TABLE I

OXIDATION OF 1-PHENYLETHANOL WITH PHENYL *N*-BROMOKETIMINE[a]

Alcohol, mmol	Bromoimine, mmol	Temp, °C	Inhibitor, mol %[b]	Yield of acetophenone, % (time)
0.49	0.98	80	None	94 (2 min)
0.49	0.98	80	Chloranil, 5	70 (2 min), 94 (4 min)
0.49	0.98	15	None	71 (15 min), 98 (30 min)
0.98	0.98	15	Chloranil, 5	41 (20 min), 80 (35 min)
0.49	0.98	15	Norbornene, 2	0 (80 min)
0.98	0.49	15	Light excluded	0 (30 min)
0.98	0.49	80	None	52[c]
2.45	0.49	80	None	21[c]

[a] All reactions were carried out in 3.0 ml of benzene at the indicated temperatures. Continuous stirring was accomplished with a magnetic stirring bar and except for the one experiment where light was excluded all reactions were under sunlamp irradiation, G.E. sunlamp at 6 in. [b] Based on bromoimine initially present. [c] Maximum accumulation of acetophenone. Yield is based on amount of alcohol initially present.

action. Evidence for the dissociation of **1** as shown in the first step and for its reaction with HBr as shown in the third step has been reported earlier.[2]

$$(C_6H_5)_2C{=}NBr \xrightarrow[\text{or } \Delta]{h\nu} (C_6H_5)_2C{=}N\cdot + Br\cdot$$

1

$$Br\cdot + {>}CHOH \longrightarrow \cdot{>}COH + HBr$$

$$HBr + \mathbf{1} \longrightarrow (C_6H_5)_2C{=}NH + Br_2$$

$$\cdot{>}COH + Br_2 \longrightarrow \begin{matrix} OH \\ | \\ C \\ | \\ Br \end{matrix} + Br\cdot$$

$$\begin{matrix} OH \\ | \\ C \\ | \\ Br \end{matrix} \longrightarrow {>}C{=}O + HBr$$

$$HBr + (C_6H_5)_2C{=}NH \longrightarrow (C_6H_5)_2C{=}NH_2^+\ Br^-\downarrow$$

Although the scope of possible oxidations with **1** has not been fully investigated, the results reported here suggest that this compound may be a very useful reagent for oxidations which need to be carried out under mild conditions. It offers certain advantages over other *N*-halo compounds in that it is extremely soluble in common organic solvents and it shows no tendency to add to olefins.[8]

Experimental Section[9]

Phenyl *N*-bromoketimine (1) was prepared from benzophenone imine hydrochloride and bromine in aqueous sodium carbonate solution.[10] The product thus obtained was crystalline, mp 34–35° (lit.[10] mp 37°), and shown to be 99.9% pure by titration for the active bromine.

Reactions of 1 with Alcohols.—All alcohols (benzhydrol, benzyl alcohol, 1-phenylethanol, 2-propanol, 2-butanol, and cyclohexanol) were purified by recrystallization or distillation prior to use and checked for the absence of the corresponding aldehyde or ketone by ir and glpc. All reactions were carried out in refluxing benzene using a 2:1 ratio of *N*-bromoimine to alcohol. The mixtures were stirred throughout the reaction and irradiated with a G.E. sun lamp from a distance of about 6 in. Aliquots were withdrawn at intervals and thermally quenched. Qualitative analyses of reaction progress were made by ir spectroscopy but quantitative analyses were made using glpc in the following manner. A series of standard solutions containing known amounts of starting alcohol and anticipated oxidation product was made up in benzene for each reaction. These solutions were then analyzed by glpc and peak area ratios were plotted against the concentration of oxidation product. The resulting working curves were used to determine percentage composition of reaction mixtures. Identification of peaks corresponding to the alcohols and oxidation product was accomplished by comparing the glpc retention volumes with the retention volumes of authentic samples on the same column.

This general procedure was used to acquire the results shown in Table I except the molar ratio of alcohol to imine was varied, the temperature was varied, and inhibitors were sometimes added.

Reaction of Bromine with 1-Phenylethanol.—A solution of 0.059 g (0.49 mmol) 1-phenylethanol in 3 ml of benzene was irradiated with a sun lamp while the temperature was maintained at 25–30°. Bromine was added at the rate of 1 drop every 15 sec until the pale yellow color produced by a drop of bromine did not disappear. At this point an aliquot of the mixture was withdrawn for analysis by glpc for percentage conversion of alcohol to ketone. The mixture was found to contain 0% alcohol and 100% acetophenone (based on initial alcohol concentration).

