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Addition of Diethyl & Dimethyl Acetylenedicarboxylates to Catechol—Synthesis of Benzodioxole Derivatives*†

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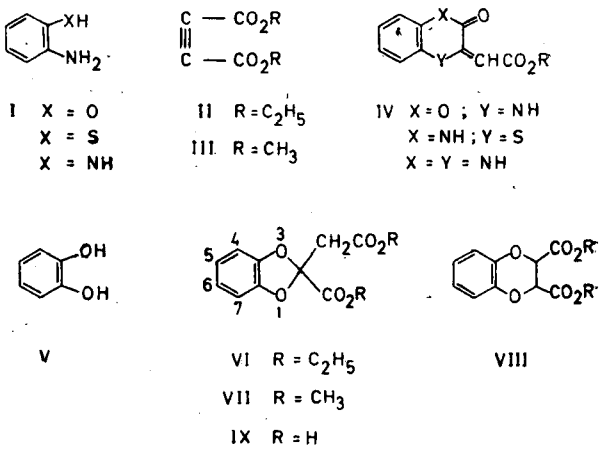
2-Ethoxycarbonylmethyl-2-ethoxycarbonyl- (VI) and 2-methoxycarbonylmethyl-2-methoxycarbonyl-(VII)-benzodioxoles are obtained in high yields by the addition of catechol to diethyl and dimethyl acetylenedicarboxylate. Alkaline hydrolysis of VI affords, besides the expected diacid IX, the rearranged benzodioxane acid X. The alkali-induced interconversions of IX and X are likely to be mediated by phenoxy-maleic acid XVIII and fumaric acid XIX. Pyrolysis of ammonium salts of diacid IX yields the novel spirosuccinimides XXX and XXXI. LAH reduction of XXXI results in the formation of a bimolecular product of likely structure XXXIX, besides the expected spiropyrrolidine XXVI.

THE reaction of anilines (I) carrying in the *ortho* position hydroxyl[1,2], mercapto[3,4] or amino[5,6] group with diethyl acetylenedicarboxylate (II) or the dimethyl ester (III) has been reported to yield products of the type (IV). The behaviour of catechol (V) towards (II) and (III) has not been investigated although phenols have been reported to add to the acetylene bond to form mixtures of phenoxy-fumarates (XV) and maleates (XVI)[7]. We find that in the absence of a base catalyst, catechol and (II) react with each other very sluggishly. However, in boiling methanol and in the presence of catalytic amounts of sodium methoxide, a liquid product was formed in 78% yield‡. Its IR spectrum showed the presence of saturated ester C=O bands. Its NMR spectrum§ in CCl_4 showed a singlet at 6·78 for 4 aromatic H, a CH_2 singlet at 3·22 and two ethyl ester groupings (quartets at 4·09, 4·23 and triplets at 1·15 and 1·23). These data indicated that the product had structure VI, arising from a 1:1 addition of V to II. Likewise, catechol and III gave the crystalline product VII in 75% yield. Analytical, IR and NMR data ruled out structure XVII (type IV) as also another possibility VIII. NMR spectra of crude total reaction products of V with II or III showed that traces of other products, possibly XVII and XX, were formed in minute yields (NMR signals due to =CH at 6·10 and 5·15).

Alkaline treatment of VI or VII followed by acidification afforded two crystalline acids in varying proportions. The major product, m.p. 177-9°,



was water-soluble. Its analysis, IR spectrum ($\nu_{C=O}$ 1700, 1720 cm^{-1}) and NMR spectrum in D_2O [δ 3·18 (*s*, $-CH_2$) and 6·67 ppm (*s*, 4 aromatic H)] showed that it had the expected structure IX. The minor product, m.p. 198-200°, was water-insoluble having the empirical formula, $C_{10}H_6O_5$. Its IR spectrum showed bands at 1780, 1740, 1680 and 1650 cm^{-1}. The NMR spectrum in DMSO-d_6 had signals at 6·25 (*s*, =CH) and 7·12 (4 aromatic H). These data indicated that it was very likely to have structure X. Catalytic reduction led to quantitative yield of dihydro acid XIII whose $CDCl_3$ NMR spectrum showed besides 4 aromatic protons at 7·08 and the CO_2H proton at 10·17, a triplet for the methine H at 5·13 (J=5·5 Hz) and a doublet for $-CH_2-$ at 3·14 (J=5·5 Hz). This observation ruled out XIII (although not very rigorously), as an alternative structure possibility for the water-insoluble acid, since XIV, the dihydroderivative of XIII, could be expected to show a quartet for the methine proton and a complex pattern for the CH_2 group.

