O-(Chloroethyl) phosphorodichloridothionate was prepared from thiophosphoryl chloride and chloroethanol in the presence of triethylamine. The *O*-phenyl and *O*-*p*-cresyl derivatives were prepared according to the procedures given by Autenrieth.[6] A solution of the phenols in aqueous sodium hydroxide was added dropwise to the cold thiophosphoryl chloride. The *p*-chlorophenol, *p*-methoxyphenol, and 4-chloro-3-methylphenol intermediates were prepared by the method according to Tolkmith[7] in which a pyrdine solution of the phenols was added to an excess of thiophosphoryl chloride in benzene. *O,O'*-Dimethyl and *O,O'*-diethyl phosphorochloridothionates were obtained from Victor Chemical Works and Monsanto Chemical Co., respectively, and benzene thiophosphonic dichloride was obtained from Eastman Kodak. All the intermediates were purified by fractional vacuum distillation.

Preparation of O-alkyl and O-aryl N,N'-diethylene phosphorodiamidothionates. Procedure A. A solution of 95.3 g. (0.88 mole) of sodium carbonate and 19.0 g. (0.44 mole) of ethylenimine dissolved in 700 ml. of water was cooled to 5°. To this solution was added dropwise 35.8 g. (0.2 mole) of *O*-ethyl phosphorodichloridothionate under rapid stirring while the temperature was maintained at 5°. After the addition was completed, stirring was continued for 1 hr. at this temperature. The organic layer was separated and dried over anhydrous magnesium sulfate. The water layer was extracted with benzene, the extract dried, and the solvent removed by distillation under vacuum at low temperatures. The dried organic layer and the solvent-free extraction residue were combined and distilled under high vacuum to obtain the purified product, *O*-ethyl *N,N'*-diethylene phosphorodiamidothionate (III).

Procedure B. A solution of 78.2 g. (1.1 moles) of 2,2-dimethylethylenimine and 111.3 g. (1.1 moles) of triethylamine in 2500 ml. of benzene was cooled to between 5° to 10°. A second solution of 96.5 g. (0.5 mole) of *O*-propylphosphorodichloridothionate in 500 ml. of benzene was added dropwise to the first solution under stirring and kept at temperatures between 5°–10°. After the addition was completed, the mixture was stirred for one hour at room temperature. The precipitated triethylamine hydrochloride was removed by filtration under suction and the solvent removed from the filtrate by distilling at 30° under vacuum. The residue was then purified by distilling under high vacuum to give the product, *O*-propyl *N,N'*-bis(2,2-dimethylethylene) phosphorodiamidothionate (IX).

Procedure C. 1. *N,N'*-Diethylene benzenethiophosphonamide (XVI) was prepared as described in procedure B except the product is a crystalline material. On removal of the solvent, a solid separates which was recrystallized twice from toluene, and gave a melting point of 103°.

2. *O*-Phenyl *N,N'*-bis(2,2-dimethylethylene) phosphorodiamidothionate (XV) was distilled in the molecular still and the distillate was recrystallized from toluene–petroleum ether and gave a melting point of 64.0°.

Procedure D. Twenty-three grams (1.0 g.-atom) of sodium was dispersed in 1 l. of dry toluene by stirring and heating to reflux. Then 174.1 g. (1.1 moles) of decyl alcohol was added dropwise. Heating of the mixture was continued until all the sodium had reacted. This mixture was added portionwise at room temperature to a solution of 169.5 g. (1.0 mole) of thiophosphoryl chloride in 2.5 liters of benzene. After the addition was completed, the mixture was heated to reflux for 3 hr. Twenty milliliters of water was added when the mixture had been cooled to room temperature. After being stirred for five minutes, the slurry was filtered and the solution dried over anhydrous magnesium sulfate, and refiltered. The clarified filtrate was then added dropwise to a precooled solution at 5° of 103.5 g. (2.4 moles) of ethylenimine and 242.0 g. (2.4 moles) of triethylamine in 300 ml. of benzene. After the addition was completed, stirring was continued for another 2 hr. at room temperature. Triethylamine hydrochloride was removed by filtration, the filtrate washed with a 5% sodium carbonate solution, dried, and the benzene removed by distillation at 30° under vacuum. The residue was then purified by distillation under high vacuum to give the product, *O*-*n*-decyl *N,N'*-diethylene phosphorodiamidothionate (XII).

