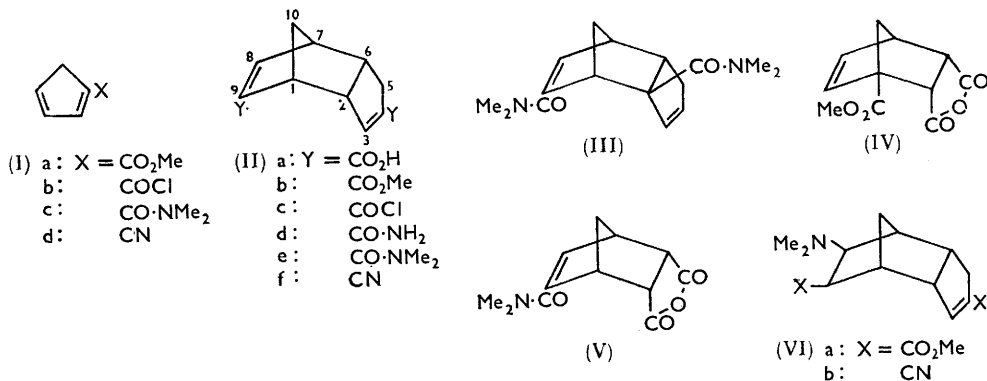**365.** *Simple Derivatives of Cyclopentadiene. Part II.**

By DAVID PETERS.

The dimer of cyclopentadienecarboxylic acid has been converted into its diacid chloride, diamide, bisdimethylamide, and dinitrile. Depolymerisation of these dimers, redimerisation of the resulting monomers, reaction of the monomers with maleic anhydride, and ultraviolet spectra of all these compounds are reported. The chloride and the nitrile behave like the ester, the dimers depolymerising to the 1-substituted cyclopentadienes which revert largely to the starting dimer. The dimethylamide monomer, however, gives mainly a new dimer and a maleic anhydride adduct which is derived from the 2-substituted cyclopentadiene. Michael addition of dimethylamine to the bicycloheptene double bond occurs readily with the dimeric ester and nitrile, but not with the dimethylamide.

INVESTIGATION of the structures and interconversion of the monomer (Ia) and the dimer (IIb)† of methyl cyclopentadiene-1-carboxylate (Ia) has recently proved the structures illustrated, though some uncertainty remains concerning the structure of the dimer. Our next objective was the preparation of cyclopentadienes carrying a range of the common

(I) a: X = CO₂Me
   b: COCl
   c: CO·NMe₂
   d: CN

(II) a: Y = CO₂H
   b: CO₂Me
   c: COCl
   d: CO·NH₂
   e: CO·NMe₂
   f: CN

(III)

(IV)

(V)

(VI) a: X = CO₂Me
    b: CN

substituents. Of such monosubstituted cyclopentadienes, only those with the alkyl,[1] phenyl,[2] carboxyl,[3] nitro-,[4] and various positively charged substituents [5] have hitherto

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* Part I, *J.*, 1959, 1761.

† Location of the substituent Y at position 4 rather than position 3, and the *endo*- rather than the *exo*-configuration of the right-hand ring in formulæ (II)—(VI), are probable but not finally proved.

[1] Alder and Holtzrichter, *Annalen*, 1936, **524**, 145; Zelinski and Levina, *Ber.*, 1933, **66**, 477; Edson, Powell, and Fischer, *Ind. Eng. Chem.*, 1948, **40**, 1526; *Analyt. Chem.*, 1948, **20**, 213, 510; Craven, *Diss. Abs.*, 1955, **15**, 2408.

[2] Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.

[3] Thiele, *Ber.*, 1901, **34**, 68.

[4] Thiele, *Ber.*, 1900, **33**, 666.

[5] Lloyd and Sneezum, *Chem. and Ind.*, 1955, 1221; Ramirez and Levy, *J. Org. Chem.*, 1956, **21**, 488, 1333; *J. Amer. Chem. Soc.*, 1957, **79**, 67, 6167; Spooncer, *Diss. Abs.*, 1956, **16**, 458.

been identified with certainty. The simplest routes would be reaction of the cyclopentadienyl anion with suitable reagents, but some preliminary experiments were not encouraging. Another possibility lay in reactions of a carboxyl group derived from the monomeric ester, but this ester is fairly strongly acidic, donating a proton to many reagents. The chosen method, therefore, was modification of the carboxyl groups of the dimeric acid (IIa), followed by depolymerisation, and it proved successful in several cases.