In a series of phenoxy-fumarates (XV) and phenoxy-maleates (XVI), it is known that the vinyl protons

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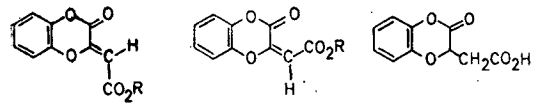
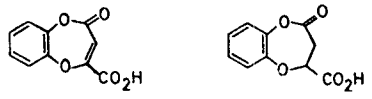
‡After this work was completed, a report by V. Rosnati, F. Sannicolo and G. Zecchi [*Gazz. chim. ital.*, **100** (1970), 3] has appeared on the formation of benzodioxole derivatives by the addition of catechol to acetylenes. Compound VII was obtained by these authors in 7% yield.

§Chemical shifts in ppm downfield with TMS as reference (Varian 60 spectrometer).

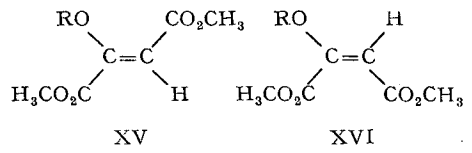


X R = H XI R = H XII

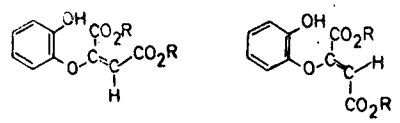
XVII R = CH_3



XIII XIV



XV XVI



XVIII R = H XIX R = H

XX R = CH_3 XXI R = CH_3

of the former appear around 6·7 and of the latter around 5·2 (ref. 7). The appearance of the vinyl proton signal in the water-insoluble acid at 6·25 suggests that its C=O functions are *trans*-oriented as in X and that they are not *cis* as in XI. Acid-catalysed esterification of X in refluxing methanol led to the formation of the corresponding ester XVII, m.p. 102-3°, in 65% yield. The mother liquor showed the presence of other products.

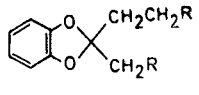
Treatment of ester XVII in methanol containing sodium methoxide led to quantitative conversion to the benzodioxole ester VII. This suggested the possibility that the primary product of reaction of (V) and (III) might be in fact, the benzodioxane XVII. But this was rendered untenable by the finding that even in THF solution in the presence of K_2CO_3, III and V interacted to form only VII. There was no evidence for the presence of XVII in the total crude product.

Attention was next focussed on the stabilities of the benzodioxole and benzodioxane acids and esters, especially in connection with the formation of both acids IX and X from VII. Ester VII was unchanged by heating at 140° for 4 hr; further it was found to be stable in methanol in the presence of either mineral acid or sodium methoxide. Acid IX was stable to aqueous acid, but treatment with aqueous NaOH, followed by acidification afforded besides starting material, a small amount of X, the two being easily separated by virtue of their very different solubilities in water. It is likely that this happened by a base-induced retro-Michael reaction, followed by lactonization. Evidence for this was obtained from NMR experiments. A D_2O solution of IX containing 2-4 equivalents of NaOD initially showed a 2 proton CH_2 singlet at 3·18 and a 4 proton aromatic singlet at 6·85. Gradually singlets of varying intensities appeared at 5·2, 6·3 and 6·55. These could be assigned to olefinic protons in XVIII, V and XIX respectively. Acidification of this mixture, evaporation and treatment with water led to the separation of acids IX and X. In one of the preparative scale hydrolysis of diester VI, acid XVIII, $C_{10}H_8O_6$, was in fact isolated in a crystalline form and characterized; m.p. 162°; ν_{OH} 3380, 3420, $\nu_{C=O}$ 1700 cm^{-1}; NMR in D_2O: 5·23 (*s*, =CH), 7·05 (4 aromatic H).

