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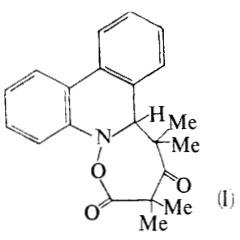
# Keten. Part V.[1] The Reaction of Dimethylketen with Heteroaromatic *N*-Oxides

By **R. N. Pratt** and **G. A. Taylor,*** Department of Chemistry, University of Sheffield

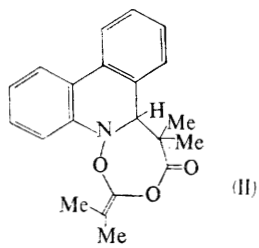
Phenanthridine *N*-oxide forms an adduct with two molecules of dimethylketen, which has been shown to be a phenanthridino[5,6-b][1,2]oxazepinedione (I). Isoquinoline *N*-oxide forms a similar adduct (VI). The reaction of phenanthridine *N*-oxide with dimethylketen in various solvents also produces phenanthridine and phenanthridone. Isoquinoline *N*-oxide reacts with dimethylketen in methanolic solution to form isoquinoline, 1-(1-methoxycarbonyl-1-methylethyl)-1,2-dihydro-2-isobutyrylisoquinoline (XVIII), and 2-methoxyisobutyric acid, the last compound indicating that deoxygenation occurs by formation of an α-lactone.

PREVIOUS studies of the reaction of dimethylketen with imines and heteroaromatic bases [2,3] have shown that cyclic adducts are frequently formed. Such adducts might, in principle, arise by reaction of a keten with any compound containing a nucleophilic centre associated with a suitable unsaturated system. It seemed to us that heteroaromatic *N*-oxides contained such a group, and we now report the results of an investigation of the reaction of dimethylketen with phenanthridine, isoquinoline, and quinoline *N*-oxides.

A suspension of phenanthridine *N*-oxide in ethyl acetate reacted with an excess of dimethylketen to give a low yield of an adduct, $C_{21}H_{21}NO_3$, formed from one molecule of the *N*-oxide and two of the keten, the spectroscopic properties of which were fully consistent with the structure (I).



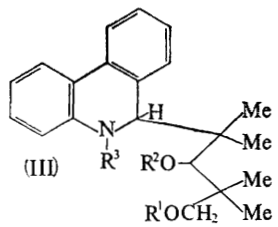

(I)




(II)

The n.m.r. spectrum of this adduct shows four methyl singlets between τ 8·2—9·2, eight aromatic protons, and singlet due to one proton at τ 5·6. This spectrum is also consistent with structure (II), which could arise by a reaction path analogous to that of heteroaromatic bases with dimethylketen.[3] However, the i.r. spectrum of the adduct shows strong absorption at 1791 and 1752 cm.$^{-1}$ indicating the presence of two carbonyl groups, one of which could be part of an *O*-acylhydroxylamine.[4] No such absorption would be expected of (II). The u.v. spectrum of the adduct is consistent with the presence of a 5,6-dihydrophenanthridine chromophore.

Reduction of the adduct with lithium aluminium hydride gave a compound $C_{21}H_{27}NO_2$, identified as (IIIa) by the n.m.r. and u.v. spectra.




(III)

(a) $R^1=R^2=R^3=H$
(b) $R^1=R^2=Ac$; $R^3=H$
(c) $R^1=R^3=Ac$; $R^2=H$

The mass spectrum of the compound confirms the structure assigned, showing a fragmentation pattern with prominent peaks corresponding to the loss of $CH_2OH$ and $Me_2CCH_2OH$. Acetylation of this reduction product gave a di-acetyl derivative, the i.r. spectrum of which contained a slightly broadened absorption at 1733 cm.$^{-1}$ but no absorption in the region 1600—1700 cm.$^{-1}$ clearly indicating that both hydroxy-groups had been acetylated, but not the amino-group. The u.v. spectrum of this di-acetyl derivative also supported structure (IIIb) showing absorption at 321 mμ, which is not observed in the spectra of 5-acyl-5,6-dihydrophenanthridines,[3] *e.g.* (IV). The mass spectrum confirms the structure (IIIb) as the fragmentation pattern showed

[1] Part IV, S. A. Procter and G. A. Taylor, *J. Chem. Soc.* (*C*), 1967, 1937.
[2] J. C. Martin, V. A. Hoyle, and K. C. Brannock, *Tetrahedron Letters*, 1965, 3589.
[3] R. N. Pratt, G. A. Taylor, and S. A. Procter, *J. Chem. Soc.* (*C*), 1967, 1569.
[4] O. Exner and B. Kakac, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2530 (*Chem. Abs.*, 1961, **55**, 3482).