Thiele's dimeric acid (IIa), which is readily available in quantity,[6] was converted into

FIG. 1. *Ultraviolet absorption of the dimers (II) in EtOH, but hexane for the acid chloride (c) [the ester (b) has λ_max. 218 mμ (log ε 4·17) in hexane].*
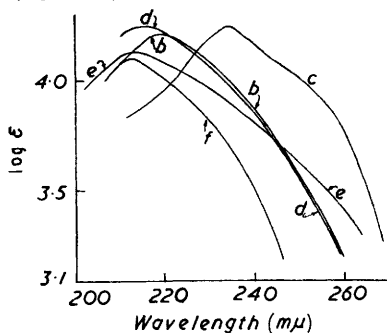
FIG. 2. *Ultraviolet absorption of the monomers (I) in EtOH, but hexane for the acid chloride (b) [the ester (a) in hexane has λ_max. 269 mμ (log ε 3·78)].*
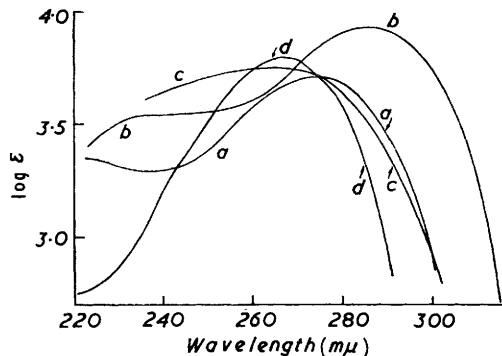
FIG. 3. *Ultraviolet absorption of (A) sorboyl chloride (in hexane), (B) NN-dimethylsorbamide, (C) methyl sorbate, (D) sorbamide, and (E) sorbonitrile (B–E in EtOH).*
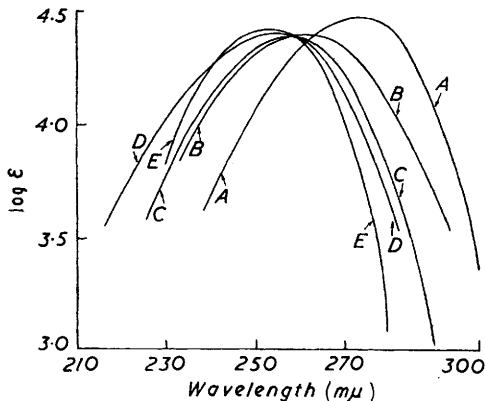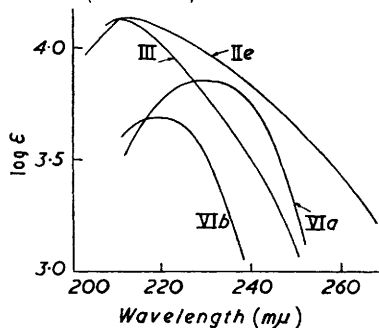
FIG. 4. *Ultraviolet absorption of the dimethylamides (IIe) and (III), and the adducts (VIa and b).*

the acid chloride (IIc) with thionyl chloride and pyridine, and thence into the amide (IId) and the dimethylamide (IIe). The amide was dehydrated to the nitrile (IIf) with benzenesulphonyl chloride and pyridine.[7] The yields were good in all cases. This acid chloride was prepared by Day,[8] and the impure nitrile was probably obtained by Courtot.[9] The structures of these compounds are established by their manner of preparation, reconversion into the parent acid (IIa) or ester (IIb), ultraviolet spectra, and other reactions described below. The ultraviolet spectra (Fig. 1) of these dimers (IIa—f) show intense maxima in

[6] Ziegler, Kühlhorn, and Hafner, *Chem. Ber.*, 1956, **89**, 434.
[7] Stephens, Bianco, and Pilgrim, *J. Amer. Chem. Soc.*, 1955, **77**, 1701.
[8] Day, *Diss. Abs.*, 1958, **19**, 39.
[9] Courtot, *Ann. Chim. (France)*, 1915, **4**, 75.

the 210—235 mμ region (Fig. 1). The curves of the dimeric acid chloride (IIc), the amide (IId) and the nitrile (IIf) are superimposable on that of the dimeric ester (IIb), showing the point of inflection on the long-wave side of the band which indicates the presence of the two conjugated systems. The order of decreasing $\lambda_{max.}$ is COCl $\gg$ COMe $>$ CO·NH$_2$ $>$ CN. The dimeric dimethylamide (IIe) has $\lambda_{max.}$ close to that of the unsubstituted amide (IId), but there is some distortion of the general shape of the band.

