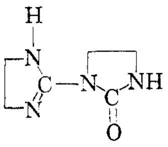
Anal. Calcd. for $C_{12}H_{15}N_6O_8$: C, 40.34; H, 4.23; N, 19.60. Found: C, 40.62; H, 4.23; N, 19.36.

A major portion (66%) of unchanged I was recovered in this case. The n-butoxy derivative IId was obtained in 47% yield; m.p. 55–58°; $\lambda_{\max}^{\text{Nujol}}$ 3.15, 6.14, 6.58, 6.71 μ; acid fumarate m.p. 126–128°.

Anal. Calcd. for $C_{11}H_{18}N_2O_5$: N, 10.85. Found: N (Kjeldahl), 10.82.

From the preparations of IIb and IId, another product was isolated in low (10–15%) yield. A consideration of the analysis (Calcd. for $C_6H_{10}N_4O$: C, 46.74; H, 6.54; N, 36.34. Found: C, 46.77; H, 6.51; N, 36.31), infrared spectrum ($\lambda_{\max}^{\text{Nujol}}$ 3.00, 3.18, 5.82, 6.22, 6.64, 6.70 μ) and other properties of this relatively high melting (210°) monoacidic base (pK_a 6.0; neut. equiv. 160) has led to assignment of the 1-(2-imidazolin-2-yl)-2-imidazolidinone structure (III) to this compound.



III

Further studies on imidazolines II and III and related compounds are in progress.

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Concerning the Structure of C_{27}-Phthienoic Acid

Sir:

The physiologically active C_{27}-phthienoic acid, isolated[1] from tubercle bacillus, has previously been reported[2] to have the partial structure, 2-methyl-4,x-dialkyl-2-alkenoic acid. Investigators at Oxford[3] have degraded by oxidation the mixture of acids with more than twenty carbons from tubercle bacillus, and on this basis assigned the structure, 2,4,6-trimethyl-2-tetracosenoic acid, to a component of this mixture termed "mycolipenic acid," although there had not been presented evidence of isolation of any pure component from the mixture. More recently, there has been reported[4] synthesis of optically active 2,4,6-trimethyl-2-tetracosenoic acid and comparison with an acid isolated from tubercle bacillus, but limited data were included. Although we have shown[5] that the mixture of higher acids from tubercle bacillus contains thirteen or more components, of which at least nine are unsaturated, it has nevertheless been stated by Bailey, Polgar, and Robinson[6] that "there can be very little doubt but that C_{27}-phthienoic and mycolipenic acid are identical." We are aware of no experimental evidence in support of this idea and much to the contrary[5]; however, it has been accepted to the point that there has appeared a paper[7] entitled "Synthesis of Racemic Methyl Phthienoate." Since we now have evidence, which appears firm, that C_{27}-phthienoic acid is *not* 2,4,6-trimethyl-2-tetracosenoic acid, this preliminary report is submitted in the hope of preventing additional confusion in the literature.

Ozonolysis at −14° in chloroform solution, followed by oxidation with silver oxide, of 2,4-dimethyl-2-docosenoic acid gave 2-methyleicosanoic acid in 60% yield and a 40% yield of neutral material which was shown to be about 3 parts 2-eicosanone and 1 part 2-eicosanol. Similar ozonolysis, in two lots, of a total of 743 mg. of pure C_{27}-phthienoic acid yielded 282 mg. of a crystalline C_{24} acid[8], m.p. 39–43°, $[\alpha]_D^{21}$ +4.96°, eq. wt. 364. In gas phase chromatography on silicone grease at 245° of the methyl ester of this acid, retention time was 6 min. 15 sec. Retention time of 6 min. 18 sec. for methyl 2,4-dimethyldocosanoate confirms the C_{27} formula for C_{27}-phthienoic acid. Chromatography on alumina of the neutral material from ozonolysis (total 302 mg.) yielded three crystalline ketone fractions and one alcohol fraction (infrared characterization), eluted in that order and weighing respectively 63, 28, 21 and 59 mg. Gas phase chromatography of the ketone fractions (numbered in order of elution from alumina), and of certain synthetic ketones, yielded retention times recorded in Table I.

Retention times in Table I, coupled with analyses for C, H, and O, show that "ketone-1" is a dioxygen

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[1] J. Cason and G. Sumrell, *J. Biol. Chem.*, **192**, 405 (1951).

[2] (a) J. Cason, N. K. Freeman, and G. Sumrell, *J. Biol. Chem.*, **192**, 415 (1951); (b) J. Cason and C. F. Allen, *J. Biol. Chem.*, **205**, 449 (1953).

[3] N. Polgar, *J. Chem. Soc.*, 1008 (1954).

[4] D. J. Millin and N. Polgar, *Proc. Chem. Soc.*, 122 (1957).

[5] J. Cason and G. J. Fonken, *J. Biol. Chem.*, **220**, 391 (1956); C. F. Allen and J. Cason, *J. Biol. Chem.*, **220**, 407 (1956).

[6] A. S. Bailey, N. Polgar, and R. Robinson, *J. Chem. Soc.*, 3031 (1953).

[7] C. Collin-Asselineau, J. Asselineau, S. Ställberg-Stenhagen, and E. Stenhagen, *Acta Chem. Scand.* **10**, 478 (1956).