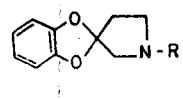
It was mentioned earlier that acid-catalysed esterification of X in the hot mainly afforded the ester XVII, which was transformed into benzodioxole derivative VII by NaOMe in MeOH. The mother liquor from the esterification of X afforded a gummy product whose NMR spectrum showed singlet signals at 3·2, 5·1, 6·3 and 6·37. These signals could be attributed respectively to $-CH_2-$ ii VII, and to =CH— in XX, XVII and XXI. This suggested that ester XVII might be unstable to acid in methanol solution. This was in fact found to be the case. A solution of XVII in methanol containing a few drops of HCl was set aside overnight at room temperature in the cold and evaporated. The residual gum was crystallized from ether-hexane to give a product, m.p. 73-75°. Analysis and NMR spectrum in $CDCl_3$ indicated it to be a mixture of XVII and XXI in the approximate ratio of 1 : 1 (signals at 6·53 due to =CH, and, at 3·75 due to $2CO_2CH_3$ in XXI, at 6·45 due to =CH and at 3·80 due to CO_2CH_3 in XVII). A four days old $CDCl_3$ solution showed partial changeover of XXI to XVII with loss of methanol.

Acid X was likewise unstable to both acid and alkali. A solution of X in a mixture of 1 : 2 $CDCl_3$-DMSO-d_6 showed a (apparent) 4 aromatic proton singlet at 7·15 and the vinyl proton singlet at 6·20. This was set aside with a drop of HCl for 24 hr and the spectrum rerun. The vinyl proton singlet had shifted down to 6·42, while the aromatic pattern changed to a complex one. It thus appeared that X was completely transformed to the lactone-opened product XIX. This could not be isolated, as it appeared mainly to cyclize to X and partially to IX (NMR signals at 6·85 and 3·35). Treatment of X with aqueous alkali and acidification again resulted in large-scale conversion to the benzodioxole acid IX, with only a small recovery of X. NMR observations of NaOD treated solution of X in D_2O indicated that maleic acid XVIII and fumaric acid XIX were being formed and converted to IX in a Michael reaction.

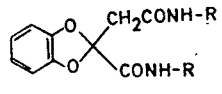
The ready availability of the novel benzodioxole derivatives VI and VII prompted us to study their usefulness in the synthesis of compounds of potential biological significance. In particular, we were interested in the preparation of the spiropyrrolidine XXIV. $LiAlH_4$ reduction of the esters gave a gummy alcohol XXII, which was converted into a crystalline dichloride XXIII. However, attempts at condensation of XXIII with methanolic ammonia or benzylamine failed to yield XXIV or XXV. The dibromide corresponding to XXIII would be more reactive for such condensations, but this



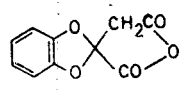
XXII R = OH
XXIII R = Cl



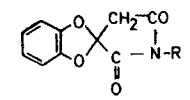
XXIV R = H
XXV R = $PhCH_2$
XXXVI R = CH_3



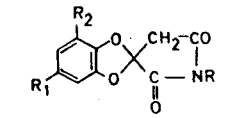
XXVII R = p-anisyl
XXVIII R = CH_3



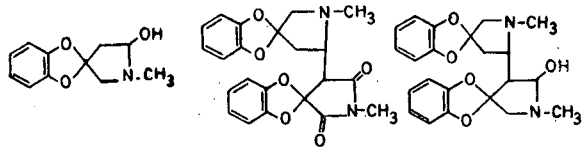
XXX



XXX R = H
XXXI R = CH_3
XXXII R = $(CH_2)_3NH_2$
XXXIII R = $(CH_2)_2N(CH_3)_2$
XXXIV R = $-CH_2CH_2CH_2N(CH_3)_2$



XXXV R = R_2=H; R_1=NO_2
XXXVI R = CH_3; R_1=R_2=NO_2



XXXVII XXXVIII XXXIX

could not be obtained from XXII by treatment with PBr_3.