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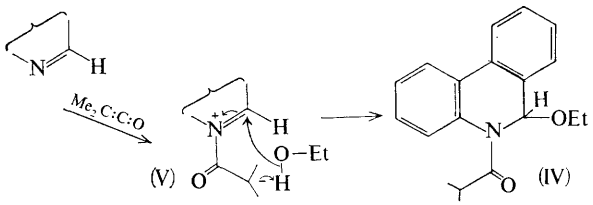
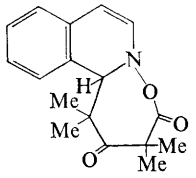
no significant peak at $(222)^+$ (*N*-acetylphenanthridium cation) but prominent peaks occur corresponding to the loss of $MeCO_2$, $MeCO_2CH_2$, $CH_3CO_2CH_2CMe_2$ and loss of the complete side chain. The final step in this process, for which a metastable peak is observed, corresponds to loss of $Me_2C{\cdot}CHOAc$, supporting the proposal that the secondary alcohol group had been acetylated. All attempts to obtain the tri-acetyl derivative of (IIIa) failed. It is remarkable that the very hindered secondary alcohol function in (IIIa) should be acylated in preference to the amino-function, as we have found that 5,6-dihydrophenanthridines normally acylate readily. It is possible that initially an *N*-acyl derivative (IIIc) is formed, that intramolecular transfer of an acetyl group occurs from the nitrogen atom onto the hindered hydroxy-group by way of a six-membered, cyclic transition state, and that subsequent re-acylation of the amino-group is then sterically hindered.

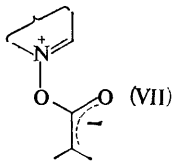
Reaction of dimethylketen with phenanthridine *N*-oxide in benzene gave a mixture of phenanthridine, phenanthridone, and the adduct (I). However, when the reaction was conducted in chloroform (laboratory reagent grade, containing ethanol), no adduct was obtained, the products being phenanthridine, phenanthridone, and a third compound, $C_{19}H_{21}NO_2$, which, on reduction with lithium aluminium hydride, gave 5,6-dihydrophenanthridine. This compound was identified as (IV), by its spectroscopic properties; the n.m.r. spectrum contained peaks characteristic of isobutyryl and ethoxy-groups, the u.v. spectrum showed no absorption below 300 mμ indicative of a 5-acyl-5,6-dihydrophenanthridine, and the i.r. spectrum showed strong absorption at 1669 cm.$^{-1}$. The mass spectrum also confirmed the structure (IV) showing loss of 45 (OEt) and 105 (OEt + $Me_2C{\cdot}CO$) mass units. We consider that this compound is formed by the reaction of dimethylketen with phenanthridine to form the zwitterion (V), which can react with ethanol in one or two steps. Attempts to increase the yield of (IV) or similar compounds by addition of more ethanol or methanol were unsuccessful; under these conditions phenanthridine and phenanthridone were the sole products of reaction.




The reaction of an excess of dimethylketen with isoquinoline *N*-oxide either as a solution in ethyl acetate or in suspension in benzene or ether gave a low yield of a 2 : 1 adduct, $C_{17}H_{19}NO_3$. This compound was unstable; in time the crystals went black, and solutions rapidly darkened. All attempts to degrade this compound by normal chemical means gave only red tars. The n.m.r. spectrum was fully consistent with the structure (VI), the i.r. spectrum showed strong absorption at 1795 and 1753 cm.$^{-1}$ and the u.v. spectrum was consistent



(VI)


(VII)

with the presence of a 1,2-dihydroisoquinoline chromophore. Confirmation of structure (VI) came from the similarity of the mass spectral fragmentation pattern of the adducts of the two *N*-oxides.

