, 6·2; N, 8·6. $C_8H_{11}O_3N$ requires C, 56·8; H, 6·6; N, 8·3%).

The product (0·4 g.) was refluxed for 5 hr. with concentrated hydrochloric acid (10 c.c.), and the solution evaporated *in vacuo*; the only crystalline material isolated from the residual tar was ammonium chloride, evidently formed by decomposition.

2 : 6-*Dibromo*-4-*methylpyridine*.—Phosphorus tribromide (20 g.) was added to 2 : 6-dihydroxy-4-methylpyridine (6·0 g.), and the mixture heated (bath, 190—200°) for 7 hr. After cooling, the mass was poured into ice-water and steam-distilled, the crystalline dibromide (4·5 g.), m. p. 76·5—77·5°, being obtained from the distillate; ether-extraction of the distillate furnished more product (0·7 g.; total yield, 43%), m. p. 76—77°. Recrystallisation from water gave the pure dibromide, m. p. 87—79° (Bernstein, Stearns, Shaw, and Lott, *J. Amer. Chem. Soc.*, 1947, **69**, 1151, give m. p. 74—75°).

2 : 6-*Dibenzyloxy*-4-*methylpyridine*.—Potassium hydroxide (20 g.) was dissolved in benzyl alcohol (100 c.c.) at 150° and, after addition of xylene (35 c.c.), water was removed azeotropically by use of a Dean and Stark separator. The foregoing dibromide (16·2 g.) was added gradually, and the mixture refluxed (bath, 200—210°) for 1 hr. Addition of water, followed by ether-extraction and removal of solvents and benzyl alcohol *in vacuo*, yielded an oil which soon solidified. Recrystallisation from methanol furnished 2 : 6-*dibenzyloxy*-4-*methylpyridine* (14·6 g.)

which separated in clusters of prismatic needles, m. p. 55·5—56° (Found: C, 78·5; H, 6·3; N, 4·4. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·3; N, 4·6%).

The amine (1·5 g.) in ethanol (100 c.c.) was hydrogenated by means of 5% palladised strontium carbonate catalyst (0·5 g.); absorption ceased when 2 mols. had been taken up. Evaporation of the filtered solution gave 2 : 6-dihydroxy-4-methylpyridine (0·55 g.), m. p. and mixed m. p. 192—194°.

α : β : N-*Trimethylglutaconimide.*—αβ-Dimethylglutaconic acid (15·7 g.) and methylamine in ethanol (60 c.c.; 35%) were heated slowly to 160°, then rapidly to 220°, and finally heated with a free flame until the product began to distil. Vacuum-distillation gave a brown viscous oil (10 g.), b. p. 95—110°/1 mm., which soon crystallised. Repeated recrystallisation from benzene–light petroleum (b. p. 60—80°) containing a little acetic acid afforded the *imide* (2·8 g.), colourless plates, m. p. 91·5—92·5° (Found: C, 62·2; H, 6·9. $C_8H_{11}O_2N$ requires C, 62·7; H, 7·2%).

N-*Benzyloxy-αβ-dimethylglutaconimide.*—A mixture of αβ-dimethylglutaconic acid (1·0 g.), benzyloxyamine (Behrend and Leuchs, *Annalen*, 1890, **257**, 206) (0·8 g.), and xylene (10 c.c.) was refluxed for 45 min., water being removed by means of a reflux-head. On cooling, crystals, m. p. 124—125° (1·1 g.), separated; recrystallisation from xylene furnished the *benzyloxy-compound* in plates, m. p. 126—127° (Found: C, 68·6; H, 6·2; N, 5·9. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·2; N, 5·7%).

1 : 6(*or* 1 : 2)-*Dihydroxy*-3 : 4-*dimethylpyrid*-2(*or* 6)-*one.*—The foregoing benzyloxy-compound (13·5 g.) was suspended in ethanol (250 c.c.) and hydrogenated in the presence of 5% palladised strontium carbonate (1 g.) until absorption ceased (1·05 mols. taken up). After the mixture had been filtered at the b. p., the solution was concentrated and, on cooling, the crude product (6·5 g.), m. p. 155—157°, crystallised. The *hydroxamic acid* separated from methanol in plates, m. p. 157—158° (Found: C, 54·0; H, 5·8; N, 9·1. $C_7H_9O_3N$ requires C, 54·2; H, 5·9; N, 9·0%)

N-*Benzyloxysuccinamic Acid.*—Benzyloxyamine (6·3 g.) in benzene (20 c.c.) was added to a boiling solution of succinic anhydride (5·0 g.) in benzene (100 c.c.); the mixture was immediately cooled, and the resulting precipitate recrystallised from benzene–ethyl methyl ketone to give thin plates of the *acid* (7·6 g.), m. p. 95—96° (Found: C, 59·6; H, 5·7; N, 6·0%; equiv., 219. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·9; N, 6·3%; equiv., 223).

