Reaction of Methyl *trans*-2,3-epoxyoctadecanoate with Phenyl Isocyanate: Synthesis of Fatty 3-phenyl-2-oxazolidones[1]

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Reaction of methyl *trans*-2,3-epoxyoctadecanoate (I) with phenyl isocyanate in dimethylformamide (DMF) in the presence of anhydrous $AlCl_3$ as catalyst has yielded 3-phenyl-4-pentadecylmethyleneoxazolid-2,5-dione (II) and 4(5)-carbomethoxy-5 (4)-pentadecyl-3-phenyl-*cis*-2-oxazolidone (III). The products have been characterized with the help of spectral data and microanalyses.

In the continuation of our studies on the synthesis of fatty 2-oxazolidones (1), we report here the synthesis of fatty 3-phenyl-2-oxazolidones, not reported earlier in the literature, by the reaction of phenyl isocyanate with methyl *trans*-2,3-epoxyoctadecanoate (I) in dimethylformamide (DMF) in the presence of $AlCl_3$ under refluxing condition.

EXPERIMENTAL PROCEDURE

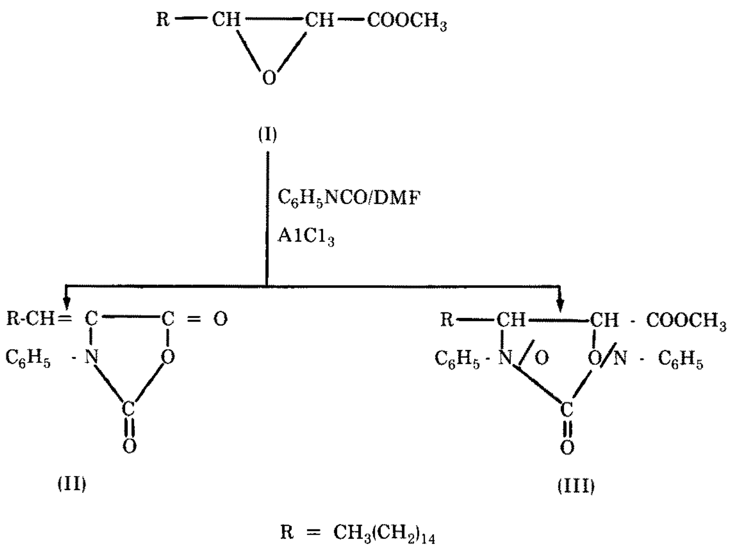
The spectroscopic and chromatographic methods used have been described in an earlier communication (1). Methyl *trans*-2,3-epoxyoctadecanoate (mp 42-43 C) was prepared by metachloroperbenzoic acid epoxidation (2) of methyl esters of *trans*-2-octadecenoic acid prepared from stearic (octadecanoic) acid by the method of Palameta and Prostenik (3).

Reaction of methyl trans-*2,3-epoxyoctadecanoate (I) with phenyl isocyanate.* A solution of I (2 g, 0.0064 mol) in DMF (10 ml) containing anhydrous $AlCl_3$ (0.05 g) as catalyst was heated to reflux, and phenyl isocyanate (0.76 g, 0.0064 mol) was added drop by drop over a period of 2-2.5 hr. After an additional 1 hr, the reaction was complete as judged by TLC. The reaction mixture was then allowed to cool to room temperature, poured into water and extracted with ether. The ether extract was washed successively with water to remove the final traces of phenyl isocyanate and DMF and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give a viscous oil (1.91 g), which showed two distinct spots on TLC. The reaction mixture was chromatographed over a column of silica gel (40 g). The elution with petroleum ether-ether (95:5 v/v) afforded II as solid (27%), mp 45-46 C (Found: C, 75.06; H, 9.28; N, 3.38. $C_{25}H_{37}NO_3$ requires: C, 75.16; H, 9.33; N, 3.5%). Further elution with petroleum ether-ether (88:12, v/v) gave III as solid (68%), mp 60-62 C (Found: C, 72.14; H, 9.44; N, 3.16. $C_{26}H_{41}NO_4$ requires: C, 72.35; H, 9.57; N, 3.25%).