A second approach for the synthesis of compounds of type XXIV envisaged the formation of imides of the diacid IX. Heating the diester VII with *p*-anisidine for several hours afforded only the diamide XXVII in poor yield. Hydrazine seemed to convert VII into catechol, but VII reacted with methanolic methylamine exothermally to give the diamide XXVIII in high yield. Pyrolysis of XXVIII alone or in *o*-dichlorobenzene or treatment of XXVIII with acetic anhydride failed to convert it into an imide. Acid IX could not be transformed to its anhydride XXIX by acetyl chloride or acetic anhydride. Successful preparations of imides XXX and XXXI were finally achieved in good yields by the pyrolysis of the respective ammonium salts *in vacuo*. This procedure could not be extended to the synthesis of XXXII and XXXIII nor could XXXIV be prepared from XXX by conventional alkylation. Nitration of XXX with HNO_3 alone afforded the mononitro derivative XXXV, while the action of HNO_3-H_2SO_4 mixture on XXXI led to a dinitro derivative, presumably XXXVI.

$LiAlH_4$ reduction of imide XXX failed to yield the spiropyrrolidine XXIV. Besides small amounts of starting material, catechol was the only other product isolable. Apparently $LiAlH_4$, acting as a strong base, had caused a retro-Michael reaction of XXX. $LiAlH_4$ reduction of imide XXXI in hot THF gave a high yield of the oily base XXVI, characterized as a crystalline maleate. When the reduction was performed in cold ether-THF mixture, a significant amount of a basic crystalline product, m.p. 98-100°, was also isolated. Its analysis and mass spectrum indicated the molecular formula $C_{22}H_{24}O_5N_2$. Its IR spectrum in CH_2Cl_2 showed OH absorption at 3540 cm^{-1}. Its NMR spectrum in $CDCl_3$ showed absorption in the aromatic region, NCH_3 singlet at 2·48 a singlet for OH at 3·1 and complex signals between 2·1 and 3·5, characteristic of methylene groups attached to carbon or nitrogen, besides a one-proton doublet at 4·33 and a two-proton singlet at 4·13. We like to formulate this tentatively as XXXIX on the reasoning that partial reduction of the imide XXXI may lead to the carbinol-amine XXXVII. This may undergo aldol condensation with itself to yield XXXIX or with a second molecule of XXXI to form XXXVIII, which can then be further reduced to the product. Partial reduction of imides to aldehydes has precedents in the literature[8]. Upon treatment with 2,4-dinitrophenylhydrazine HCl in alcohol, XXXIX formed the dinitrophenylhydrazone HCl of XXXVII, m.p. 201-3° (d) (from ethanol) (Found: C, 48·48; H, 4·73; N, 16·81; Cl, 9·13. $C_{17}H_{18}ClN_5O_6$ requires C, 48·17; H, 4·28; N, 16·53; Cl, 8·37%).

Experimental Procedure

IR spectra were run for Nujol mulls, unless otherwise stated, on a Perkin-Elmer infracord spectrophotometer.

2-Methoxycarbonylmethyl-2-methoxycarbonyl-benzodioxole (VII) — To a solution of catechol (V) (22 g) in methanol (85 ml) in which a small piece of sodium (~25 mg) had been dissolved, was added slowly dimethylacetylene dicarboxylate (III) (30 g), when an exothermic reaction took place. After 24 hr reflux, the solution was concentrated and cooled to give VII, which recrystallized from MeOH (38 g, 75%), m.p. 65-66°; $\nu_{C=O}$ 1720, 1740 cm^{-1}; NMR: CCl_4: 3·22 (*s*, 2H, $-CH_2$), 3·62 (*s*, CO_2CH_3), 3·73 (*s*, CO_2CH_3), 6·77 (*s*, 4 aromatic H) (Found: C, 57·41; H, 5·04. $C_{12}H_{12}O_6$ requires C, 57·14; H, 4·80%).

