drawal. This unlikely "explanation" requires that the magnitude of inductive electron withdrawal be unaffected by the presence or absence of a positive charge on iodine. Alternatively, one may say that iodine withdraws electrons conjugatively more from the *ortho* position than from the *para* position in both iodobenzene and the diphenyliodonium ion.

As for electrostatic effect of the positively charged iodine, we can perhaps ascribe to it the whole shift downfield of the hydrogens in the diphenyliodonium cation relative to those in iodobenzene, but we cannot use it to explain the relative chemical shifts of the hydrogens within the diphenyliodonium cation.

It has been shown[10,13] that shielding parameters for substituents *para* to H^1, C^{13}, and F^{19} are well correlated by Hammett's σ constants. In the present work σ_p for the phenyliodonio group has been calculated from the equation obtained for the straight-line plot of Hammett's substituent constants[25] σ_p against the shielding parameters $d^x{}_p$ of the various substituents (x) obtained by Martin and Dailey.[12] The values for $d^x{}_p$ given by Spiesecke and Schneider[10a] give slightly lower values for σ_p for the phenyliodonio group.

$$d^x{}_p = -0.658\sigma_p + 0.21$$

The correlation between σ_m and $d^x{}_m$ is not as good as for σ_p and $d^x{}_p$ since the differences in the shielding at this position are small and give scattered points on a graph. This has also been observed in the C^{13} studies.[10a,13e] In the F^{19} studies there seems to be a better correlation for certain *meta* substituents only, with Taft's σ_I values.[13c-e] The poor correlation with σ_m has been attributed,[10] although inconclusively, to anisotropy[26] of the substituents (effect should be small on this position), to specific solvent interactions and to small "field effects" due to polar groups. While a plot of the $d^x{}_m$ values given by Martin and Dailey[12] *vs.* σ_m values[25] shows widely scattered points, the best line drawn through the two extremes of the scale, NH_2 and NO_2, gives a value for σ_m for the phenyliodonio group ($C_6H_5I^+$) which is in good agreement with previously found values. The equation of this line is given by

$$d^x{}_m = -0.47\sigma_m + 0.17$$

These values are included in Table I. It can be seen that in methanol, where ionization is almost complete, σ_m and σ_p are indeed very close ($\sigma_p - \sigma_m = 0.07$).

Table III summarizes the above constants of the phenyliodonio, trimethylammonio, dimethylsulfonio, diphenylcarbonio, and diazonio groups. It is seen that values obtained by nmr agree fairly well with those obtained by other methods.

From the available data the order of decreasing tendency for electron withdrawal appears to be as follows.

	N_2^+	>	$(C_6H_5)_2C^+$	>	$(CH_3)_2S^+$	>	$C_6H_5I^+$	~	$(CH_3)_3N^+$
σ_p:	3.04		2.48		1.16		0.88		0.86

Buckingham[16] has shown that the change in the proton screening constant Δd^x of a C–X bond when subjected to an electric field E, arising from polar groups in other parts of the molecule, is given by

$$\Delta d^x = -2 \times 10^{-12}E_z - 10^{-18}E^2$$

where E_z is the component of E in the bond direction. Recently Musher[20] showed that for most intramolecular fields the E^2 term is negligible and the nuclear magnetic shielding can be considered as varying linearly with the electric field.

Shaefer and Schneider[21] applied this linear relationship to several aromatic compounds and found a generally good agreement with values by simple MO calculations. Difficulties arise from the magnetic anisotropies of the substituents, affecting mostly the *ortho* positions. The following equation was derived[21] where

$$d^x = k\Delta\rho$$

d^x is the proton chemical shift in the x-substituted benzene relative to benzene (shielding parameter); $\Delta\rho$ is the "excess" local charge on the carbon atom in the aromatic system. In benzene the π-electron density ρ at each carbon atom is unity ($\Delta\rho = 0$). The constant k is found from the slope of the line when the proton chemical shifts d^x (with appropriate corrections for ring size) in the six π-electron system $C_5H_5^-$, C_6H_6, and $C_7H_7^+$ were plotted against $\Delta\rho$. The value of 10.7 ppm/electron thus obtained is in good agreement with previous values.[19,20] With this value for k, the electron densities ρ for the phenyliodonio group and iodobenzene were calculated and are included in Table I.