Attempts to prepare an adduct from quinoline *N*-oxide were inconclusive. The reaction of dimethylketen with quinoline *N*-oxide in benzene gave a yellow oil, from which no pure compound could be isolated. Attempted vacuum distillation caused decomposition, quinoline and 2-isopropylquinoline being isolated from the distillate. It is possible that the latter compound arises from pyrolytic decomposition of a labile cyclic adduct.

The formation of phenanthridone during the reaction might occur by either of two processes, starting from the zwitterion (VII), which is presumably an intermediate in the formation of (I). This zwitterion could be converted into 6-isobutyrylphenanthridine by way of a cyclic intermediate similar to that proposed for the formation of acridone in the reaction of acetic anhydride with acridine *N*-oxide,[5] with subsequent hydrolysis of the ester. Alternatively, (VII) might react directly with water, as in the conversion of pyridine *N*-oxide into pyridone.[6] The water required for these processes might be present in traces in the solvent, or produced during the preparation of the keten by pyrolysis of its dimer.

The formation of phenanthridine in the reaction of the *N*-oxide with dimethylketen must involve a deoxygenation, and such reactions are already known to occur with ketens. Staudinger has reported that the reaction of diphenylketen with dimethylaniline *N*-oxide gives an almost quantitative yield of dimethylaniline[7] along with benzophenone or a polymeric compound also obtained by the reaction of diphenylketen with oxygen, which, on hydrolysis, gives benzilic acid. More recently, Koenig showed that the kinetics of the reaction of pyridine *N*-oxide with diphenylketen were consistent with the initial production of a zwitterion (VIIIa) followed by formation of an α-lactone (IXa),[8] but he was unable to trap this intermediate. A species such as (IX) might either polymerise to (X), or react with more *N*-oxide, to give the ketone *via* the intermediate (XI), which is fully in accord with Staudinger's observation that, in the deoxygenation of dimethylaniline *N*-oxide, the production of benzophenone was only significant when the molar ratio of keten : *N*-oxide was 1 : 2.

[5] J. H. Markgraf and M. K. Ahn, *J. Amer. Chem. Soc.*, 1964, **86**, 2699.

[6] S. Oae and S. Kozuka, *Tetrahedron*, 1965, **21**, 1971.

[7] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 608.

[8] T. Koenig, *Tetrahedron Letters*, 1965, 3127.

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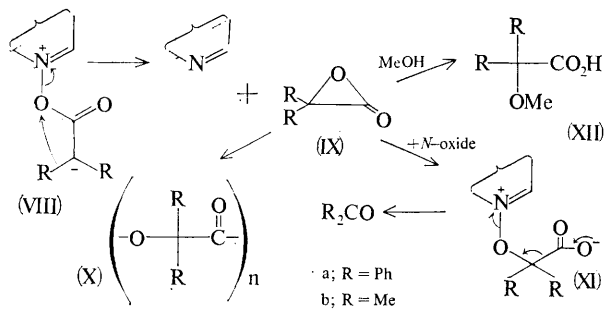
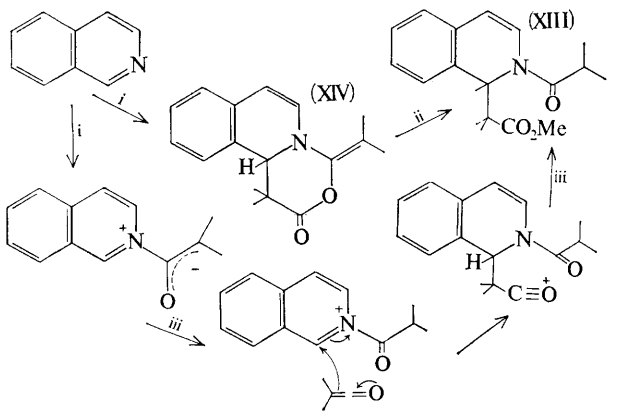
α-Lactones have been proposed as intermediates in the alcoholysis of α-halocarboxylate anions,[9] and also in the decomposition of di-t-butylperoxymalonic esters.[10,11]