The same ester was also formed in about 50% yield (NMR estimation) when V (1·1 g) and III (1·42 g) were left in THF (15 ml) containing anhydrous potassium carbonate (0·1 g) overnight and the mixture then refluxed for 2 hr.

Diethyl acetylenedicarboxylate (II) (17 g) and catechol (11 g) underwent reaction in ethanol (50 ml) in which sodium (~20 mg) had been dissolved to give 2-ethoxycarbonylmethyl-2-ethoxycarbonyl-benzodioxole VI (22 g) as an oil. In one experiment, where this reaction was run inadvertently in methanol, a crystalline product was obtained; m.p. 88-90°; $\nu_{C=O}$ 1740, 1750 cm^{-1}; NMR 1·18 (*t*, 3H, CH_2-CH_3), 3·20 (*s*, 2H, $-CH_2-\overset{\overset{O}{\|}}{C}-O-$), 3·75 (*s*, 3H, CO_2CH_3), 4·12 (*q*, 2H, $CO_2CH_2CH_3$), 6·77 (*s*, 4 aromatic H) (Found: C, 58·95; H, 5·18. $C_{13}H_{14}O_6$ requires C, 58·64; H, 5·30%). This is probably 2-methoxycarbonylmethyl-2-ethoxycarbonyl-benzodioxole, arising from VI by base-catalysed exchange of the less hindered ethyl ester with methanol.

Alkaline hydrolysis of ester VI — A solution of the diester VI (5·6 g) in ethanol (10 ml) was mixed with water (20 ml) containing NaOH (2 g). After being left overnight at room temp., the solution was acidified and extracted with ether to give a gummy product (5·5 g), which was triturated with water (10 ml) and filtered. The insoluble part (0·4 g) was crystallized from aq. ethanol to give the benzodioxane acid X, m.p. 198-200° (Found: C, 58·43; H, 3·35. $C_{10}H_6O_5$ requires C, 58·26; H, 2·93%). The water-soluble part was recovered by evaporation to dryness and crystallized from $CHCl_3$-ether to afford diacid IX (4 g), m.p. 177-9° (Found: C, 53·35; H, 3·60. $C_{10}H_8O_6$ requires C, 53·58; H, 3·60%).

Reduction of acid X — A solution of acid X (10 g) in MeOH (100 ml) was shaken with hydrogen (1 atm) at room temperature using 10% Pd-C (1 g), until 1 mole of hydrogen was taken up. The mixture was filtered and the filtrate evaporated to dryness. The residual oil crystallized after several days standing and recrystallized from ether-hexane to afford XII (7·7 g), m.p. 160-61°; $\nu_{C=O}$ 1700, 1780 cm^{-1} (Found: C, 57·95; H, 3·93. $C_{10}H_8O_5$ requires C, 57·69; H, 3·87%).

Esterification of acid X — A solution of X (5 g) in methanol (100 ml) containing conc. H_2SO_4 (5 drops) was heated under reflux overnight. The gummy ester became crystalline on rubbing with methanol and was recrystallized from the same solvent to yield lactone-ester XVII (3·3 g); m.p. 102-3°; $\nu_{C=O}$ 1780, 1720, $\nu_{C=C}$ 1650 cm^{-1}; NMR in $CDCl_3$: 3·78 (*s*, CO_2CH_3), 6·38 (*s*, =CH) and 7·13 (approx. *s*, 4 aromatic H) (Found: C, 60·62; H, 3·99. $C_{11}H_8O_5$ requires C, 60·00; H, 3·66%).

Acid treatment of ester XVII — A solution of XVII (0·3 g) in methanol (10 ml), containing 3 drops of 2*N* HCl was left overnight at room temp. It was then concentrated, treated with water and extracted with ether to give a gum (0·25 g) whose NMR spectrum indicated it to be a 1:1 mixture of XXI and XVII. The gum became crystalline when rubbed with hexane and was recrystallized from the same solvent; m.p. 73-75°; ν_{OH} 3400, 3490; $\nu_{C=O}$ 1700, 1720, 1760; $\nu_{C=C}$ 1640 cm^{-1} [Found: C, 58·96; H, 4·24. $C_{11}H_8O_5+C_{12}H_{12}O_6$ (1:1) requires C, 58·57; H, 4·22%].