(25) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(26) The correction for anisotropy of iodine was determined from C^{13} nmr studies: G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

Reaction of 1-(*p*-Chlorophenyloxycarbonyl)-azetidine with Aromatic Amines

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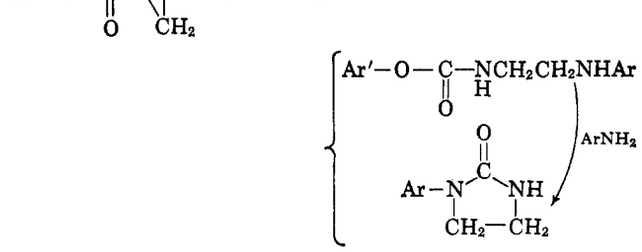
In a previous paper,[1] it has been reported that the reaction of 1-(aryloxycarbonyl)aziridines with aromatic amines gives 1-aryl-1,3-imidazolidin-2-ones along with 2-arylaminoethylcarbamic acid aryl esters at comparatively low temperatures.



Further, it has been shown that the imidazolidinones are formed from the ring-opened products in the presence of amines.

Now the study was extended to an azetidine derivative, 1-(*p*-chlorophenyloxycarbonyl)azetidine (I). I was prepard by the interfacial condensation reaction of *p*-chlorophenyl chloroformate with azetidine. Reactions of I with arylamines (II) were carried out at several temperatures. In contrast to the results with aziridine

(1) Y. Iwakura and A. Nabeya, *J. Org. Chem.*, **25**, 1118 (1960).

TABLE I

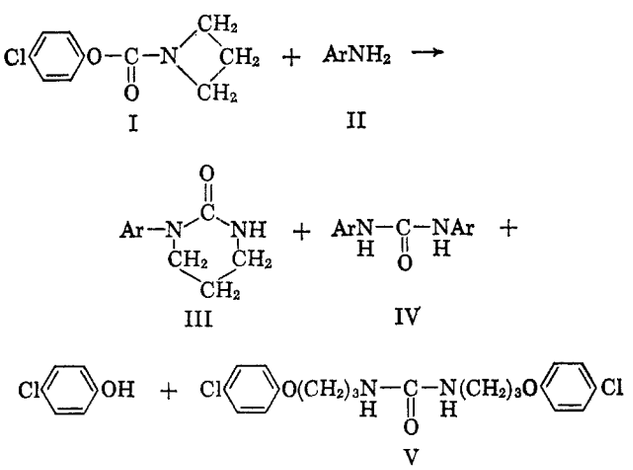
1-ARYLTETRAHYDRO-1H-PYRIMIDIN-2-ONES (III)

Compd	Ar	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IIIa	*p*-Ethoxyphenyl	199–200	$C_{12}H_{16}N_2O_2$	65.43	7.32	12.72	65.92	7.24	12.76
IIIb	*p*-Methoxyphenyl	202–203.5	$C_{11}H_{14}N_2O_2$	64.06	6.86	13.58	63.65	6.95	13.39
IIIc	*p*-Tolyl	203–204[a]	$C_{11}H_{14}N_2O$	69.44	7.42	14.73	68.72	7.00	14.69
IIId	Phenyl	201.5–202.5[b]	$C_{10}H_{12}N_2O$	68.16	6.86	15.90	67.62	6.96	15.65
IIIe	*p*-Chlorophenyl	166–168	$C_{10}H_{11}ClN_2O$	57.01	5.26	13.30	57.04	5.18	13.56

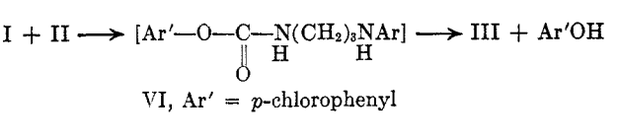
[a] M. Frankel [*Ber.*, **30**, 2497 (1897)] reported mp 207°. [b] A. Goldenring [*ibid.*, **23**, 1173 (1890)] and R. Delaby, R. Daomiens, and G. d'Huytéza [*Compt. Rend.*, **239**, 674 (1954)] reported mp 213–215°; R. Delaby and R. Damiens [*Festschr. Arthur Stoll*, 474 (1959); *Chem. Abstr.*, **53**, 376 (1959)] reported mp 215°. A sample prepared from 1-(3′-chloropropyl)-3-phenylurea by treatment with potassium hydroxide solution melted at 203.5–205.5°. Admixture of both samples gave no depression of melting point. The infrared spectra had bands at 3290, 3200 (NH), and at 1650 cm^{-1} (C=O).