RESULTS AND DISCUSSION

Methyl *trans*-2,3-epoxyoctadecanoate (I) on refluxing with phenyl isocyanate in DMF in the presence of $AlCl_3$ as catalyst (4) afforded two products (II and III) (Scheme 1).

The product (II) on microanalysis gave composition $C_{25}H_{37}NO_3$. Its IR spectrum instead of showing a band at ~980 cm^{-1} (*trans* epoxy function) gave bands at 1820 and 1750 cm^{-1}, indicating the formation of a five-mem-



$R = CH_3(CH_2)_{14}$

SCHEME 1. Reaction scheme.

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[1] Presented at the 41st Annual Convention and Symposium of the Oil Technologists' Association of India (OTAI) in Hyderabad in February, 1986.

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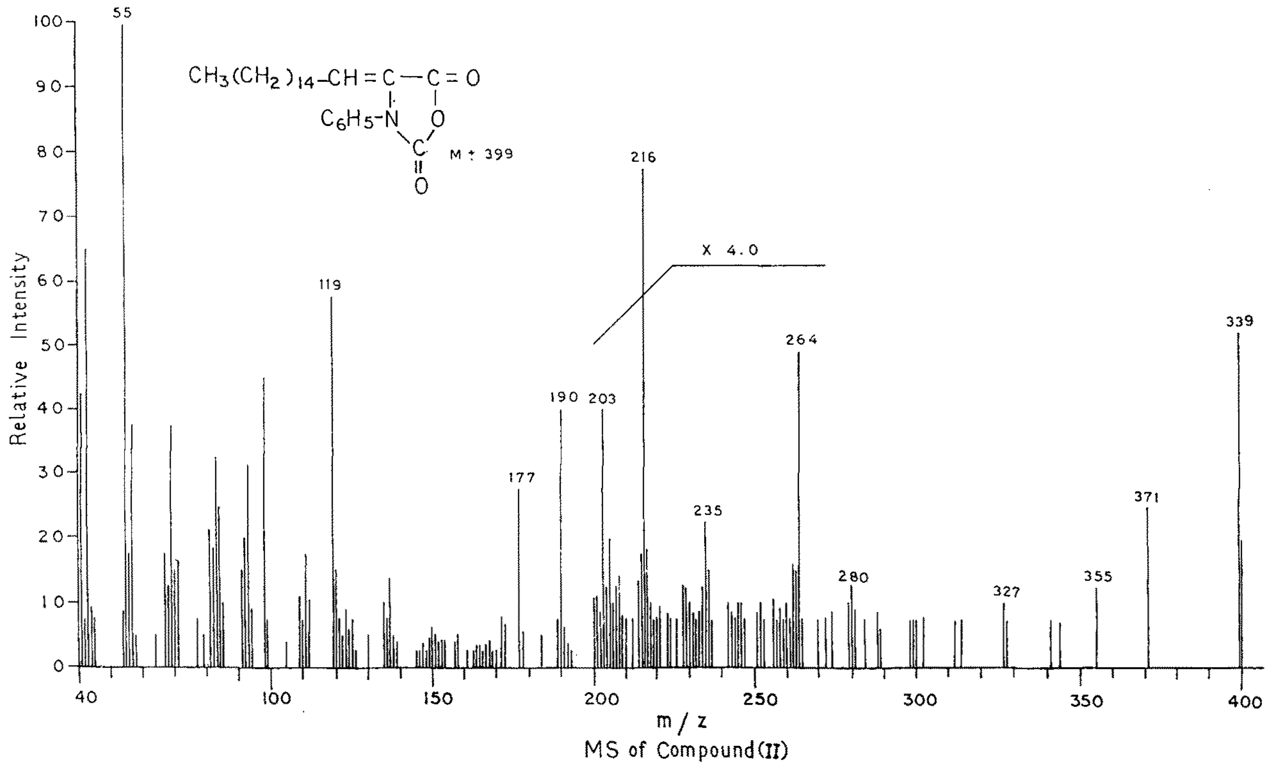


FIG. 1. Mass spectrum of II.