Esterification of acid IX — Acid IX (0·5 g) was esterified as before with methanol to afford diester VII (0·5 g), m.p. and m.m.p. 63-65°.

Interconversion of acids IX *and* X — A solution of benzodioxole and IX (0·44 g) in ethanol (1 ml) and water (2 ml) containing NaOH (0·2 g) was left at room temp. overnight. It was then acidified and extracted with ether. The ether layer was evaporated and separated into water-soluble (320 mg) and water-insoluble (4·5 mg) compounds, identified by m.m.p. determinations as IX and X respectively.

Similarly, benzodioxane acid X (1 g) was treated with NaOH (0·5 g) in ethanol (5 ml) and water (10 ml) to give X (0·15 g) and IX (0·6 g).

Reduction of diester VI — A solution of VI (10 g) in ether (50 ml) was added slowly to a stirred suspension of $LiAlH_4$ (6 g) in ether (50 ml). The mixture was stirred overnight, decomposed with water, and the ether layer decanted off. Evaporation gave the alcohol XXII as an oil (6·1 g).

2-(β-Chloroethyl)-2-chloromethylbenzodioxole (XXIII) — The above alcohol (1 g) was treated with thionyl chloride (5 ml) in dry benzene (25 ml) at room temp. overnight to afford the dichloride XXIII (0·95 g) which crystallized from hexane; m.p. 105-7° (Found: C, 51·53; H, 4·55. $C_{10}H_{10}Cl_2O_2$ requires C, 51·52; H, 4·32%).

Reaction of diester VII *with p-anisidine* — VII (2·5 g) and *p*-anisidine (2·5 g) were heated together at 100° for 6 hr. The product was dissolved in ether and the ether layer washed with 2*N* HCl and then with water. Evaporation of the residue from MeOH afforded the bis-amide XXVII (0·7 g), m.p. 152-3° (Found: C, 66·16; H, 5·40; N, 6·84. $C_{24}H_{22}N_2O_6$ requires C, 66·25; H, 5·10; N, 6·45%).

Reaction of diester VII *with methylamine* — VII (5 g) was added to 33% methylamine in ethanol (25 ml). An exothermic reaction occurred and a clear solution was obtained. This was followed by separation of a crystalline product. Recrystallization from ethanol gave the bis-amide XXVIII (3·8 g); m.p. 205-7°; ν_{NH} 3260, $\nu_{C=O}$ 1650 cm^{-1} (Found: C, 57·46; H, 5·70; N, 10·96. $C_{12}H_{14}N_2O_4$ requires C, 57·59; H, 5·64; N, 11·20%).

Spirosuccinimide XXX — Diacid IX (25 g) was dissolved in ethanol (130 ml) saturated with ammonia and the resultant solution evaporated to dryness. The residual salt was distilled *in vacuo* and the imide distilled at 200-15°/1-2 mm, as an oil which rapidly crystallized (19 g). Recrystallization from ether-hexane gave the pure imide XXX; m.p. 160-61°; ν_{NH} 3200; $\nu_{C=O}$ 1720, 1800 cm^{-1} (Found: C, 58·73; H, 3·35; N, 7·13. $C_{10}H_7NO_4$ requires C, 58·54; H, 3·44; N, 6·83%).

Spirosuccinimide XXXI — Sublimation of the methylamine salt of diacid IX (5 g) *in vacuo* at 160-70°/1-2 mm gave the methyl imide XXXI, which crystallized from methanol; yield 3·5 g; m.p. 110-12°; $\nu_{C=O}$ 1700, 1790 cm^{-1}; NMR in CCl_4: 3·03 (*s*, 3H, NCH_3), 3·13 (*s*, 2H, $-CH_2-$) and 6·82 (*s*, 4 aromatic H) (Found: C, 60·36; H, 4·47; N, 6·62. $C_{11}H_9NO_4$ requires C, 60·27; H, 4·14; N, 6·39%).

