Triphenylmethyl Nitrate.—For the preparation of solid triphenylmethyl nitrate the reaction mixture with carbon tetrachloride as the solvent was stirred magnetically for four hours, the supernatant liquid was decanted into a receiver, and the solvent distilled back into the reaction flask at room temperature. The entire operation was done in a closed system. Part of the residual pale yellow solid was removed for a melting point and the rest was decomposed *in vacuo* without solvent. It gave (from 2.0 g. of triphenylmethyl chloride) 200 mg. of benzophenone, 600 mg. of carbinol and a mixture of highly colored substances. The solid melted at 73° when heated rapidly, became red, and evolved a gas. When heating was continued, the mixture resolidified (with lightening of color) and remelted to a light orange liquid at 145–160°.

N-Triphenylmethylacetamide.—A solution of 16 g. of triphenylchloromethane in acetonitrile was added to a solution of 10 g. of silver nitrate in acetonitrile. After a short while, the precipitated silver chloride was removed by filtration, and the solvent was removed. The residue was crystallized from toluene giving about 12.5 g. of solid, m.p. 95–125° (dec. with formation of nitrogen oxides). When this material was recrystallized from commercial acetone or from 95% ethanol, it was converted to N-triphenylmethylacetamide,[6] m.p. 214–218°.

Anal. Calcd. for $C_{24}H_{19}ON$: C, 83.69; H, 6.35. Found: C, 83.84; H, 6.52.

When this compound was submitted to hydrolysis in aqueous acetic acid, using a trace of hydrochloric acid catalyst, triphenylcarbinol, m.p. and mixed m.p. 162–163° was obtained.[6]

NOTE ADDED IN PROOF.—G. W. H. Cheeseman, *Chem. and Ind.*, 281 (1954), recently has noted the high reactivity of triphenylmethyl nitrate.

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[6] W. Hemelian and H. Silberstein, *Monatsh.*, **17**, 741 (1884).

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On the Expansion of the Sulfur Octet[1]

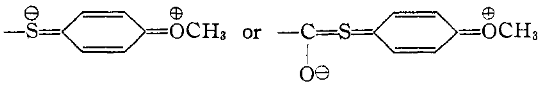
BY G. CILENTO AND WOLFGANG FERDINAND WALTER

RECEIVED DECEMBER 8, 1953

As reported in previous papers,[2] the ultraviolet absorption spectra of fully aromatic esters and thiolesters show that the three main electronic transitions expected in these compounds are largely independent of one another and strongly indicate that in certain of these thiolesters, in an activated state, the sulfur atom uses a 3d-orbital, expanding its valence shell to a decet.

In the light of these results, it was expected that an indication of expansion would also be found in the spectra of certain partially aromatic thiolesters, such as *p*-anisyl thiolacetate. The spectra of this compound, of the analogous ester and of both corresponding unsubstituted compounds have been investigated and are shown in Fig. 1.

It can be seen that introduction of a methoxyl in the ring of phenyl acetate produces essentially the same spectral changes which are to be observed on passing from benzene to anisole. However, the same substitution in the case of phenyl thiolacetate produces a very strong absorption maximum at around 240 mμ. This almost certainly indicates that the sulfur atom participates in the electronic transition corresponding to this band by using a 3d-orbital



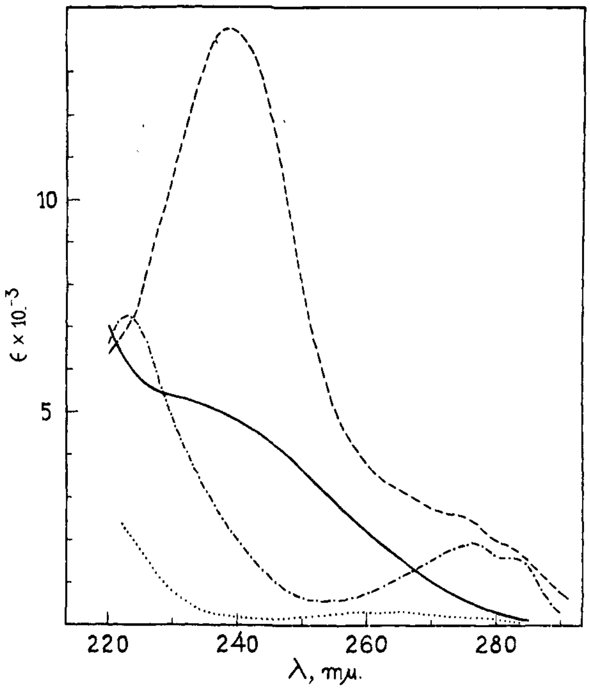


Fig. 1.—Absorption spectra in C_2H_5OH of: CH_3–CO–O–C_6H_5.........; CH_3–CO–S–C_6H_5———; CH_3–CO–O–C_6H_4–OCH_3-·-·-·-·; CH_3–CO–S–C_6H_4–OCH_3- - - - - -.