Registry No.—**1**, 7699-75-4; 1-phenylethanol, 98-85-1.

(8) C. G. McCarty and C. G. Leeper, unpublished results.

(9) Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer and a Beckman Model IR-8 spectrophotometer. A Micro-Tek GC-2503R gas chromatograph equipped with a Sargent GC recorder and Disc integrator was used for all glpc analyses.

(10) W. Theilacker and K. Fauser, *Justus Liebigs Ann. Chem.*, **539**, 103 (1939).

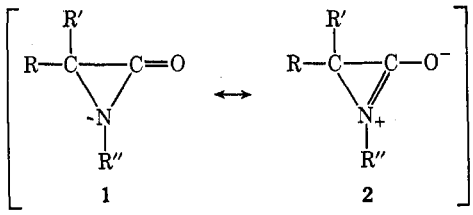
α-Lactams. VIII.[1,2] *O*-Alkylation of α-Lactams

JOHN C. SHEEHAN[3] AND M. MEHDI NAFISSI-V

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received December 29, 1969

In an earlier report[4] on the photochemistry of α-lactams **1**, a dipolar resonance form **2** was proposed in



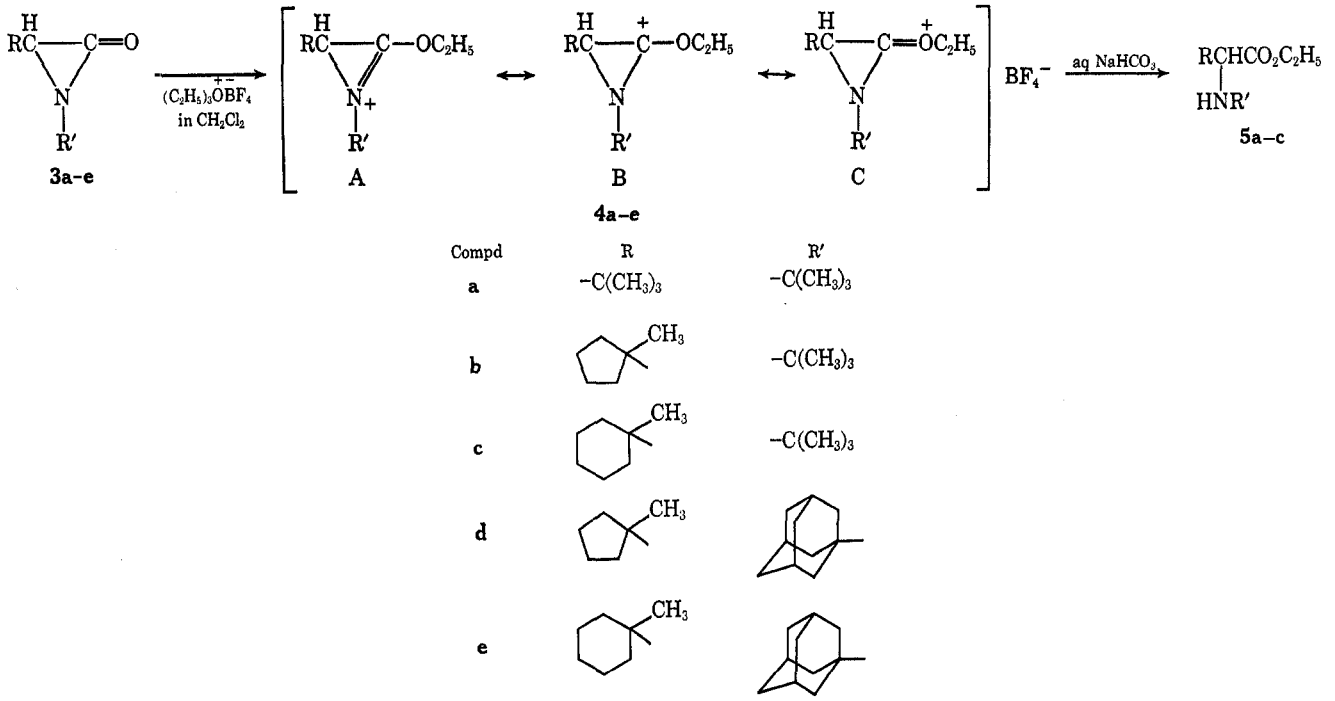
(1) α-Lactams. VII: J. C. Sheehan and M. M. Nafissi-V, *J. Amer. Chem. Soc.*, **91**, 4596 (1969).