derivatives, reaction of I with *p*-phenetidine (IIa) at 150° resulted in the recovery of large quantities of I (Scheme I), and only a small quantity of 1,3-di(*p*-ethoxyphenyl)urea (IVa) was obtained after 20 hr. However, at higher temperatures (180, 200, and 220°), I and arylamines (II) gave 1-aryltetrahydro-1H-pyrimidin-2-ones (III) and 1,3-diarylureas (IV) along with *p*-chlorophenol. At 220°, 1,3-di[3′-(*p*-chlorophenyloxy)propyl]urea (V) was also obtained, which was presumably formed *via* the ring-opened product of I with *p*-chlorophenol [3-(*p*-chlorophenyloxy)propylcarbamic acid *p*-chlorophenyl ester] in the presence of a small amount of water.[2]

SCHEME I



Possible mechanisms for the formation of III and IV were investigated (Table I). When an amine attacks I, two possible points of attack exist: the carbon adjacent to the nitrogen of the azetidine ring and the carbonyl carbon. If the ring carbon is attacked, 3-(arylamino)propylcarbamic acid *p*-chlorophenyl ester (VI) may be produced at first. Such a urethan (VI) may be rapidly changed to III by a cyclization reaction under the reaction conditions. 3-(*p*-Ethoxyphenylamino)-

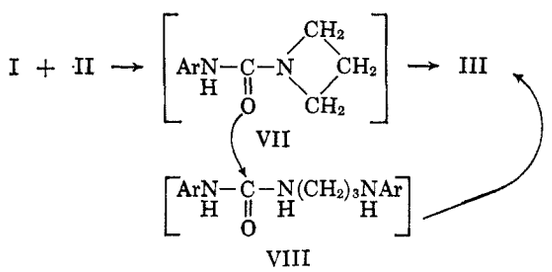


VI, Ar′ = *p*-chlorophenyl

propylcarbamic acid *p*-chlorophenyl ester (VIa) was heated in the presence of *p*-phenetidine at 200° for 5 hr. IIIa was obtained in 95% yield, and only a small quantity (<1%) of IVa was obtained.

(2) Y. Iwakura and A. Nabeya, *J. Org. Chem.*, **26**, 4384 (1961).

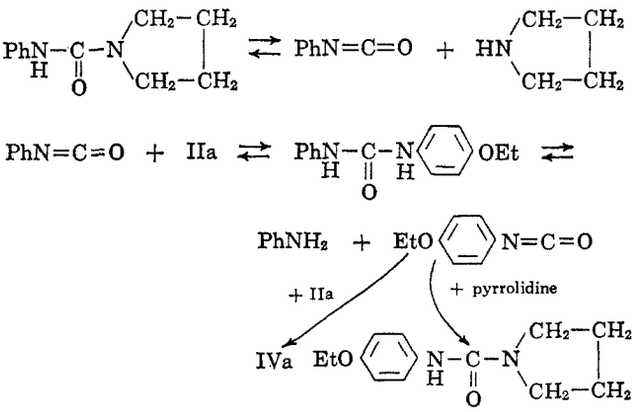
If an amine attacks the carbonyl carbon, an intermediate such as 1-(N-arylcarbamyl)azetidine (VII) has the possibility of giving III either by an isomerization reaction or by the cyclization reaction of the ring-opened product of VII with the amine, 1-[3′-(arylamino)propyl]-3-arylurea (VIII). Actually, 1-[3′-(*p*-ethoxyphenylamino)propyl]-3-phenylurea (VIIIa) was



changed to IIIa in high yield (87%) in the presence of IIa. However, 1-(N-phenylcarbamyl)azetidine (VIIa) and IIa gave IIIa only in 13% yield,[3] and IVa in 7% yield in the presence of *p*-chlorophenol at 200° after 20 hr. Therefore, the mechanism involving VI is more likely for the formation of III than the one involving VII, though the latter is not excluded.