It is pertinent to note that there seems to exist a counterpart of this finding in chemical reactivity. Thus, Tarbell and Herz[3] have connected the failure of aryl thiolesters to undergo the Fries rearrangement with deactivation of the aromatic nucleus by resonating structures in which sulfur expands its octet.[3]

As suggested by chemical or physicochemical evidence, this peculiarity of the sulfur atom to enlarge the outer shell presents itself in various other classes of compounds.[4] Nonet structures also have been formulated.[5] Very probably this peculiarity is involved also in the explanation of the behavior of triphenylmethyl radicals in liquid sulfur dioxide. These radicals transfer their unpaired electron to the solvent, most likely to a d-orbital of the sulfur atom.

It would not be going too far to suggest that the ability of sulfur to use a d-orbital might, in certain cases, be of significance—or at least should not be overlooked—in the elucidation of the biological role of certain sulfur-containing groups or molecules. Such a suggestion would in a way remind one of the importance of vacant d-orbitals in the activity of certain cations in some biological systems.[6]

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[1] Presented at the 5th Meeting of the "Sociedade Brasileira para o Progresso da Ciência," Curitiba, November, 1953.

[2] G. Cilento, *Experientia*, **8**, 421 (1952); THIS JOURNAL, **75**, 3748 (1953).

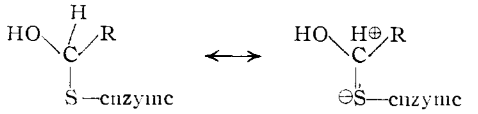
[3] D. S. Tarbell and A. H. Herz, *ibid.*, **75**, 1668 (1953).

[4] Several references are given by D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).

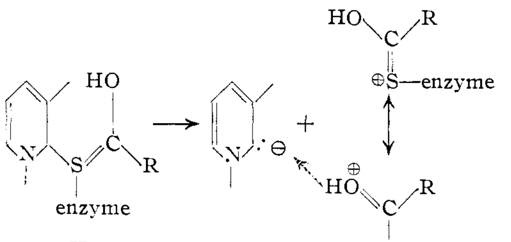
[5] C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950).

[6] See, for instance, A. L. Lehninger, *Physiol. Rev.*, **30**, 393 (1950).

Consider, for example, reactions involving carbonyl groups under the influence of –SH groups either from an enzyme or a coenzyme. It is assumed that in certain cases, as a first step, a hemimercaptal Ia is formed. Contribution of a resonating structure Ib, in which the sulfur atom expands the octet, would give considerable proton-releasing effect on the attached carbon atom[7] and this may be of importance in relation to the mechanism of these reactions.


Ia Ib

For instance, one may conceive of removal of a proton from the hemimercaptal, followed by formation of an unstable intermediate II from DPN$^+$ and the anion.[8] This intermediate would decompose forming DPNH and a thiolester


II

Experimental

The compounds were obtained by condensation of the phenol or thiophenol with acetyl chloride, extracted from the reaction mixture by current procedures and distilled (phenyl acetate, b.p. 189.5–191.5° at 701 mm.; phenyl thiolacetate, b.p. 117–118° at 21 mm.; anisyl acetate, b.p. 135–137° at 19 mm.; anisyl thiolacetate, b.p. 168–169° at 16 mm.). Anisyl acetate was also recrystallized from ether (m.p. 29–32°).

For absorption measurements, solutions in especially purified ethyl alcohol were prepared. Readings were taken with a Beckman D.U. quartz spectrophotometer at 2-mμ intervals, employing a constant band width of 10 Å.

Acknowledgments.—We wish to express our gratitude to the Rockefeller Foundation for the gift of the Beckman Spectrophotometer and to Prof. H. Hauptmann for his stimulating interest.

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[7] (a) E. Rothstein, *J. Chem. Soc.*, 1550, 1553, 1558 (1940); (b) R. B. Woodward and R. H. Eastman, THIS JOURNAL, **68**, 2229 (1946).