Nitration of imide XXX — XXX (5 g) was added in small portions to conc. HNO_3 (10 ml) at room temp. during 15 min. After being set aside for another 15 min, the solution was diluted with water. The precipitate was recrystallized from acetone-ethanol to afford XXXV (5·2 g); m.p. 231-3°; $\nu_{C=O}$ 1720, 1780, 1800 cm^{-1}; NMR in 1:2 $CDCl_3$-DMSO-d_6: 3·43 (*s*, 2H, $-CH_2$), 7·15 (*d*, J=8·5 Hz, 1H), 7·78 (*d*, J=2 Hz, 1H), 7·97 (*q*, J=8·5, 2Hz, H), 12·08 (broad *s*, 1H, NH) (Found: C, 48·39; H, 2·58; N, 11·09. $C_{10}H_6N_2O_6$ requires C, 48·01; H, 2·42; N, 11·20%).

Nitration of imide XXXI — Methyl imide XXXI (0·5 g) was added to a mixture of conc. HNO_3 (0·5 ml) and conc. H_2SO_4 (0·5 ml) cooled in an ice-bath. The resultant solution was left at 0-5° for 1½ hr and poured into water. The precipitate was crystallized from ethanol to afford dinitroimide XXXVI (0·6 g), m.p. 229-31°; $\nu_{C=O}$ 1710, 1780, 1800 cm^{-1} (Found: C, 43·03; H, 2·65; N, 13·94. $C_{11}H_7N_3O_8$ requires C, 42·73; H, 2·28; N, 13·59%).

LAH reduction of imide XXXI — A solution of the imide (6·7 g) in dry THF (25 ml) and dry ether (100 ml) was added to a stirred suspension of $LiAlH_4$ (4 g) in ether (50 ml) at room temperature. The mixture was stirred overnight and decomposed with ether. The ether layer was evaporated and the residue treated with maleic acid (4 g) in ether (20 ml). The resultant gummy salt was rubbed with ethanol to give a crystalline maleate (2 g), m.p. 145-55°, which was recrystallized from methanol-ether to yield the maleate of spiropyrrolidine XXVI (1·3 g), m.p. 166-8° (Found: C, 58·87; H, 5·68; N, 4·49. $C_{15}H_{17}NO_6$ requires C, 58·63; H, 5·58; N, 4·56%). NMR of free base in CCl_4: 6·68 (*s*, 4 aromatic H); broad absorption between 2 and 3·5 for 9H. The mother liquors from the crystallization of the maleate were combined and evaporated and the free base liberated from it. This became crystalline when rubbed with hexane; 0·9 g, m.p. 90-93°; two recrystallizations from hexane gave pure XXXIX, m.p. 98-100° (Found: C, 66·35; H, 6·21; N, 6·96. $C_{22}H_{24}N_2O_5$ requires C, 66·65; H, 6·10; N, 7·07%). The mass spectrum showed the molecular ion peak at 296. Small peaks at *m/e* 278 and 266 were also seen.

When the reduction of XXXI (5·7 g) was carried out in refluxing THF, only XXVI was isolable as the crystalline maleate (2·6 g), m.p. 166-7°.

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References

1. Iwanami, Y., *Bull. chem. Soc. Japan*, (1964), 1745.
2. Nair, M. D., *Indian J. Chem.*, **7** (1969), 229.
3. Iwanami, Y., *J. chem. Soc. Japan*, **83** (1962), 100.
4. Kalbag, S. M., Nair, M. D., Rajagopalan, P. & Talaty, C. N., *Tetrahedron*, **23** (1967), 1911.
5. Iwanami, Y., *J. chem. Soc. Japan*, **83** (1962), 590.
6. Nair, M. D. & Mehta, S. R., *Indian J. Chem.*, **6** (1968), 490.
7. Gudi, M. N., Hiriyakkanavar, J. G. & George, M. V., *Indian J. Chem.*, **7** (1969), 971.
8. Tagmann, E., Sury, E. & Hoffmann, K., *Helv. chim. Acta*, **37** (1954), 185.