Similarly (but using the anhydride in cold benzene) were prepared N-*benzyloxyglutaramic*, plates (92% yield) (from benzene–chloroform), m. p. 85—85·5° (Found: C, 60·5; H, 6·2; N, 6·0. $C_{12}H_{15}ON$ requires C, 60·7; H, 6·5; N, 5·9%), and N-*benzyloxymaleinamic acid*, rods (95% yield) [from ethyl methyl ketone–light petroleum (b. p. 60—80°)], m. p. 121—122° (Found: C, 59·7; H, 4·9; N, 6·1. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0; N, 6·3%).

N-*Hydroxysuccinamic Acid.*—The benzyloxy-acid (4·3 g.) in ethyl methyl ketone was hydrogenated as above, yielding the acid (1·45 g.), which separated from ethyl methyl ketone in prisms, m. p. 105—106° (Found: C, 36·5; H, 5·6; N, 10·0. Calc. for $C_4H_7O_4N$: C, 36·1; H, 5·3; N, 10·5%). Errara (*Gazzetta*, 1895, **25**, II, 25) described the preparation of this *compound* from succinic anhydride and hydroxylamine in ethanol but did not report the m. p.

N-*Hydroxyglutaramic acid* (77% yield), obtained similarly, formed prismatic needles, m. p. 122—124°, from ethyl methyl ketone (Found: C, 41·0; H, 6·2; N, 9·7. $C_5H_9O_4N$ requires C, 40·8; H, 6·2; N, 9·5%).

N-*Benzyloxysuccinimide.*—Succinic anhydride (0·8 g.) and benzyloxyamine (1·0 g.) were heated for 30 min. (bath, 180°). On cooling, the mass solidified and recrystallisation from benzene yielded the *imide* (1·25 g.) as prismatic needles, m. p. 140—141° (Found: C, 64·5; H, 5·3; N, 6·7. $C_{11}H_{11}O_3N$ requires C, 64·4; H, 5·4; N, 6·8%).

The following were prepared similarly: N-*Benzyloxyglutarimide* (44%), prismatic needles (from ether–chloroform), m. p. 140—141° (Found: C, 65·3; H, 5·9; N, 6·3. $C_{12}H_{13}O_3N$ requires C, 65·7; H, 6·0; N, 6·4%). N-*Benzyloxy-α-dodecylglutarimide* (60%), needles [from light petroleum (b. p. 60—80°)], m. p. 69—70° (Found: C, 74·3; H, 9·8; N, 3·7. $C_{24}H_{37}O_3N$ requires C, 74·4; H, 9·6; N, 3·6%). N-*Benzyloxy-αβ-dimethylmaleinimide* (76%), plates, m. p. 87·5—89°, from light petroleum (b. p. 60—80°) (Found: C, 67·8; H, 5·5; N, 6·0. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·1%).

N-*Hydroxysuccinimide.*—Hydrogenation of the benzyloxyimide (5 g.) in ethyl methyl ketone (60 c.c.; dried over K_2CO_3) was carried out as in the previous example. The product crystallised from xylene–ethyl methyl ketone in plates, m. p. 94—95° (Found: C, 42·0; H, 4·4; N, 12·1. Calc. for $C_4H_5O_3N$: C, 41·7; H, 4·4; N, 12·2%). Dried solvents were used for the hydrogenation and recrystallisation since the substance is decomposed by warm water. [Errara (*loc. cit.*) probably obtained the same product by dehydration of *N*-hydroxysuccinamic

acid with sulphuric acid but did not give the m. p. Groth ("Chemische Krystallographie," 1910, **3**, 272) described the crystalline form and reported m. p. *ca.* 87° but gave no experimental details.] Treatment with acetic anhydride gave the acetyl derivative, m. p. 131—132°; Hurd, Buess, and Bauer (*J. Org. Chem.*, 1954, **19**, 1140) give m. p. 131°.

In the same manner were prepared *N-hydroxyglutarimide* (83%), fine needles, m. p. 108—109°, from xylene–ethyl methyl ketone (Found: C, 47·1; H, 5·6; N, 10·9. $C_5H_7O_3N$ requires C, 46·6; H, 5·5; N, 10·9%), and *α-dodecyl-N-hydroxyglutarimide* (95%), needles, m. p. 89—90°, from light petroleum (b. p. 60—80°) (Found: C, 69·0; H, 10·4; N, 4·9. $C_{17}H_{31}O_3N$ requires C, 68·6; H, 10·5; N, 4·7%).