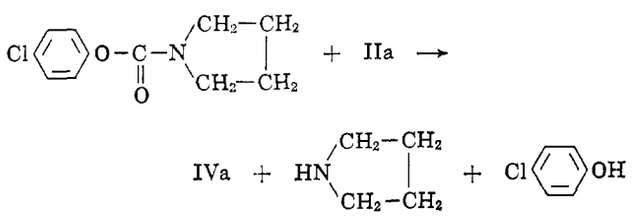
As mentioned above, VIa gave only a trace of IVa after being heated with IIa at 200°. Further, it was shown that in the reaction of I with IIa, the ratio IV: III was larger at shorter reaction times than at longer

(3) VII and amines cannot be expected to give VIII in high yield, because such a urea (having at least one hydrogen atom on the nitrogen) is apt to dissociate [T. Mukaiyama, *J. Soc. Org. Syn. Chem., Japan*, **16**, 55 (1958)] to the isocyanate and azetidine, followed by several amine interchange reactions, before the ring-opening reaction takes place under the reaction condition. Such is just considered to be the reason why VII and IIa gave a mixture of several products. In this connection, it was found that 1-(N-phenylcarbamyl)pyrrolidine and IIa gave 1-[-(*p*-ethoxyphenyl)carbamyl]-pyrrolidine in 54%, and IVa in 9% yield in the presence of *p*-chlorophenol at 200° after 20 hr. The reaction sequence may be as follows.



ones (the 20-hr reaction of I with IIa gave IVa in 5% and IIIa in 54% yield, while the 4-hr reaction gave IVa in 3.3% and IIIa in 1.4% yield at 200°). These facts suggest that the main route to IV probably does not involve VI.

To test the possibility that IV results from attack on the carbonyl carbon of I, 1-(*p*-chlorophenyloxycarbonyl)pyrrolidine was heated with IIa at 200° for 20 hr. Attack at the ring carbon of this pyrrolidine derivative is expected to be less likely than in the case of I, owing to the strain-free, five-membered ring. IVa was obtained in 5% yield, and the formation of pyrrolidine



was confirmed. This fact suggests that the formation of IV involves direct attack on the carbonyl carbon of I by an amine.

Experimental Section[4]

Azetidine was prepared by the procedure previously described.[5]

1-(*p*-Chlorophenyloxycarbonyl)azetidine (I).—*p*-Chlorophenyl chloroformate (19.1 g, 0.100 mole), azetidine (5.8 g, 0.102 mole), benzene (75 ml), and water (50 ml) were placed in a blender. The mixture was stirred vigorously while an aqueous solution of sodium hydroxide (4.2 g in 50 ml of water) was added dropwise, the temperature being kept below 10°. After addition was completed, stirring was continued for 3 hr. The benzene layer was separated and washed with water. After removal of benzene by distillation, the oily residue was recrystallized from petroleum ether (bp 40–80°) to give 17.1 g (81%) of I, mp 59–60.5°. Infrared spectrum had bands at 1720 and 1735 cm^{-1} (both C=O).

Anal. Calcd for $C_{10}H_{10}ClNO_2$: N, 6.63. Found: N, 6.48.

Examples of the Reaction of I with Arylamines (II). Reaction of I with *p*-Phenetidine (IIa) A. At 220°.—A sample of 1.06 g (0.005 mole) of I and 0.69 g (0.005 mole) of IIa was placed in a glass tube and sealed under an atmosphere of nitrogen. The tube was immersed in an oil bath maintained at 220 ± 5° for 20 hr. To the reaction mixture, which solidified on cooling, 30 ml of ether was added, and crystals were collected on a filter. The residue which was obtained from the ethereal filtrate after removal of ether, *p*-chlorophenol, and IIa, by distillation under reduced pressure was washed with ether–petroleum ether to give additional product, which was combined with the previous one. The combined product was separated into two parts: the one soluble in boiling water (150 ml) and the other insoluble. From the water-soluble part, 0.51 g (46%) of 1-(*p*-ethoxyphenyltetrahydro-1H-pyrimidin-2-one (IIIa) was obtained, mp 196–199°, and was recrystallized from water to give an analytical sample. The infrared spectrum of IIIa had bands at 3320, 3330 cm^{-1} (NH) and at 1660 cm^{-1} (C=O).