[8] It is interesting that DPN$^+$, in fact, forms dissociable addition complexes with cyanide and bisulfite (O. Meyerhof, P. Ohlmeyer and W. Möhle, *Biochem. Z.*, **297**, 113 (1938)).

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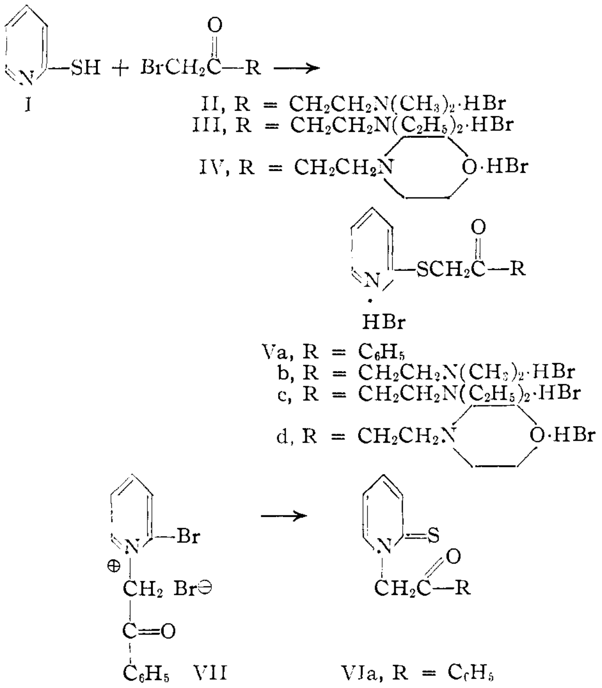
The Reaction of α-Halo Ketones with 2-Pyridinethiol[1]

BY CARL DJERASSI AND GEORGE R. PETTIT

RECEIVED APRIL 7, 1954

In connection with another project, it was necessary to determine the course of the reaction of 2-pyridinethiol (I) with certain α-halo ketones, notably brominated Mannich bases.[2] The condensation was carried out in glacial acetic acid solution with the following ketones: phenacyl bromide, 1-bromo-4-dimethylamino-2-butanone hydrobromide (II), 1-bromo-4-diethylamino-2-butanone hydrobromide (III) and 1-bromo-4-morpholino-2-butanone hydrobromide (IV). The solubility characteristics of the resulting products and especially the presence of a carbonyl function, detected by infrared and chemical means, excluded a cyclic (quaternary) pyridothioazole structure and indicated that the compounds must be the products of S- (V) or N-alkylation (VI). A decision in favor of structure V was arrived at as follows: The quaternary salt, 1-phenacyl-2-bromopyridinium bromide (VII), prepared from 2-bromopyridine and phenacyl bromide, was converted to 1-phenacyl-2-pyridinethione (VIa) with sodium hydrogen sulfide. The ultraviolet absorption spectrum (see Experimental) of this substance, though very similar to that of 1-ethyl-2-pyridinethione,[3,4] was completely different from that of the pyridinethiol–phenacyl bromide condensation product (as the free base), which is therefore assigned structure Va. The analogous condensation products with the Mannich bases II–IV exhibited essentially the same ultraviolet absorption spectra (see Experimental), as did 2-ethylthiopyridine[3,5] and it is clear, therefore, that all of these substances are the products of S-alkylation (V). This was confirmed further by the stability of Vd toward boiling 42% hydrobromic acid; 1-alkyl-2-pyridinethiones are converted to


I
II, R = $CH_2CH_2N(CH_3)_2 \cdot HBr$
III, R = $CH_2CH_2N(C_2H_5)_2 \cdot HBr$
IV, R = CH_2CH_2N O·HBr
Va, R = C_6H_5
b, R = $CH_2CH_2N(CH_3)_2 \cdot HBr$
c, R = $CH_2CH_2N(C_2H_5)_2 \cdot HBr$
d, R = CH_2CH_2N O·HBr
VII
VIa, R = C_6H_5

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[1] Taken in part from the M.S. thesis of G. R. P.

[2] For the reaction of thioamides with brominated Mannich bases, see C. Djerassi, R. H. Mizzoni and C. R. Scholz, *J. Org. Chem.*, **15**, 700 (1950).

[3] D. J. Fry and J. D. Kendall, *J. Chem. Soc.*, 1716 (1951).

[4] The ultraviolet absorption spectrum of 2-pyridinethiol (I) is given for comparison and indicates that in ethanol solution it exists primarily in the thione form.

[5] H. J. Backer and J. A. K. Buisman, *Rec. trav. chim.*, **64**, 102 (1945).