[8] Polgar[3] reported data only for the crude acid from permanganate oxidation, m.p. 34–35°, $[\alpha]_D^{16}$ +7.1°; for synthetic (+)-2,4-dimethyldocosanoic acid, after purification *via* the quinine salt, $[\alpha]_D^{22}$ +7.4°, no m.p. reported [G. I. Fray and N. Polgar, *J. Chem. Soc.*, 2036 (1956)].

TABLE I

RETENTION TIMES OF KETONES

Ketone	Retention Time (min., sec.) at 180°	220°
6-Hexadecanone	6'15"	
6-Heptadecanone	8'34"	2'46"
2-Heptadecanone	9'32"	
2-Octadecanone	12'53"	
2-Eicosanone		5'06"
6-Tricosanone		9'49"
5,11-Pentadecanedione	7'44"	
Pentadecan-5-ol-11-one	9'12"	
5,12-Hexadecanedione	10'50"	
5,14-Octadecanedione	20'35"	4'36"
"Ketone-1"		13'48"
"Ketone-2"		9'00"[a]
"Ketone-3"	10'44"	3'14"[b]

[a] Minor bands at 5'11" (6% of total area) and 3'14" ("ketone-3," 1% of total). [b] Minor band at 6'23" (13% of total), no band at 9'.

compound (probably a C_{23} keto alcohol) and that "ketone-2" is a mono-oxygen compound (probably a C_{23} ketone with one branch in chain). Of most interest is "ketone-3," whose properties are those of a C_{16} diketone. *Anal.* Calcd. for $C_{16}H_{30}O_2$: C, 75.5; H, 11.9. Found: C, 75.8; H, 11.5. A C_{16} diketone cannot be obtained by oxidation of 2,4,6-trimethyl-2-tetracosenoic acid; and 2-eicosanone, which would be expected and should be isolated by our procedure, has not been found among our degradation products.

The x-ray diffraction pattern[9] of C_{27}-phthienoic acid gives good, but not entirely rigorous, evidence that the longest chain in the substance contains 20 carbons. Infrared evidence[10] suggests that the substituent in the 4-position is methyl, and shows the absence[2a] of ethyl or propyl groups. If these data and other firm evidence[2] be combined with the C_{16} formula for the diketone, the structure for C_{27}-phthienoic acid may be deduced to be *trans*-2,4-dimethyl-13-*n*-amyl-2-eicosenoic acid; however, this structure must be regarded as tentative until more rigorous evidence is secured.

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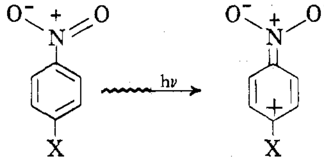
[9] Dr. E. S. Lutton of the Miami Valley Laboratories, Procter and Gamble Co., carried out x-ray diffraction on a sample of phthienoic acid isolated by one of us (C.F.A.), and advised us on June 7, 1956, that the unstable polymorph of this acid melting at about 21° appears to crystallize in an "alpha" form, which allows direct calculation of the chain length.

[10] J. Cason and K. L. Rinehart, Jr., *J. Org. Chem.*, **20**, 1591 (1955).

Example of Net Electron Release by Formyl, Nitro, Cyano, and Carbomethoxy Groups

Sir:

We have found that normally electron accepting substituents such as formyl can give a net *release*, relative to hydrogen, in the "principal" ultraviolet transition of *para* substituted nitrobenzenes. This transition involves excitation to a highly dipolar state, with the transition moment lying in the long axis of the molecule toward the nitro group.[1] It is approximately described by equation 1.[2] The energy of the excited state should be lowered, relative to that of nitrobenzene, whenever X is able to release electrons and absorb some of the electron deficiency created in the neighborhood of the *para* position to a greater extent than does a *para* hydrogen. If this stabilization is greater than that of the ground state, the transition energy would be expected to be lowered. Presumably this accounts for the fact that *p*-alkylnitrobenzenes absorb at a lower energy (*i.e.* lower frequency, higher wave length) than nitrobenzene (*cf.* ref. 2).



(1)

The results for the *para* halonitrobenzenes (Table I) show that stabilization of excited relative to the ground state is in the order I>Br>Cl>F, indicating a net electron release, on excitation, in the same order. This order is opposite to the accepted normal order of electromeric release, but corresponds to the polarizability order.[3,4] The *p*-halonitrobenzene results prompted the authors to study nitrobenzene substituted in the *para* position with CHO, NO_2, CN and $COOCH_3$. These substituents are considered to be electron acceptors, by both the inductomeric and electromeric mechanisms.[3] The gas phase results of Table I indicate that, on excitation, there is a greater net electron *release* by these substituents than by hydrogen. The authors interpret this as meaning that the formal aromatic (*p*-nitrophenyl) moiety in the excited state is more electronegative than the

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[1] A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (1955); *J. Am. Chem. Soc.*, **77**, 4454 (1955).

[2] W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957).

[3] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, New York, 1953, Chapters II and III.

[4] While this work was in progress, A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956) published results on *p*-halonitrobenzene spectra in hexane that parallel the authors' observations in heptane. An explanation in terms of polarizability, similar to that of the authors, was advanced to account for the order of excitation energy observed.