The water-insoluble portion gave 0.06 g (3%) of 1,3-di(*p*-ethoxyphenyl)urea (IVa) and 0.06 g (2% based on I) of 1,3-di[3′-(*p*-chlorophenyloxy)propyl]urea (V) after several fractional recrystallization from acetone and methanol.

V melted at 159–161° and had bands at 3350 cm^{-1} (NH) and 1617 cm^{-1} (C=O) in the infrared spectrum. An authentic sample of V was prepared from phosgene and 3-(*p*-chlorophenyloxy)propylamine, and melted at 160–161.5°. Infrared spectra of the two samples were identical.

Anal. Calcd for $C_{16}H_{22}Cl_2N_2O_3$: C, 57.43; H, 5.58; N, 7.05. Found: C, 57.27; H, 5.54; N, 6.87.

B. At 200° (or at 180°).—Reactions of I with II at 200° (or at 180°) were carried out in a quite similar manner. Treatment of the reaction products as described under A gave III from the water-soluble fraction but only IV from the insoluble portion.

C. At 150°.—Reaction of 1.06 g of I with 0.69 g of IIa at 150° for 20 hr resulted in the formation of a small amount of IVa (0.01 g) and recovery of 0.73 g of I, mp 54–56°.

Results obtained by the reaction of I with II are summarized in Table II.

TABLE II

RESULTS OBTAINED BY THE REACTION OF 1-*p*-CHLOROPHENYLOXYCARBONYL)AZETIDINE (I) WITH AROMATIC AMINES (II)

Compd	Ar	Temp, °C	Yields[a] (%) of— III	IV	V
IIa	*p*-Ethoxyphenyl	180	13	8	0
		200	54	5	0
		220	46	3	2
IIb	*p*-Methoxyphenyl	200	57	3	0
		220	50	3	4
IIc	*p*-Tolyl	200	9	5	0
		220	10	*b*	*b*
IId	Phenyl	180	5	<1	0
IIe	*p*-Chlorophenyl	200	9	4	0
		220	13	9	5

[a] Based on I. [b] Several attempts to isolate IV and V were unsuccessful.

The melting points and the analytical data of IV are summarized in Table III.

TABLE III

1,3-DIARYLUREA (IV)

Compd	Ar	Mp, °C	Formula	N, % Calcd	N, % Found
IVa	*p*-Ethoxyphenyl	225.5–226.5	$C_{17}H_{20}N_2O_3$	9.33	9.32
IVb	*p*-Methoxyphenyl	225–227	$C_{15}H_{16}N_2O_3$	10.29	10.26
IVc	*p*-Tolyl	259–260.5	$C_{15}H_{16}N_2O$	11.66	12.01
IVd	Phenyl	235	$C_{13}H_{12}N_2O$	13.20	13.52
IVe	*p*-Chlorophenyl	286–289	$C_{13}H_{10}Cl_2N_2O$	9.79	9.88

Preparation of 3-(*p*-Ethoxyphenylamino)propylcarbamic Acid *p*-Chlorophenyl Ester (VIa).—3-(*p*-Ethoxyphenylamino)propylamine was prepared from 3-(*p*-ethoxyphenylamino)propionitrile (mp 64–68°). Reduction of the nitrile carried out by a modification of a published procedure[6] with sodium in boiling 1-butanol. Crude amine distilled at 145–156° (0.5 mm), and was recrystallized from ether to give a 49% yield of a sample melting at 48–50.5°.

Condensation of *p*-chlorophenyl chloroformate (1 mole) with 3-(*p*-ethoxyphenylamino)propylamine (1 mole) using triethylamine as an acid acceptor gave VIa, mp 111–112° after several recrystallizations. The infrared spectrum of VIa had bands at 3350 (NH) and 1702 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{21}ClN_2O$: C, 61.96; H, 6.07; N, 8.03. Found: C, 62.31; H, 6.08; N, 8.18.

Reaction of VIa with IIa.—VIa (0.87 g, 0.0025 mole) and IIa (0.34 g, 0.0025 mole) were heated in a sealed glass tube (nitrogen) at 200 ± 3° for 5 hr. The reaction mixture was worked up in a manner similar to that described in A. From the fraction insoluble in boiling water, a small quantity of IVa was detected. The water-soluble portion gave 0.53 g (95%) of IIIa, melting at 196–199°.