In the latter case attempts to demonstrate their formation were inconclusive.[10] Attempts to trap the α-lactone (IXb) formed by deoxygenation of phenanthridine *N*-oxide were unsuccessful, as phenanthridine *N*-oxide in methanol solution failed to react with dimethylketen. It is conceivable that the *N*-oxide behaves as a nucleophilic catalyst for the reaction of dimethylketen with methanol. However, treatment of a methanol solution of isoquinoline *N*-oxide with dimethylketen gave isoquinoline, 2-methoxyisobutyric acid (XIIb), and a compound identified as (XIII), which could also be obtained by the reaction of dimethylketen with a solution of isoquinoline in methanol. The formation of (XIIb) is a clear indication that α-lactones are formed in the deoxygenation, and it is immaterial whether the acid arises directly from the free α-lactone (IXb) or the polyester (Xb).[10]




SCHEME
Reagents: i, $Me_2C{:}C{:}O$; ii, MeOH–$H^+$; iii, MeOH

The formation of (XIII) in this reaction raises an interesting mechanistic problem. In aprotic solvents isoquinoline gives the adduct (XIV), which on acid-catalysed methanolysis gives the ester (XIII).[3] However (XIV), which is not detectable in the product of reaction of isoquinoline *N*-oxide with dimethylketen in methanol, is not converted into (XIII) under the reaction conditions, and can be recrystallized from neutral methanol without appreciable loss. We propose that direct formation of (XIII) may occur by an alternative path, outlined in the Scheme, in which an acylisoquinolinium ion is subject to nucleophilic attack by a keten molecule. Ketens are known to act as nucleophiles, *e.g.* in their reaction with acyl chloride [12] or trityl chloride,[13] but reaction with such weak electrophiles as heteroaromatic cations has not been reported hitherto.

## EXPERIMENTAL

N.m.r. spectra were measured in deuteriochloroform with a Varian A60 spectrometer, i.r. spectra with a Unicam SP 100 spectrometer, and mass spectra with an A.E.I. MS9 mass spectrometer.

Dimethylketen was prepared by the pyrolysis of tetramethylcyclobutan-1,3-dione in a modified version of Johnson and Witzel's apparatus [14] and used without further purification.

*The Reaction of Phenanthridine* N-*Oxide with Dimethylketen.* (*a*) Dimethylketen (*ca.* 2 g.) was passed into a suspension of phenanthridine *N*-oxide (1·2 g.) in dry ethyl acetate (180 ml.) and the solution was set aside for 3 days. Evaporation of the solvent and addition of light petroleum (40 ml.) deposited a gummy solid, which, after recyrstallisation from light petroleum gave 2,3,4,5-*tetrahydro*-3,3,5,5-*tetramethyl*-5α*H*-*phenanthridino*[5,6-b][1,2]*oxazepine*-2,4-*dione* (I) as pale yellow prisms (0·33 g., 16%), m.p. 154° (Found: C, 75·0; H, 6·2; N, 4·1. $C_{21}H_{21}NO_3$ requires C, 75·2; H, 6·3; N, 4·2%), $\lambda_{max.}$ (ethanol) 254, 282, and 328 mμ (log ε 4·31, 3·68, and 3·50), $\nu_{max.}$ (KBr disc) 1791 and 1752 cm.$^{-1}$, τ 2·0—3·1 (8H, m), 5·62 (1H, s), 8·23 (3H, s), 8·60 (3H, s), 8·63 (3H, s), and 9·17 (3H, s), mass spectrum: *m/e* 335 (24%), 307 (1), 266 (48), 221 (48), 220 (33), 207 (14), 191 (9), 180 (100), and 179 (66), *m** 281·3 (335 ⟶ 307), 219 (221 ⟶ 220), and 178 (180 ⟶ 179).

(*b*) Repetition of the above reaction, using benzene as solvent gave phenanthridine, phenanthridone, and the adduct (I), which were identified by t.l.c.