(2) Taken in part from the Ph.D. Thesis of M. M. N. V., Massachusetts Institute of Technology, Aug 1969.

(3) To whom inquiries concerning this paper should be addressed.

(4) J. C. Sheehan and M. M. Nafissi-V., *J. Amer. Chem. Soc.*, **91**, 1176 (1969).

SCHEME I



order to explain the ultraviolet absorption at 250 mμ of this class of compounds. As a test for the reactivity of the carbonyl group in this class of compounds, five α-lactams were treated with triethyloxonium fluoroborate.

The alkylation of amides, larger lactams, and other carbonyl compounds at the oxygen atom of the carbonyl group by trialkyloxonium fluoroborate has been reported by Meerwein and his coworkers.[5-7] Kornblum and Coffey[8,9] obtained oxygen ethylation as well as nitrogen ethylation when α-pyridones were treated with triethyloxonium fluoroborate. The *O*-alkylation of amides by the oxonium salt was also reported by Weintraub, Oles, and Kalish.[10]

The structural similarity between α-lactams and amides suggests that α-lactams should also undergo *O*-alkylation when they are allowed to react with trialkyloxonium fluoroborate. The *N*-alkylation observed with α-pyridones was not significant in the case of di-*tert*-alkyl aziridinones, probably because of steric hindrance. Thus, when 1,3-di-*tert*-butylaziridinone (**3a**) was allowed to react with triethyloxonium fluoroborate in methylene chloride, the ir carbonyl absorption of α-lactam at 1835 cm^{-1} was completely replaced by a new absorption at 1670 cm^{-1}. This latter absorption band was assigned to [C=N$^+$ ↔ C$^+$—N] stretching and an azirinium salt **4** structure was proposed for this intermediate. Thus, the low ir absorption of C=N stretching in salt **4**, compared to that of azirine,[11] was attributed to the delocalization of π electrons as represented by three canonical structures A, B, and C.[12]

Evaporation of the solvent from the mixture gave a very hygroscopic solid which could not be purified for further characterization. It was treated with aqueous sodium bicarbonate solution to give ethyl 2-(*N*-*tert*-butylamino)-3,3-dimethylbutyrate **5a** (Scheme I). Compound **5a** was obtained as a colorless oil, the microanalytical data, infrared, nmr and mass spectra of which were consistent with the assigned structure (Table I).

TABLE I

SPECTRAL PROPERTIES AND ANALYTICAL DATA OF COMPOUNDS **5a-e**[a]

Compd 5	Infrared (film), cm^{-1}	Nmr ($CDCl_3$), R and R′, -CH(NHR′)	δ, ppm NH, $-CH_2-$, $-CH_3$
a	3425, 1735, 1225	0.98, 1.2, 3.1	1.7, 4.05, 1.08
b	3410, 1730, 1225	1.6, 1, 1.38, 3.12	2.1, 4.15, 1.18
c	3415, 1733, 1225	1.56, 1, 1.14, 3.18	2.2, 4.2, 1.18
d	3420, 1735, 1225	2–1.65, 1, 3.15	2.25, 4.1, 1.18
e	3425, 1730, 1225	2–1.4, 0.98, 3.10	2.2, 4.0, 1.02

[a] Satisfactory analytical values (±0.35% for C, H, and N) were reported for compounds **5a-e**, Ed.

Similar results were obtained when 1-*tert*-butyl-3-(1-methylcyclopentyl)aziridinone (**3b**), 1-*tert*-butyl-3-(1-methylcyclohexyl)aziridinone (**3c**), 1-(1-adamantyl)-3-(1-methylcyclopentyl)aziridinone (**3d**), and 1-(1-adamantyl)-3-(1-methylcyclohexyl)aziridinone (**3e**) were treated with triethyloxonium fluoroborate (Scheme I). The results are summarized in Table I. All of the *O*-alkylation reactions were carried out in a drybox at nearly zero humidity.