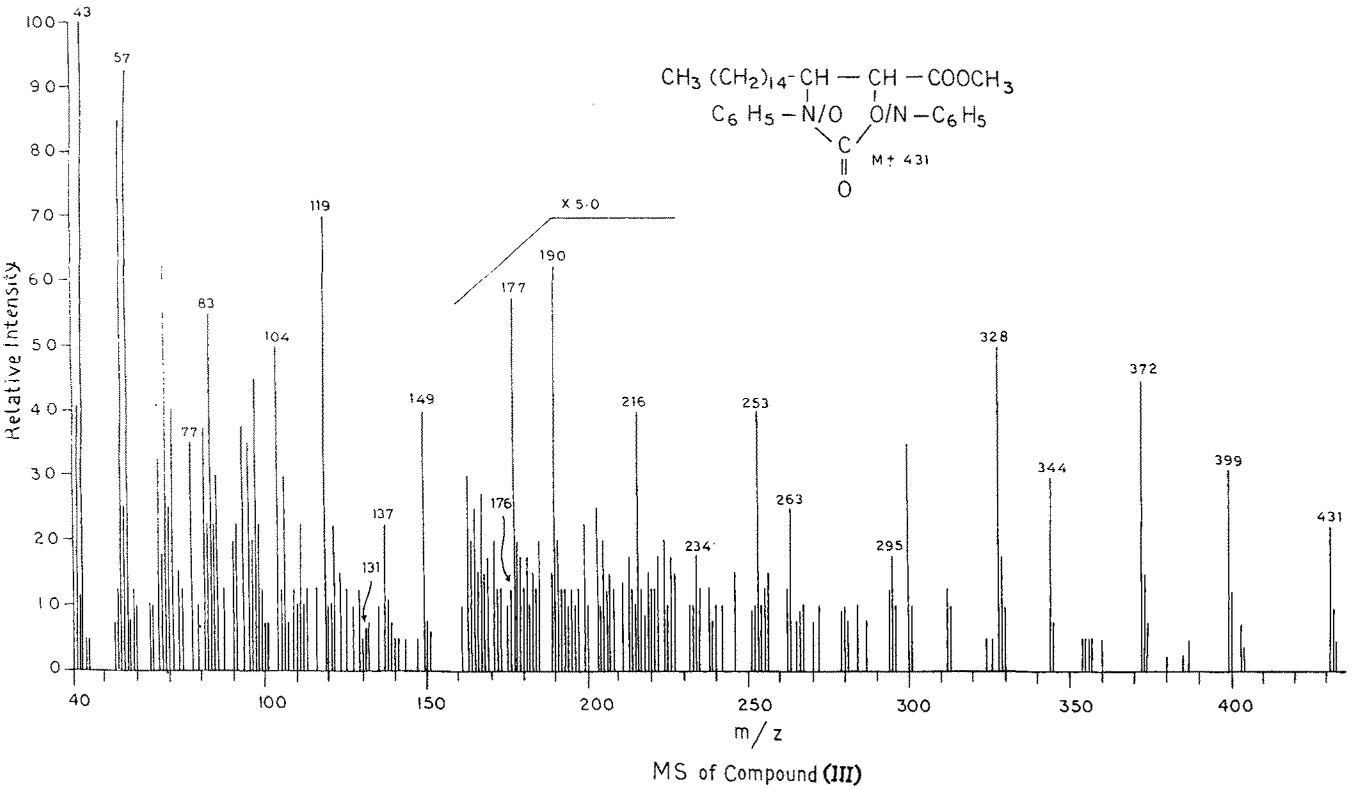