All but one of the new dimers (IIc—f) are easily depolymerised, and in good yield, to the monomeric cyclopentadienes (I) by distillation at reduced pressure. The exception is the unsubstituted amide (IId) which, because of its high melting point (202°), decomposes before depolymerising: the free acid (IIa) behaves in the same way. There is a difference in the ease of depolymerisation between the dimethylamide (IIe) and the other dimers (IIb, c, f). These three depolymerise rapidly at ~150°, but the dimethylamide requires a temperature of 200°. Unsubstituted cyclopentadiene dimer depolymerises at 200°, so the carboxyl, chlorocarbonyl, and nitrile groups increase the ease of depolymerisation considerably,* but the reason for this awaits unravelling of the reaction path.[10]

The probable structures of the resulting monomeric substituted cyclopentadienes (I) follow from their ultraviolet spectra (Fig. 2). The monomers absorb intensely in the 250—280 mμ region and the curves of the acid chloride (Ib) and the nitrile (Id) are superimposable on that of the ester (Ia). From the size of the bathochromic shift from unsubstituted cyclopentadiene, these compounds are the 1-substituted cyclopentadienes, as discussed in Part I. The curve for the monomeric dimethylamide (Ic), like that of the dimer (IIe), is considerably distorted from that of the other monomers (Fig. 2). This may be due to the bulk of the dimethylamido-group or to the presence of some 2-substituted isomer. To ensure that no product with a different carbon skeleton had been formed, the monomeric dimethylamide (Ic) was hydrogenated to *NN*-dimethylcyclopentanecarboxamide in good yield. The order of decreasing $\lambda_{max.}$ for the monomers is almost identical with that of the dimers, *i.e.*, COCl $\gg$ CO$_2$Me $>$ CO·NMe$_2$ $\approx$ CN. No systematic investigation of the effect of these substituents on the ultraviolet spectrum of the butadienyl system could be found in the literature, so the sorbyl derivatives were examined. The order of decreasing $\lambda_{max.}$ in this series of compounds (Fig. 3) was COCl $\gg$ CO·NMe$_2$ $>$ CO$_2$Me $>$ CO·NH$_2$ $\approx$ CN. Apart from the dimethylamide, which again behaves abnormally, the sequence is as for the dimeric and monomeric cyclopentadienes.

The monomeric substituted cyclopentadienes (Ia—d) redimerise in a few hours at room temperature. The monomeric acid chloride (Ib) and the monomeric nitrile (Id) resemble the monomeric ester (Ia) in returning largely, but not completely, to the starting dimer. The monomeric dimethylamide (Ic) again behaves differently, dimerising largely to a new dimer. In the ultraviolet spectrum, this new dimer shows the bicycloheptene chromophore, but the point of inflection on the long-wavelength side of the band (the cyclopentene chromophore) is missing (Fig. 4). This new dimer, then, is conjugated in the bicycloheptene system, but not in the cyclopentene ring and so is a compound such as (III). From the ultraviolet spectrum of the original dimerised mixture, it appears that some 70% of the new isomer is formed together with 30% of the original dimer (IIe). The free acid corresponding to (III) could not be obtained, decomposition occurring during attempted hydrolysis with acid or base.

In the Diels–Alder reaction with maleic anhydride, there are substantial differences in the behaviour of the monomeric cyclopentadienes (IIa—d). The ester (Ia) gives compound (IV), as discussed in Part I. The acid chloride (Ib) gives no adduct with the dienophile, perhaps because of interaction between the functional groups of the diene and the dienophile. An ethereal solution of the monomeric acid chloride, however, when treated with methanol, gave the adduct (IV) of the monomeric ester. The monomeric

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* These comparisons were made during simple distillations. The temperatures are those of the heating bath at which distillation proceeds steadily.