The alkylation of α-lactams on the carbonyl–oxygen atom by oxonium salts has not been reported previously, and it was found to be a general reaction for this class of compounds. This process can be considered as a new method to achieve the synthesis of the esters of N-substituted amino acids.

(5) H. Meerwein, E. Bhattenberg, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939).
(6) H. Meerwein, *et al.*, *Chem. Ber.*, **89**, 2060 (1956).
(7) H. Meerwein, W. Florian, N. Schon, and G. Stopp, *Justus Liebigs Ann. Chem.*, **641**, 1 (1961).
(8) N. Kornblum and G. P. Coffey, *J. Org. Chem.*, **31**, 3447 (1966).
(9) N. Kornblum and G. P. Coffey, *ibid.*, **31**, 3449 (1966).
(10) L. Weintraub, S. R. Oles, and N. Kalish, *ibid.*, **33**, 1679 (1968).
(11) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968).
(12) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, pp 282–284.

Experimental Section[13]

The following general procedure is representative for this reaction. To a stirred solution of 1,3-di-*tert*-butylaziridinone (**3a**),[14] 553.5 mg (3.35 mmol), in methylene chloride was added a molar solution of triethyloxonium fluoroborate[15] in methylene chloride (3.5 ml) in a drybox. After 4 hr of stirring at room temperature, the solvent was removed by evaporation at low pressure to give a hygroscopic solid, infrared (Nujol) 1670, 1250, and 1150–1020 cm^{-1}. The residue was treated with a 5% aqueous sodium bicarbonate solution and extracted with a diethyl ether, 4 × 15 ml. The combined ether extract was dried over anhydrous magnesium sulfate and the ether was evaporated to give 540 mg of ethyl 2-*N*-*tert*-butylamino-3,3-dimethylbutyrate (**5a**): infrared (film) 3425, 1735, and 1225 cm^{-1}; nmr ($CDCl_3$) δ 4.05 (quartet, 2 H), 3.1 (quartet, 1 H), 1.7 (broad, 1 H), 1.2 (singlet, 9 H), 1.08 (triplet, 3 H), and 0.98 ppm (singlet, 9 H). *Anal.* Calcd for $C_{12}H_{25}NO_2$: C, 66.93; H, 11.70; N, 6.50. Found: C, 66.74; H, 11.63; N, 6.38.

Registry No.—**5a**, 26153-99-1; **5b**, 26154-00-7; **5c**, 26154-01-8; **5d**, 26154-02-9; **5e**, 26154-03-0.

Acknowledgment.—This research was supported in part by Sloan Basic Research account 27609, and one of us (M. M. N. V.) is grateful to the Schering Corporation of Bloomfield, N. J., for a E. B. Hershberg Fellowship.

(13) The infrared spectra were obtained on a Perkin-Elmer 237 spectrophotometer, and nmr spectra were recorded on a Varian A-60 and/or T-60 spectrometer. The mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Microanalyses were performed at the Microanalytical Laboratory of the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., and/or by Galbraith Laboratories, Inc., Knoxville, Tenn.

(14) J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, **89**, 292 (1967).

(15) H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

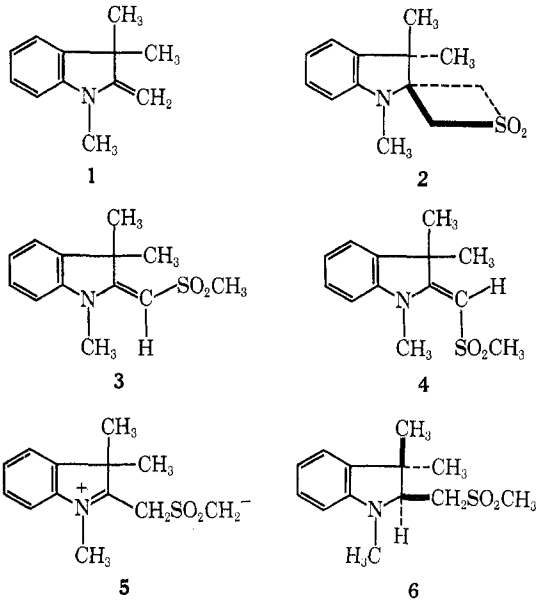
Reactions of 1,3,3-Trimethyl-2-methyleneindoline (Fischer's Base) with Sulfonyl Chlorides[1]