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(6) W. Autenrieth and Mayer, *Ber.*, **58**, 840 (1925).
(7) H. Tolkmith, *J. Org. Chem.*, **23**, 1685–1690 (1958).

The Proton Magnetic Resonance Spectrum of Ethyl 1-Diacetylamino-3-acetamido-4-(α-ethoxycarbonylbenzyl)-2-naphthoate

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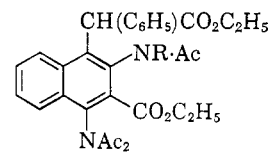
A compound obtained by the reductive acetylation of ethyl 3-amino-4-(α-ethoxycarbonylbenzylidine)-1,4-dihydro-1-imino-2-naphthoate was previously formulated[1] as either ethyl-1-diacetylamino-3-acetamido-4-(α-ethoxycarbonylbenzyl)-2-naphthoate (I. R = H) or ethyl 1,3-di(diacetylamino)-4-(α-ethoxycarbonylbenzyl)-2-naphthoate (I. R = Ac) with a preference, on infrared evidence. for the latter. Proton nuclear magnetic evidence (see Fig. 1), strongly favors the former structure and thus the ν(NH) band in the infrared must be weak or absent[2] for the compound.



I

In Fig. 1, the absorption of the phenyl substituent is seen at $\tau = 2.72$ p.p.m. as a sharp peak of intensity corresponding to five protons, the complex pattern at lower τ values arises from naphthalenic protons. This evidence clearly confirms the tricyclic nature of the precursor, ethyl 3-amino-4-(α - ethoxycarbonylbenzylidine) - 1,4 - dihydro-1-imino-2-naphthoate, as, had cyclization to a naphthalene not occurred, a phenyl peak of intensity corresponding to ten protons could be expected for compound I.

The integral curve (Fig. 1, inset) was consistent with a total of either 30 or 32 protons and thus did not distinguish between I. R = H and I. R = Ac; however the three acetyl peaks at τ = 7.64, 7.58, and 7.40 p.p.m. clearly prove the triacetyl formulation—*e.g.*, I. R = H, as they show absorption peaks of three "*N*-acetyl" CH_3 groups in different environments. This further indicates

(1) J. E. Banfield, *J. Chem. Soc.*, 2098 (1961).
(2) A. G. Cairns-Smith, *J. Chem. Soc.*, 184 (1961).