[10] Woodward and Katz, *Tetrahedron*, 1959, **5**, 70.

nitrile (Id) gives a complex mixture of adducts with maleic anhydride. The monomeric dimethylamide (Ic) gives an adduct which has strong ultraviolet absorption in the 210 mμ region and so is presumably the conjugated isomer (V).

The bicycloheptene double bond (8, 9 in II) which carries a carbonyl group is known [11] to be very reactive in the Michael addition of amines and other nucleophiles. This is also true when the substituent is carboxyl or cyano, since dimethylamine adds to this double bond of the dimeric ester (IIb) and nitrile (IIf) under mild conditions to give compounds (VIa and b respectively). The structures of these compounds are established by the absence of the short-wavelength bicycloheptene chromophore and the presence of the cyclopentene one (Fig. 4). There is no indication of addition to the other (cyclopentene) double bond. The dimeric dimethylamide (IIe) does not add dimethylamine under the same conditions; steric or electronic factors may prevent the addition in this case and one could distinguish between them with the unsubstituted amide (IId) which has comparable electronic but no greater steric effect than the ester (IIb); unfortunately, this comparison is frustrated by the fact that the unsubstituted amide (IId) is insoluble in dimethylamine and the common solvents, and its reactivity towards dimethylamine cannot be deter-mined under the conditions which were used for the other compounds.

EXPERIMENTAL

Ultraviolet spectra were recorded on a Hilger Uvispek, the solvent, unless otherwise specified, being absolute ethanol.

Preparation and Reactions of the Dimeric Acid Chloride (IIc).—Pyridine (14 ml.) in dry ether (25 ml.) was added dropwise to a stirred suspension of Thiele's acid (IIa) (26 g.) and thionyl chloride (24 ml.; freshly purified) in dry ether at 0°. The appearance of the precipitate changed, but no heat was evolved. The mixture was stirred for 1 hr., filtered, and left in a vacuum until free from solvent. This gave the dimeric *acid chloride*, which, on crystallisation from light petroleum (b. p. 60—80°; 200 ml.; charcoal), was white (24·5 g., 81%) and had m. p. 60—61°. Two further crystallisations gave a sample of m. p. 62° (Found: C, 56·4; H, 4·3; Cl, 26·0. $C_{12}H_{10}O_2Cl_2$ requires C, 56·0; H, 3·9; Cl, 27·6%), $\lambda_{max.}$ 235 mμ (log ε 4·24) in hexane. The acid chloride (0·5 g.) with sodium hydroxide solution gave the dimeric acid (0·4 g.), m. p. and mixed m. p. 208—210°. With methanol the acid chloride (0·3 g.) gave the dimeric ester, (0·2 g.), m. p. and mixed m. p. 85°.

Preparation and Reactions of the Monomeric Acid Chloride (Ib).—The dimeric acid chloride (2·7 g.) was distilled (vapour-temp. 80—94°) at 0·5 mm. (bath-temp. 140—160°) into a receiver at −70°, to give the monomeric acid chloride (2·0 g.) as a glass, $\lambda_{max.}$ in hexane 286 mμ (log ε 3·94); there was no long-wavelength fulvene-type band. In ethanol, it had the ultraviolet spectrum of the monomeric ester (Ia) reported in Part I. From ether at −70° the oil (2·0 g.) gave the dimeric acid chloride (0·8 g.), m. p. and mixed m. p. 60—61°, in a few hr. A solution of the monomeric acid chloride (2·1 g.) in ether (25 ml.) containing methanol (2 ml.) was stirred with calcium carbonate (2 g.) for 30 min.; maleic anhydride (2 g.) was then added and the mixture stirred for 24 hr.; filtration gave a residue (3·5 g.) from which chloroform extracted the adduct (0·75 g.), m. p. and mixed m. p. 148—150° (Part I), of the monomeric ester.

Preparation and Reactions of the Dimeric Amide (IId).—The dimeric acid chloride (14 g.) was added in portions to aqueous ammonia (*d* 0·88) (25 ml.). The mixture boiled, either spon-taneously or on gentle warming. The dimeric *amide* (*tricyclo*[5,2,1,0^{2,6}]*deca-3,8-diene*-4,9-*dicarboxyamide*) (IId) (8 g., 67%), precipitated at 0° overnight, was twice crystallised from water, then having m. p. 202° (Found: C, 66·4; H, 6·7; N, 12·9. $C_{12}H_{14}O_2N_2$ requires C, 66·0; H, 6·5; N, 12·85%), $\lambda_{max.}$ 215 mμ (log ε 4·25). This compound is insoluble in all the common solvents. Attempted distillation at 10 mm. resulted in decomposition after melting. Refluxing the dimeric amide (1·0 g.) with sulphuric acid (1·0 ml.) and water (10 ml.) for 3 hr. gave the dimeric acid (0·77 g.), m. p. 205—207°, elevated to 208—210° with an authentic sample.