Reaction of 1-[3′-(*p*-Ethoxyphenylamino)propyl]-3-phenylurea (VIIIa) with IIa.—VIIIa was prepared from 3-(*p*-ethoxyphenylamino)propylamine and phenyl isocyanate, mp 109–110.5°.

Anal. Calcd for $C_{18}H_{10}N_3O_2$: C, 71.75; H, 6.36; N, 13.95. Found: C, 72.06; H, 6.19; N, 13.89.

VIIIa (1.5 g, 0.005 mole) and IIa (1.37 g, 0.01 mole) were heated in a sealed glass tube as in A at 200 ± 5° for 5 hr. The reaction mixture, after being washed with hot ether, gave 0.96 g (87%) of IIIa, mp 197–199°, and 0.03 g (2%) of IVa from the ethereal filtrate. Addition of *p*-chlorophenol to the above reaction system (in a half equimolar amount of VIIIa) gave little change in the yields of IIIa (89%) and IVa (1%).

Reaction of 1-(N-Phenylcarbamyl)azetidine (VIIa) with IIa.—A sample of 2.64 g (0.015 mole) of VIIa, 4.11 g (0.03 mole) of IIa,

(4) Melting points and boiling points are uncorrected.

(5) W. R. Vaughan, R. S. Klonowski, R. S. McElhinney, and B. B. Millward, *J. Org. Chem.*, **26**, 138 (1961).

(6) C. M. Suter and E. W. Moffett, *J. Am. Chem. Soc.*, **56**, 487 (1934).

and 0.97 g (0.0075 mole) of *p*-chlorophenol was heated in a glass tube, which was not closed but formed a long vertical capillary, at 200 ± 8° for 20 hr. IIa and *p*-chlorophenol were distilled under reduced pressure. From the residue which contained much oily part, 0.44 g (13%) of IIIa and 0.32 g (7%) of IVa were obtained after recrystallizations from tetrahydrofuran. Absence of *p*-chlorophenol resulted in the marked change in the yields of IIIa (4%) and IVa (31%).

Reaction of 1-(*p*-Chlorophenyloxycarbonyl)pyrrolidine with IIa. —Reaction of 1-(*p*-chlorophenyloxycarbonyl)pyrrolidine (mp 55–56°) (2.25 g, 0.01 mole) and IIa (1.37 g, 0.01 mole) was carried out as in A at 200 ± 5° for 20 hr. The odor of pyrrolidine was quite pronounced when the reaction tube was opened after cooling. Dry toluene was added to the reaction mixture, and the mixture was submitted to fractional distillation. To the distillate (up to 110°) phenyl isocyanate was added. After removal of toluene and excess phenyl isocyanate by distillation under reduced pressure, a small amount of crystals was obtained, the infrared spectrum of which was identical with that of 1-(N-phenylcarbamyl)pyrrolidine. The distillation residue, after removal of toluene and a part of IIa, consisted almost entirely of unchanged 1-(*p*-chlorophenyloxycarbonyl)pyrrolidine and gave only 0.15 g (5%) of IVa on treatment with ether.

The Reaction of *p*-Nitrostyrene Oxide with Sodiomalonic Ester. II

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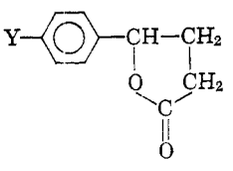
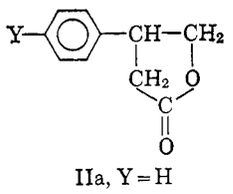
Received November 22, 1965

Recent work[1,2] on the reaction of sodiomalonic ester with styrene oxide has made it clear that products result from attack of malonate ester anion on both the α and β atoms of the epoxide, and that earlier reports[3] that only β attack occurs were erroneous. Presumably, the earlier errors were caused by similarities in melting points of the lactones Ia and IIa, which were produced by hydrolysis and decarboxylation of the initial condensation products. Proton magnetic resonance data have now established the structural assignments of both isomeric lactones without question.[1]



Ia, Y = H
Ib, Y = NO_2



IIa, Y = H
IIb, Y = NO_2

Some years ago one of us[4] studied the reaction of *p*-nitrostyrene oxide with sodiomalonic ester and reported that the resulting lactone (after hydrolysis and decarboxylation) had structure Ib, basing our conclusion on the early reports and on the fact that the product was identical with the product of nitration of the presumed Ia. The newer reports[1,2] suggested that our conclusion was in doubt, and was in fact probably incorrect (as turned out to be the case). The purpose of this note is to correct our earlier communication.