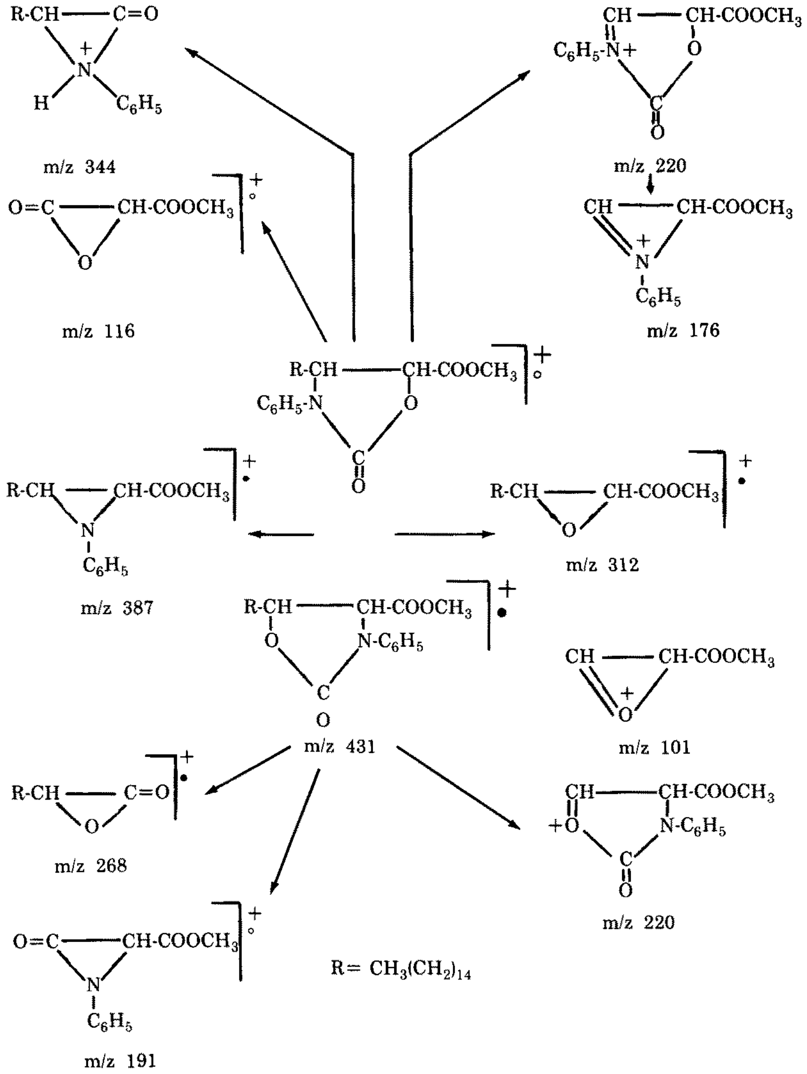