Preparation and Reactions of the Dimeric Dimethylamide (IIe).—Dimethylamine (30 ml.) in dry benzene (20 ml.) was added dropwise to a stirred solution of the dimeric chloride (15 g.) in dry benzene (50 ml.) at 0°. The mixture was stirred for 3 hr., filtered, and freed in a vacuum

[11] Petrov and Sopov, *J. Gen. Chem. (U.S.S.R.),* 1953, **23**, 1085; Kochetov and Yhorlin, *ibid.,* 1957, **27**, 3217.

from solvent, to give a white solid. Crystallisation from light petroleum (b. p. 80—100°) gave the dimeric *dimethylamide* (14 g., 88%), m. p. 103—104° (Found: C, 69·9; H, 8·3; N, 9·1, 8·3. $C_{16}H_{22}O_2N_2$ requires C, 70·1; H, 8·0; N, 10·2%), $\lambda_{max.}$ 212 mμ (log ε 4·14). This compound is readily soluble in water. Refluxing the dimethylamide (0·5 g.) with sulphuric acid (2 g.) in water (20 ml.) for 16 hr. and crystallisation of the precipitate from butyl acetate gave the dimeric acid (0·2 g.), m. p. and mixed m. p. 212°. There was no addition of dimethylamine to the dimethylamide after the latter had been kept in a large excess of dimethylamine for a week at 0°.

Preparation and Reactions of the Monomeric Dimethylamide (Ic).—The dimeric dimethyl-amide (2 g.) was distilled (vapour-temp. 120—140°) at 10 mm. (bath-temp. 200—210°) into a receiver at −70° to give the monomeric dimethylamide (1·4 g.) as a yellow glass, $\lambda_{max.}$ 265 mμ (log ε 3·76) (no fulvene-type band). Hydrogenation of this monomer (3·2 g.) over platinum in ethanol at room temperature and atmospheric pressure led to the uptake of 860 ml. of hydrogen ($2H_2 = 1050$ ml.). Distillation of the product (2·95 g.) gave *NN*-dimethylcyclopentane-carboxyamide (2·1 g.), b. p. 124—125°/20 mm. (lit.,[12] 115°/20 mm.), and a non-volatile residue (0·7 g.). Redistillation gave an analytical sample (Found: C, 67·0; H, 10·5; N, 10·4. Calc. for $C_8H_{15}ON$: C, 68·0; H, 10·7; N, 9·9%). Hydrolysis of this amide (1·4 g.) with refluxing 20% sulphuric acid gave cyclopentanecarboxylic acid (0·62 g.), b. p. 122°/22 mm. (lit.,[12] 126°/20 mm.) whose 4-bromophenacyl ester had m. p. and mixed m. p. 76° (cf. Part I). In 24 hr. at room temperature, the monomeric dimethylamide (1·41 g.) partly solidified. Several recrystallisations from light petroleum (b. p. 80—100°) gave an isomeric *dimer* (*NNN'N'-tetra-methyltricyclo*[5,2,1,0²,⁶]*deca-3,8-diene-2,9-dicarboxyamide*) (0·43 g.), m. p. 115—116° (Found: C, 70·4; H, 7·9; N, 10·0%; *M*, 260. $C_{16}H_{22}O_2N_2$ requires C, 70·1; H, 8·0; N, 10·2%; *M*, 274), $\lambda_{max.}$ 211 mμ (log ε 4·13). This isomer is readily soluble in water. Attempted hydrolysis with acid or base under a variety of conditions gave no identifiable material. Chromatography of the mother-liquors from the dimerisation gave oils. The monomeric dimethylamide (3·3 g.) was treated with maleic anhydride (2·7 g.) in benzene (30 ml.). After 8 hr. at room temperature, precipitation was complete and filtration removed the *adduct* (1·8 g.), m. p. 180—185°. Two crystallisations from butyl acetate gave a sample (1·2 g.) of m. p. 186—187° (Found: C, 61·6; H, 5·8; N, 5·8%; *M*, 239. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·6; N, 6·0%; *M*, 235), $\lambda_{max.}$ 210 mμ (log ε 3·79).