(*c*) Dimethylketen (*ca.* 2 g.) was passed into a solution of phenanthridine *N*-oxide (2·89 g.) in chloroform (150 ml.; laboratory reagent grade) and the solution was set aside overnight. A colourless precipitate, which formed, was collected and identified as phenanthridone by a mixed m.p. determination. Evaporation of the chloroform solution and addition of dry ether deposited more phenanthridone (total 0·73 g., 25%). Evaporation of the ether solution and addition of light petroleum gave pink crystals, which, on recrystallisation from ethanol gave 6-*ethoxy*-5-*isobutyryl*-5,6-*dihydrophenanthridine* (IV) as needles (0·53 g., 12%), m.p. 170° (Found: C, 77·5; H, 7·3; N, 4·7. $C_{19}H_{21}NO_2$ requires C, 77·3; H, 7·1; N, 4·7%), $\lambda_{max.}$ (ethanol) 245 and 271 mμ (log ε 4·32 and 4·12), $\nu_{max.}$ (KBr disc) 1659 cm.$^{-1}$, τ 2·0—3·0 (8H, m), 3·34 (1H, s), 6·32 (2H, quartet, *J* 7 c./sec.),

[9] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 841.
[10] P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, 1963, **85**, 1864.
[11] L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, 1966, **31**, 3821.
[12] J. Beranek, J. Smrt, and F. Sorm, *Chem. Listy*, 1954, **48**, 679; 1955, **49**, 73 (*Chem. Abs.*, 1955, **49**, 9545, 15773).
[13] A. T. Blomquist, R. W. Holley, and O. J. Sweeting, *J. Amer. Chem. Soc.*, 1947, **69**, 2356.
[14] J. R. Johnson and J. M. Witzel, *Org. Reactions*, 1946, **3**, 136.

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6·78 (1H, septet, $J$ 6·5 c./sec.), 8·73 (3H, d, $J$ 6·5 c./sec.), 8·92 (3H, t, $J$ 7 c./sec.), and 9·20 (3H, d, $J$ 6·5 c./sec.), mass spectrum: *m/e* 295 (5%), 250 (15), 196 (6), 180 (100), 179 (76), 152 (23), 151 (19), 71 (11), and 43 (48), *m** 211·8 (295 ⟶ 250), 129·6 (250 ⟶ 180).

The solution in light petroleum was evaporated, ether (100 ml.) was added, and the solution was extracted with hydrochloric acid. From the acidic extract, phenanthridine (0·5 g., 19%) was isolated and identified by a mixed m.p. determination.

(*d*) Treatment of a solution of phenanthridine *N*-oxide in mixtures of chloroform and ethanol or methanol (10% by vol. of the alcohol) with excess of dimethylketen gave only phenanthridine and phenanthridone along with unchanged *N*-oxide.

(*e*) A solution of phenanthridine *N*-oxide in methanol was treated with excess dimethylketen and set aside overnight. From the mixture unchanged *N*-oxide (99%) was subsequently recovered.

*Lithium Aluminium Hydride Reduction of the Adduct* (I).—To a solution of lithium aluminium hydride (0·5 g.) in ether (150 ml.) was added the adduct (I) (0·3 g.), and the mixture was then boiled under reflux overnight. After decomposition of the excess of hydride, the ether solution was dried ($Na_2SO_4$) and evaporated. Recrystallisation of the residue from light petroleum gave 6-(2,4-*dihydroxy*-1,1,3,3-*tetramethylbutyl*)-5,6-*dihydrophenanthridine* (IIIa) as needles (0·19 g., 65%), m.p. 122° (Found: C, 77·7; H, 8·2; N, 4·5. $C_{21}H_{27}NO_2$ requires C, 77·5; H, 8·3; N, 4·3%), $\lambda_{max.}$ (ethanol) 255, 275s, and 318 mμ (log ε 4·31, 3·96, and 3·47), τ 2·1—3·0 (8H, m), 5·3—5·7 (2H, broad signal, disappearing after treatment with $D_2O$), 5·57 (1H, s), 6·1—6·8 (4H, complex band, 1H removed after treatment with $D_2O$), 9·16 (9H, s), and 9·85 (3H, s), mass spectrum: *m/e* 325 (0·1%), 294 (2), 252 (24), 180 (100), 179 (5), *m** 128·6 (252 ⟶ 180).