N-Hydroxy-αβ-dimethylmaleinimide.—5% Palladised strontium carbonate (0·5 g.) was reduced with hydrogen, and the benzyloxy-imide (2·0 g.) was then added. Absorption almost ceased when 1 mol. of hydrogen had been taken up; evaporation of the filtered solution and crystallisation of the residue from benzene furnished *N-hydroxy-αβ-dimethylmaleinimide* (0·45 g.), plates, m. p. 126—127° (Found: C, 51·3; H, 5·1; N, 9·8. $C_6H_7O_3N$ requires C, 51·1; H, 5·0; N, 9·9%).

N-Hydroxy-meso-*αβ-dimethylsuccinimide.*—*N*-Benzyloxy-αβ-dimethylmaleinimide (7·0 g.) was hydrogenated in the presence of palladium oxide on strontium carbonate (1·0 g.; 5% of Pd); 2 mols. of hydrogen were rapidly absorbed. Isolated in the usual manner, the *imide* separated from ethyl methyl ketone–light petroleum (b. p. 60—80°) in rectangular plates, m. p. 71—72° (Found: C, 47·2; H, 6·3; N, 9·5. $C_6H_9O_3N,\frac{1}{2}H_2O$ requires C, 47·4; H, 6·6; N, 9·2%). The substance was hygroscopic; the analytical sample was dried at room temperature in a high vacuum.

α : β : *N-Trimethylmaleinimide.*—Xylene (25 c.c.) and methylamine in ethanol (1 c.c.; 32%) were added to αβ-dimethylmaleic anhydride (1·0 g.) dissolved in benzene (5·5 c.c.), and the mixture was refluxed until no more aqueous phase could be collected. Concentration to *ca.* 10 c.c., followed by vacuum-distillation, gave the *imide* (0·6 g.), b. p. 130—133°/60 mm., n_D^{20} 1·4896 (Found: C, 60·4; H, 6·7. $C_7H_9O_2N$ requires C, 60·4; H, 6·5%).

NN'-Dibenzyloxy-α-dodecylglutaramide.—α-Dodecylglutaric anhydride (10 g.) and benzyloxyamine (4·3 g.) were refluxed with xylene (50 c.c.) for 30 min. Evaporation under reduced pressure and repeated recrystallisation of the residue from benzene–light petroleum (b. p. 60—80°) furnished the *diamide* (3·4 g.), plates, m. p. 113—114° (Found: C, 72·8; H, 9·2; N, 5·6. $C_{21}H_{46}O_4N_2$ requires C, 72·9; H, 9·1; N, 5·5%).

N-Benzyloxymaleinimide.—A suspension of *N*-benzyloxymaleinamic acid (13 g.) in benzene (300 c.c.) was refluxed for 2·5 hr. with thionyl chloride (26 c.c.). The solution was stirred at 5—10° while pyridine (26 c.c.) was slowly added, and then for another 15 min. After addition of water (500 c.c.), the separated aqueous layer was extracted with ether; the combined organic layers were washed with sodium hydrogen carbonate solution and water and dried ($MgSO_4$). Evaporation and crystallisation from light petroleum (b. p. 60—80°) yielded the *imide* (9·1 g.), needles, m. p. 80—81° (Found: C, 65·4; H, 4·6; N, 6·7. $C_{11}H_9O_3N$ requires C, 65·0; H, 4·5; N, 6·9%).

NN-Diacetyl-O-benzylhydroxylamine.—*N*-Benzyloxymaleinamic acid (5 g.) was heated with acetic anhydride (50 c.c.) at 150° (b. p.) for 5 min. Evaporation *in vacuo* and crystallisation from light petroleum (b. p. 60—80°) afforded needles of the *imide* (3·35 g.), m. p. 101—102° (Found: C, 63·9; H, 6·1; N, 6·3; Ac, 43·6. $C_{11}H_{13}O_3N$ requires C, 63·8; H, 6·3; N, 6·8; Ac, 41·5%). The same product, m. p. and mixed m. p., was obtained directly from benzyloxyamine and acetic anhydride in the same manner.

NN-Diacetylhydroxylamine.—Catalytic hydrogenation of the foregoing benzyloxy-compound yielded the *hydroxy-imide*, needles, m. p. 88—88·5°, from benzene–light petroleum (b. p. 60—80°). On admixture with *ON*-diacetylhydroxylamine (Hantzsch, *Ber.*, 1892, **25**, 701), the m. p. was depressed to 63—67° (Found: C, 40·9; H, 5·9; N, 11·7. $C_4H_7O_3N$ requires C, 41·0; H, 6·0; N, 12·0%).

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RESEARCH DEPARTMENT, PARKE, DAVIS AND COMPANY, LTD.,
HOUNSLOW, MIDDLESEX.

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