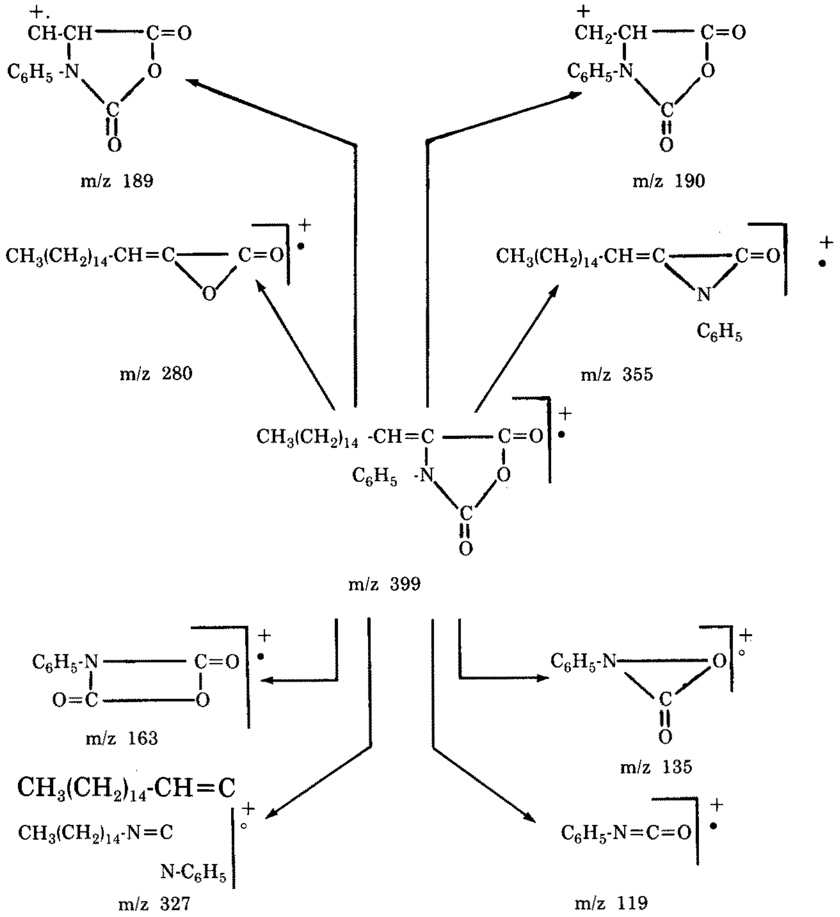
FIG. 2. Mass spectrum of III.