Preparation and Reactions of the Dimeric Nitrile (IIf).—A slurry of the dimeric amide (5 g.), dry pyridine (10 ml.) and benzenesulphonyl chloride (redistilled; 9 g.) was stirred at 100° for 1 hr. The mixture was then cooled, diluted with water, and extracted with ether. The ethereal extract was washed with aqueous acid, base, and water, dried, and evaporated, to give the nitrile (3·4 g.) as a pink solid. One crystallisation from methylcyclohexane (250 ml.; charcoal) gave a solid (3·0 g.), m. p. 60—62° (this compound is apparently dimorphic since a pure sample melting at 67° was obtained on one occasion). Several further such crystallisations gave a sample of m. p. 62° (Found: C, 78·5; H, 5·7; N, 15·4%; *M*, 189. $C_{12}H_{10}N_2$ requires C, 79·1; H, 5·5; N, 15·6%; *M*, 182), $\lambda_{max.}$ 212 mμ (log ε 4·12). This *compound* appears first as an oil during recrystallisation. Attempted hydrolysis with acid or base led to decomposition. The Michael addition product was prepared by keeping the dimeric nitrile (0·34 g.) in dimethyl-amine (5 ml.) at 0° for 16 hr. The excess of amine was then removed and the residue recrystal-lised from methylcyclohexane, to give *4,9-dicyano-8-dimethylaminotricyclo*[5,2,1,0²,⁶]*dec-3-ene* (VIb) (0·32 g.), m. p. 93° (Found: C, 73·6; H, 7·1; N, 18·4%; *M*, 226. $C_{14}H_{17}N_3$ requires C, 74·0; H, 7·5; N, 18·5%; *M*, 227), $\lambda_{max.}$ 218 mμ (log ε 3·70).

Preparation and Reactions of the Monomeric Nitrile (Id).—The dimeric nitrile (2·0 g.) was distilled (vapour-temp. 80—96°) at 10 mm. (bath-temp. 150—160°) into a receiver at −70°. The monomeric nitrile (1·7 g.) is a white solid at this temperature, and has $\lambda_{max.}$ 266 mμ (log ε 3·81). After 24 hr. at room temperature, the oily monomer (0·78 g.) became more viscous and three crystallisations from methylcyclohexane gave a semisolid material (0·49 g.). The ultra-violet and infrared spectra of this were essentially identical with those of the starting dimer. The monomeric nitrile with maleic anhydride in benzene solution gave no precipitate: in ether, only an oil was obtained.

Preparation of the Michael Addition Product of the Dimeric Ester and Dimethylamine (VIa).— The dimeric ester (5 g.) was kept in dimethylamine (50 ml.) at 0° for 16 hr. The excess of amine was then removed, and the residue crystallised twice from light petroleum (b. p. 60—80°;

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[12] Mousseron, Jullien, and Jolchine, *Bull. Soc. chim. France*, 1952, **19**, 765.

charcoal) to give *dimethyl 8-dimethylaminotricyclo*[5,2,1,0^{2,6}]*dec-3-ene-4,9-dicarboxylate* (4·8 g.), m. p. 110—111° (Found: C, 65·3; H, 8·0; N, 4·9%; *M*, 256. $C_{16}H_{23}O_4N$ requires C, 65·5; H, 7·8; N, 4·8%; *M*, 293), $\lambda_{max.}$ 228 mμ (log ε 3·88). This compound evolved dimethylamine in boiling water, but the product was a mixture.

Ultraviolet Spectra of Sorbamide, NN-*Dimethylsorbamide, Methyl Sorbate, Sorboyl Chloride, and Sorbonitrile.*—These compounds were obtained by conventional methods. All are well-known, except NN-dimethylsorbamide which decomposed before analytical figures could be obtained. The ultraviolet absorption maxima were, respectively, at 254 (log ε 4·43), 262 (log ε 4·41), 258 (log ε 4·39), 273 (log ε 4·48), and 254 mμ (log ε 4·43) (cf. Fig. 3).

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