β-Phenyl-γ-butyrolactone (IIa), mp 46–47°, was isolated from the reaction of styrene oxide with sodiomalonic ester, as described earlier.[1-3] Its pmr spectrum corresponded with that described by DePuy and coworkers,[1] and we therefore agree[1,2] that α attack by diethyl malonate anion on styrene oxide is of greater importance than β attack. γ-Phenyl-γ-butyrolactone (Ia), mp 37°, was prepared[5] by catalytic reduction of β-benzoylpropionic acid.

When the β-phenyl lactone IIa was nitrated as described earlier,[4] β-nitrophenyl-γ-butyrolactone (IIb), mp 112–113°, was isolated. This had properties similar to those described earlier, and its synthesis and pmr spectrum led to the conclusion that it has structure IIb rather than that (Ib) assigned earlier. Genuine Ib was prepared by nitration of Ia and had mp 76–77°. Its pmr spectrum is described in the Experimental Section.

Repetition of the condensation of sodiomalonic ester with *p*-nitrostyrene oxide with careful scrutiny of intermediates in the reaction confirms the report[4] that only one product is formed in amounts substantial enough to observe. This product leads to IIb on hydrolysis and decarboxylation; it is the result of attack by ethyl malonate anion on the α position of *p*-nitrostyrene oxide. The powerful electron-attracting effect of the *p*-nitro group should enhance markedly the reactivity of the α position in styrene oxide toward nucleophilic attack, as suggested earlier,[4] and this is in fact observed.

Experimental Section

β-Phenyl-γ-butyrolactone (IIa), mp 46–47°, was prepared as described earlier by condensation of sodiomalonic ester with styrene oxide.[1-3] γ-Phenyl-γ-butyrolactone (Ia), mp 37°, was prepared[5] by hydrogenation of β-benzoylpropionic acid over palladium-on-charcoal catalyst.

β-*p*-Nitrophenyl-γ-butyrolactone (IIb), mp 112–113°, was prepared by nitration of Ib with acetyl nitrate, as described earlier.[4] Its pmr spectrum, taken in acetone in the aromatic (downfield) region and in chloroform in the remaining region, was very similar to that reported by DePuy for IIa.[6] A multiplet of about seven peaks assignable to the two dissimilar α-methylene protons was observed in the range τ 6.7–7.7, the benzylic hydrogen was assigned to the doublet of triplets in the τ 5.9–6.7 region, and the γ-methylene protons appear as two triplets in the τ 5.1–5.9 region. Cristol and Helmreich[4] had proven the location of the nitro group by oxidation of IIb to *p*-nitrobenzoic acid. The pmr spectrum confirms this by giving two doublets (J = 9 cps) of equal intensity (two protons each). The one at τ 1.80 is assigned to the protons *ortho* to the nitro group and that at τ 2.35 to those *meta* to the nitro group.

γ-Nitrophenyl-γ-butyrolactone (Ib) was prepared from γ-phenyl-γ-butyrolactone (Ia) by nitration with acetyl nitrate at below 0°, substantially as described for IIb. Chromatography on silica gel, using methylene chloride–chloroform (1:1) as eluting solvent, followed by recrystallization from chloroform–carbon tetrachloride (4:1), gave Ib, mp 76–77°, in 20% yield.

Anal. Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.38. Found: C, 58.04; H, 4.39.

Oxidation with sodium dichromate and sulfuric acid[7] gave *p*-nitrobenzoic acid, mp 236°, proving the position of the nitro group.[7]

Pmr spectra were taken in both acetone and chloroform, and showed great similarity to that reported for Ia. The four methylene protons (α and β to the carbonyl) give a complex

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(5) N. H. Cromwell, P. L. Creger, and K. E. Cook, *ibid.*, **78**, 4412 (1956).
(6) Pmr spectra were obtained using a Varian A-60 nmr instrument using tetramethylsilane (τ 10.00) as internal standard.
(7) The general procedure of O. Kamm and A. O. Mathews, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p 393.