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).

$$(1)$$
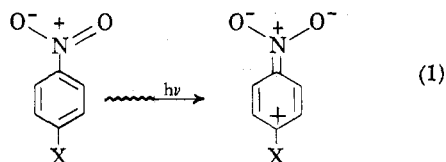
The results for the *para* halonitrobenzenes (Table I) show that stabilization of excited relative to the ground state is in the order $I > Br > Cl > F$, indicating a net electron release, on excitation, in the same order. This order is opposite to the accepted normal order of electromeric release, but 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

(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.

TABLE I

VALUES OF ν_{max} (CM.$^{-1}$) FOR para SUBSTITUTED NITROBENZENES[a]

Substituent	Gas Phase $\nu \times 10^{-1}$	$\epsilon_{max} \times 10^{-2}$	95% EtOH $\nu \times 10^{-1}$	H_2O $\nu \times 10^{-1}$	20.6% HClO$_4$ $\nu \times 10^{-1}$
H	4182[b]	96	3850	3739	3722
F	4080	84	3786	3667	3651
Cl	3979	118	3686	3583	3564
Br	3928	137	3625	3524	3516
I	3786[c]	129	3394	3316	3303
CHO	4058	150	...	3736	3724
CN	4114	143	3896	3836	3820
NO$_2$	4102	155	3848	3755	3747
COOCH$_3$	4120	138	3867	3785	3771

[a] Determined by methods previously described;[2] the ν_{max} values are averages of at least two determinations and were duplicated to ±20 cm.$^{-1}$ [b] Erroneously reported previously.[2] [c] The same order of ν_{max} was observed for p-haloacetophenones.

substituent and consider the amount of electron release by the substituent to be a function of both the electronegativity difference between the aromatic moiety and the substituent and the polarizability of the Ar-X bond. The electronegativity difference between the excited p-nitrophenyl moiety and the substituent would be greatest for hydrogen, but the polarizability of the Ar-X bond is sufficiently greater than that of the Ar-H bond to result in a greater electron release by X. Similar considerations can be applied to the ground state, but presumably the effects would be smaller, due to the smaller electronegativity difference between the aromatic moiety and the various substituents. The authors are exploring the possibility that such factors play a role in the effect of substituents in ordinary chemical reactions and are attempting to incorporate these ideas in a semi-empirical quantitative relationship.[5] Obviously, the Hammett equation is of little use here, since the sigma constants

not only have the wrong magnitude, but also are of the wrong sign.

The nature of the electronic transition being studied is also revealed in the solvent effects on the excitation energies. Note that the red shift accompanying increased solvent acidity is greater for the substituted nitrobenzenes than for nitrobenzene. Electron withdrawal by the para substituent in the ground state reduces hydrogen bond solvation of the nitro-group; in view of the Franck-Condon principle, this would act to reduce solvent stabilization of the excited relative to the ground state, thus contributing to a less pronounced red shift (cf. ref. 2). The solvent red shift is decreased even more for the nitrobenzenes substituted with the hydrogen bonding substituents such as formyl; thus in 20% perchloric acid the excitation energy of these compounds is now greater than that of nitrobenzene. This can be attributed to a decrease in hydrogen bond solvation of these groups in proceeding from the ground state (in which they have a partial negative charge) to the excited state (in which they have a partial positive charge).

(5) The polarizability of the Ar-X bond is dependent on the orbital character of the bonding. Within limits, this polarizability is assumed to be a constant in the hypothetical reaction: purely covalent Ar:X → actual Ar-X. Thus the polarizability of the bond in X attached to aromatic carbon (some π as well as σ bonding may be involved) may have a different value than that of the bond in X attached to aliphatic carbon.

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