*Acetylation of the Diol* (IIIa).—A mixture of the diol (IIIa) (0·12 g.), ether (150 ml.), pyridine (5 ml.), and acetyl chloride (5 ml.), was set aside overnight. The mixture was then washed with water, dried, and evaporated. Recrystallisation of the residue from light petroleum gave 6-(2,4-*diacetoxy*-1,1,3,3-*tetramethylbutyl*)-5,6-*dihydrophenanthridine* (IIIb) as prisms (0·13 g., 86%) m.p. 113—114° (Found: C, 73·4; H, 7·5; N, 3·4. $C_{25}H_{31}NO_4$ requires C, 73·4; H, 7·6; N, 3·4%), $\lambda_{max.}$ (ethanol) 255, 274, and 321 mμ (log ε 4·33, 3·91, and 3·43), $\nu_{max.}$ (KBr disc) 1733 cm.$^{-1}$, τ 2·1—3·0 (8H, m), 5·63 (1H, s), 5·95 and 6·23 (2H, AB quartet, $J$ 10·5 c./sec.), 6·14 (1H, s), 6·2 (1H, broad signal, NH), 7·92 (3H, s), 8·08 (3H, s), 8·95 (3H, s), 9·01 (3H, s), 9·33 (3H, s), and 9·54 (3H, s), mass spectrum: *m/e* 409 (0·1%), 350 (0·4), 336 (1), 294 (37), 234 (5), 220 (2), 180 (100), 179 (12), 152 (4), 115 (41), 43 (68), *m** 110·2 (294 ⟶ 180), 45 (294 ⟶ 115).

*Lithium Aluminium Hydride Reduction of* (IV).—To a solution of lithium aluminium hydride (0·3 g.) in ether (100 ml.) was added (IV) (90 mg.), and the mixture was then boiled under reflux for 18 hr. The excess of hydride was decomposed by cautious addition of water and the ether solution was filtered, dried, and evaporated. Recrystallisation of the residue from light petroleum gave 5,6-dihydrophenanthridine as needles, m.p. and mixed m.p. 122°.

*The Reaction of Dimethylketen with Isoquinoline N-Oxide.*—(*a*) Dimethylketen (*ca.* 11 g.) was passed into a solution of isoquinoline *N*-oxide hemihydrate (11 g.) in ethyl acetate (450 ml.) and the solution was set aside for six days. Evaporation of the solution and addition of ether (100 ml.) to the residue deposited a solid, which on recrystallisation from ether gave 1,2,3,4-*tetrahydro*-1,1,3,3-*tetramethyl*-11bH-*isoquinolino*[2,1-b][1,2]*oxazepine*-2,4-*dione* (VI) as prisms (4·3 g., 20%), m.p. 139° (decomp.) (Found: C, 71·3; H, 6·4; N, 5·0. $C_{17}H_{19}NO_3$ requires C, 71·6; H, 6·7; N, 4·9%), $\lambda_{max.}$ (ethanol) 236 and 314 mμ (log ε 3·99 and 3·88), $\nu_{max.}$ (KBr disc) 1795 and 1753 cm.$^{-1}$, τ 2·7—3·3 (4H, m), 3·83 (1H, quartet, $J$ 1·5, 7·5 c./sec.), 4·46 (1H, d), $J$ 7·5 c./sec.) 5·39 (1H, narrow unresolved multiplet), 8·38 (3H, s), 8·55 (3H, s), 8·68 (3H, s), and 8·87 (3H, s), mass spectrum: *m/e* 285 (9%), 257 (0·5), 216 (54), 171 (68), 170 (40), 157 (8), 156 (8), 141 (10), 130 (100), 129 (38), 128 (13), 115 (15), 103 (13), 102 (13), 77 (15), 70 (80), *m** 231·7 (285 ⟶ 257), 163·8 (285 ⟶ 216), 99·4 (170 ⟶ 130), 78·2 (216 ⟶ 130), and 58·4 (285 ⟶ 129).

(*b*) The dione (VI) was also obtained from the reaction of dimethylketen with isoquinoline *N*-oxide hemihydrate in ether (yield 6%), and benzene (yield 22%).