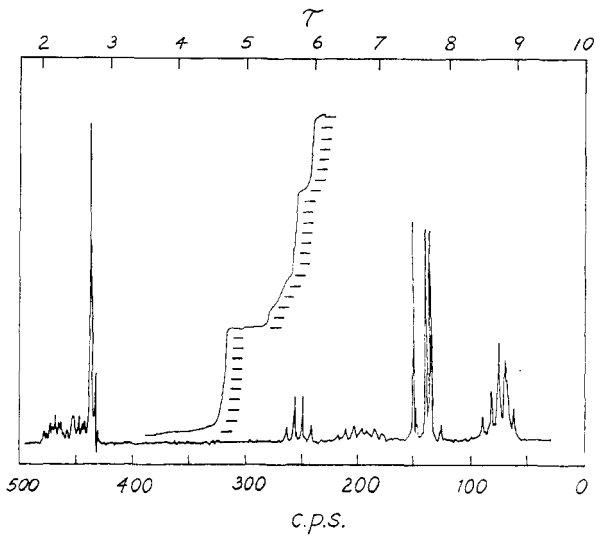


Figure 1

that the *N*-acetyl groups above and below the plane of the naphthalenic nucleus are differently situated which implies that the rotation of the benzyl and other substituents is restricted, with a time of half rotation long compared with the observed frequency. The quartet of lines centered at $\tau = 5.7$ p.p.m. can be attributed to the methylene hydrogens of the aliphatic carbethoxy group, while the lines of the three protons absorbing in the $\tau = 6.7$ p.p.m. region must include a quartet expected from the aromatic carbethoxy group; for a discussion of the unexpectedly high shielding of this group and of the assignments see below; the coupling is similar (J = 7 c.p.s.) for the lines of both groups. The over-lapping triplets at $\tau =$ 8.73 and $\tau = 8.51$ p.p.m. are due to the aromatic and aliphatic carbethoxy groups.

As it is inconceivable that more than 9 aromatic hydrogen atoms are present in the compound, the peaks in the region $\tau = 2.5$ p.p.m. of intensity corresponding to 10–11 protons must include absorption due to a nonaromatic proton. Of the two possibilities, the NH and the benzyl CH, the former is favored on the grounds of the observed shielding.[3] Four nonequivalent protons, as in an unsymmetrically *o*-disubstituted benzene, would (neglecting the weak *m*-coupling) give rise to a maximum of 16 lines shoud there be slightly different coupling constants between each pair of protons; in this case, no doubt, this would be due to different steric interactions at the peri postions. In fact, (neglecting the fine structure possibly due to *m*-coupling), about thirteen lines can be distinguished at lower τ values than the phenyl peak, one or more (see below) of which could be due to the NH group.

(3) L. M. Jackman, *Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, London, 1959, p. 126.

The group of lines at *ca.* $\tau = 6.7$ p.p.m. of relative intensity corresponding to three protons, and partly due to two methylene protons, must include at least two peaks due to a third proton; this must be, by elimination, the benzyl proton. Coupling through space being discounted, these peaks must originate from the diasteriomers (by restriction of rotation) of (I) present in approximately equal amounts.

Detailed examination of the pattern of the five main lines at *ca.* $\tau = 8.6$ p.p.m. reveals an intensity pattern not wholly consistent with two overlapping triplets (*e.g.*, 1:2:2:2:1); this suggests that the diasteriomers have slightly different chemical shifts for at least one of their respective ethoxy groups and that the pattern is that of either three, four, or five over-lapping triplets. The ethyl of the aromatic carbethoxy group may lie above or below the plane of the ring giving rise in all to four configurations (enantiomers not being counted) of compound I. R = H; thus the environment of the methyl group of the aromatic carbethoxy group will be influenced by the configuration of the adjacent amide group (a similar situation will arise with respect to the benzylic hydrogen); this may account for the fine structure of the methyl band. In a similar way,the above-mentioned ill-defined group of peaks in the $\tau =$ 6.58 p.p.m. region, partly due to a methylene group, may represent the contribution of overlapping quartets, the relative position of these depending on the relative configuration of the aromatic carbethoxy and acetamido groups. The sharpness of the lines of the quartet at τ *ca.* 5.7 p.p.m. supports its assignment to the aliphatic carbethoxy group, this being further away from centers of asymmetry and thus less subject to this environmental disturbance. The chemical shift of the methylene hydrogen atoms of the aromatic carbethoxy group (which apparently lies at τ values higher than those of the aliphatic group) may be due to the nonplanarity of the former group with the ring thus placing the protons in the region of space partly shielded by the aromatic ring currents in some of the conformations.

Examination of Catalin models of structure (I. R = H) shows, in support of the above argument, that considerable steric hinderance to rotation would be expected for each of the substituents on the naphthalenic nucleus.

EXPERIMENTAL

The proton resonance spectrum was determined at 60 m.c. for deuterochloroform solutions by Varian Associates, Calif. I am indebted to Dr. J. N. Shoolery for helpful comment on the results.

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