K. NAGARAJAN* AND S. R. MEHTA

CIBA Research Centre, Bombay 63, India

Received February 12, 1970

Among the reported enamine reactions of Fischer's Base [2–4] (**1**), there is no mention of its behavior toward organic sulfonyl chlorides.[5] We find that the reaction of methane sulfonyl chloride with Fischer's Base affords in about 50% yield, a mixture of two isomeric products in the ratio of approximately 2:1. The major part, mp 139–141°, was recognized as the cycloaddition product of methylene sulfene[6] to **1**. The ir spectrum of **2** had bands at 1145 and 1320 cm^{-1} for the SO_2 group.[7] The uv spectrum had maxima at 257 nm (log ϵ 3.97) and 297 (3.46) and was characteristic of an indoline.[8] The 60-Mc nmr spectrum of **2** in $CDCl_3$ showed signals at 1.33 [singlet, 6 H, $C(CH_3)_2$], 2.95 (singlet, 3 H, NCH_3), and 4.28 ppm (center of a complex A_2B_2 multiplet for 4 H from two CH_2 groups) and the four aromatic protons as multiplets from 6.5 to 7.3 ppm.



The minor product, mp 120–121°, was identified as the methanesulfonyl derivative **3**. Its ir spectrum showed, in addition to the bands due to the SO_2 group at 1130 and 1300 cm^{-1}, strong absorption for C=C at 1550 cm^{-1}.[9] Its uv spectrum, with maxima at 220 nm (log ϵ 4.33) and 292 (4.43), indicated that the indoline chromophore was distorted. The nmr spectrum of a fresh solution of **3** in DMSO-d_6 showed signals at 1.67 [singlet, 6 H, $C(CH_3)_2$], 3.07 (singlet, 3 H, $-SO_2CH_3$), 3.15 (singlet, 3 H, $-NCH_3$), and 5.33 ppm (singlet, 1 H, =CH), besides 4 aromatic proton signals spread between 6.7 and 7.4 ppm. The C–CH_3 signals were shifted significantly downfield from their respective positions in **1** (1.27 ppm), **2** (1.33 ppm), and *N*-benzoyl-3,3-dimethyl indoline[10] (1.30 ppm), indicating that this product had the *gem*-dimethyl and $-SO_2CH_3$ groups cis as in **3** and not trans as in **4**. The smaller shift to downfield of the *N*-methyl group in **3** in comparison with its position in **1** (2.87 ppm) and **2** (2.95 ppm) is to be attributed to its conjugation with the $-SO_2CH_3$ group. Interestingly, a 24-hr old DMSO-d_6 solution showed new signals (whose intensities did not change further on keeping) at 1.33 ppm [singlet, $C(CH_3)_2$, ~20% of 6 H], 3.13 ppm (singlet, $-SO_2CH_3$, ~20% of 3H), and 3.63 ppm (singlet, $-NCH_3$, ~20% of 3 H). This is best interpreted by assuming that **3** had set up an equilibrium with the cis isomer **4**, using the partial single bond character of the enamine double bond. Compound **4** had the $-NCH_3$ and $-SO_2CH_3$ groups cis, accounting for the marked downfield shift of the former, while the *gem*-dimethyl group has the "normal" chemical shift of about 1.3 ppm. Similar equilibria were set up rapidly in pyridine and old samples of $CDCl_3$ but at measurable rates in fresh $CDCl_3$. However the ratios of **3** and **4** at equilibrium in the three different solvents were approximately the same (4:1).

It was established that the cycloaddition product **2** was not the precursor of the methanesulfonyl derivative

* To whom correspondence should be addressed.

(1) Contribution No. 180 from CIBA Research Centre, Bombay 63, India.

(2) M. Coenen, *Angew. Chem.*, **61**, 11 (1949).

(3) K. Blaha and O. Cervinka, *Advan. Heterocycl. Chem.*, **6**, 147 (1966).

(4) A. G. Cook, "Enamines: Synthesis, Structure and Reactions," Marcel Dekker, New York, N. Y., 1969.

(5) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(6) J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 69 (1963).

(7) I. J. Borowitz, *J. Amer. Chem. Soc.*, **86**, 1146 (1964).

(8) T. R. Govindachari, K. Nagarajan, and H. Schmid, *Helv. Chim. Acta*, **46**, 433 (1963).

(9) J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966).

(10) K. Nagarajan and P. M. Pillai, *Indian J. Chem.*, **7**, 848 (1969).