(*c*) Dimethylketen (*ca.* 2·4 g.) was passed into a solution of isoquinoline *N*-oxide hemihydrate (4·5 g.) in methanol (180 ml.) and the mixture was set aside overnight. The solution was then evaporated and the residue was heated at 100° for 1 hr. with aqueous sodium hydroxide (100 ml., 3%). The mixture was cooled, extracted with chloroform, and the organic layer was dried ($K_2CO_3$) and evaporated. Addition of ether (100 ml.) to the residue deposited unchanged *N*-oxide (1·5 g., 33%). The ether solution was evaporated and the residue was shaken with light petroleum (30 ml., b.p. 60—80°) when the ester (XIII) (1·43 g., 15%) was deposited and identified by a mixed m.p. determination with an authentic specimen.[3] From the residual petroleum solution, isoquinoline was isolated as the picrate (0·97 g., 9%) and identified by a mixed m.p. determination.

The aqueous layer from the chloroform extraction was acidified with dilute hydrochloric acid and extracted with ether (5 × 30 ml.). The ether extract was dried and evaporated to leave an oil, which, on distillation, gave 2-methoxyisobutyric acid (0·46 g., 17% based on the keten used), b.p. 120—130°/35 mm. identified by comparison of its *S*-benzylthiuronium salt with an authentic specimen.

(*d*) Treatment of a methanol solution of isoquinoline *N*-oxide hemihydrate with a large excess of dimethylketen gave the ester (XIII) (32%) b.p. 138—140°/0·07 mm., m.p. 115—116° (lit.,[3] 115—116°).

*The Reaction of Dimethylketen with Isoquinoline.*—(*a*) Treatment of a solution of isoquinoline in methanol with an excess of dimethylketen followed by work up in the usual way gave the ester (XIII) (40%) m.p. and mixed m.p. 114—115°.

(*b*) A solution of the adduct (XIV) in 5% aqueous methanol was treated with an excess of dimethylketen, and the mixture was set aside overnight. Examination of the solution by t.l.c. showed no trace of the ester (XIII) and much unchanged adduct. (The authors thank Mr. D. P. Stokes for this experiment.)

2-*Methoxyisobutyric Acid* (XIIb).—2-Bromoisobutyryl bromide (15 g.) was added slowly to methanol (100 ml.) and the solution was set aside for ½ hr. and then evaporated. The residue was added slowly to a solution of sodium methoxide in methanol, and the mixture was boiled under reflux for 2 hr. The solution was evaporated, and the residue boiled under reflux with aqueous sodium hydroxide (100 ml., 10%) for 2 hr. The resulting solution was ex-

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tracted with ether and the ethereal extract was discarded. Acidification of the aqueous layer followed by extraction with ether (3 × 100 ml.), drying, and evaporation of the ether solution gave a colourless liquid which on distillation afforded 2-methoxyisobutyric acid (3·9 g., 51%) b.p. 124—125°/35 mm. (lit.,[16] 98—99°/20 mm.), $\tau$ ($CCl_4$) −1·07 (1H, s), 6·72 (3H, s) and 8·58 (6H, s). With time, the acid slowly polymerised to a waxy solid.

The S-*benzylthiuronium salt* was prepared in the usual manner. Recrystallisation from ethanol gave plates, m.p. 155° (Found: C, 55·1; H, 6·8; N, 9·7. $C_{13}H_{20}N_2O_3S$ requires C, 54·9; H, 7·0; N, 9·9%).

*The Reaction of Dimethylketen with Quinoline* N-*Oxide*.—Dimethylketen (*ca.* 5 g.) was passed into a solution of freshly distilled quinoline *N*-oxide (4·5 g.) in benzene and the solution was set aside overnight. Evaporation left a dark oil from which no crystalline material could be isolated. Vacuum distillation gave a colourless oil b.p. 40—90°/0·05 mm. Separation of the basic components of this oil by the usual techniques gave a pale yellow liquid (0·5 g.), which, on addition of an ethanolic solution of picric acid deposited yellow needles of quinoline picrate (0·35 g.) m.p. and mixed m.p. 201°. After a prolonged period a further crop of yellow needles (0·6 g.), m.p. 154° (from ethanol), was deposited and identified as 2-isopropylquinoline picrate (lit.,[15] m.p. 155—157°) (from the n.m.r. spectrum of the free base: $\tau$ 6·78 (1H, septet, $J$ 7 c./sec.), 8·65 (d, 6H, $J$ 7 c./sec.).

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