SCHEME 3. Mass fragmentation pattern of III.

bered anhydride ring (5). The bands at 1680 cm^{-1} showed the presence of a carbonyl group conjugated with double bond; at 1600, 1465 and 830 cm^{-1} accounted for the presence of the benzene ring. Its NMR spectrum gave signals at δ7.47 br, m (5H, aromatic), 6.1 t (1H, $-CH_2CH=C-CO$), 2.7 m (2H, $-CH_2-CH=C-CO$), 1.27 br, s (chain-CH_2) and 0.9 t (3H, terminal-CH_3). The mass spectrum of II (Fig. 1) showed a molecular ion peak at m/z 399 along with an ion peak at 400 (M+1). It gave dominant ion peaks (Scheme 2) at m/z 355, 327, 264, 189, 177 and 119. Other characteristic peaks were observed at m/z 371 (M-CO), 280, 216 ($202+CH_2$), 203 (202+H), 202 ($188+CH_2$), 190, 188 [M - $CH_3(CH_2)_{14}$], 158 ($202-CO_2$), 135, 130 ($202-CO_2$ and -CO), 120 (119+H), 111, 83 and 55 (base peak). These data finally confirmed the structure of II as 3-phenyl-4-pentadecylmethyleneoxazolid-2,5-dione.

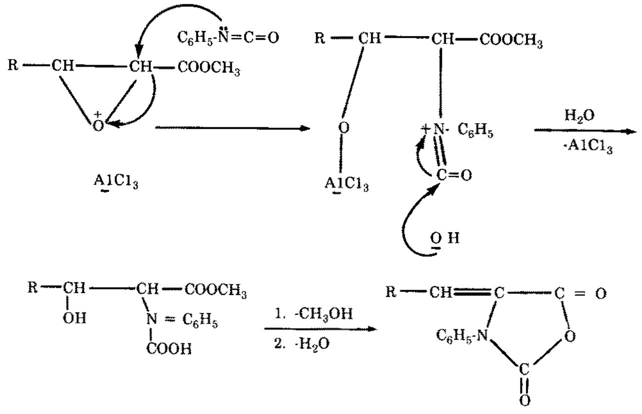
The product (III) analyzed for $C_{26}H_{41}NO_4$. Its IR spectrum showed bands at 1755 [2-oxazolidone ring (6)], 1735 (ester CO), 1500, 1440 (C-N), 1400, 1210, 1130, 1070 (C-O) and 720 cm^{-1}. The bands observed at 1600, 1465 and 840 cm^{-1} were characteristic of benzene ring. The NMR of III revealed signals at δ7.44 m (2H, aromatic), 7.35 m (3H, aromatic), 5.2 d (J=8.5 Hz, oxazolidone 5-CH attached to a $COOCH_3$ group), 4.17 m (oxazolidone 4-CH), 3.77 s (3H, $COOCH_3$), 1.27 br, s (chain-CH_2) and 0.90 t (terminal-CH_3). Appearance of a doublet at δ4.4 (J=8.5 Hz, oxazolidone 4-CH attached to a $COOCH_3$ group) and a multiplet at δ4.51 (oxazolidone 5-CH) indicated the formation of another isomer. On the basis of the above data, III was characterized as 4(5)-carbomethoxy-5(4)-pentadecyl-3-phenyl-*cis*-2-oxazolidone. The *cis* configuration of 4- and 5-methine protons in the ring was established by their coupling constants (7,8). The isomeric nature of III was further confirmed by its mass spectral fragmentation data (Scheme 3). The mass spectrum of III (Fig. 2) gave a molecular ion peak at m/z 431 along with ion peaks at 432 (M+1) and 433 (M+2). The ion peaks at m/z 344, 268, 191, 176, 116 and 101 confirmed the isomeric nature of III. Other ion peaks appeared at m/z 403 (M-CO), 400 (M-OCH_3), 399 (M-CH_3OH), 387 (M-CO_2), 373 (M-$COOCH_3$), 354 (M-C_6H_5), 328 (372-CO_2 or 387 -$COOCH_3$), 312 (M-C_6H_5NCO), 295 (M-$C_6H_5NCO_2H$), 253 (312-$COOCH_3$), 220, 189 (220-OCH_3), 163 (191-CO), 160 (191-OCH_3), 149, 137, 132 (191-$COOCH_3$), 131



SCHEME 2. Mass fragmentation pattern of II.

(163-CH_3OH), 119, 104 (163-$COOCH_3$), 85 (116-OCH_3), 77 ($C_6H_5^+$) and 43 (base peak).

The mechanism for the formation of 2-oxazolidone from the reaction of epoxide with phenyl isocyanate in the presence of a Lewis acid such as LiCl is already known (9). The possible mechanism for the formation of oxazolid-2,5-dione (II) from the reaction of methyl 2,3-epoxy ester (I) with phenyl isocyanate in the presence of $AlCl_3$ may be formulated as under:



R = $CH_3(CH_2)_{14}$

(II)

ACKNOWLEDGMENT

Prof. M.S. Ahmad, chairman of the Department of Chemistry provided research facilities. The council of Scientific and Industrial Research, New Delhi, provided a Senior Research Fellowship to M.H. Ansari.

REFERENCES

1. Ansari, M.H., M.S. Ahmad Jr. and M. Ahmad, *J.Am. Oil Chem. Soc. 62*:1659 (1985).
2. Gunstone, F.D., and F.R. Jacobsberg, *Chem. Phys. Lipids 9*:26 (1972).
3. Palameta, B., and M. Prostenik, *Tetrahedron 19*:1463 (1963).
4. Irwin, W.J., and D.L. Wheelar, *J. Chem. Soc. (C)* 3166 (1971).
5. Colthup, N.B., L.H. Daly and S.E. Wiberley, in *Introduction to Infrared and Raman Spectroscopy*, Academic Press Inc., New York, 1972, p. 297.
6. Pinchas, S., and D. Ben Ishai, *J. Am. Chem. Soc. 79*:4099 (1957).
7. Herweh, J.E., T.A. Foglia and D. Swern, *J. Org. Chem. 33*:4029 (1968).
8. Foglia, T.A., and D. Swern, *Ibid. 34*:1680 (1969).
9. Dyen, M.E., and D. Swern, *Chem. Rev. 67*:197 (1967).

[Received October 20, 1986]